



# $C^{\text{em}}$ QUANT<sup>®</sup> software Mathematical modeling in quantitative phase analysis of Portland cement

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Received 8 December 1998; accepted 21 June 1999

## Abstract

It is necessary to determine a complete mineralogy of clinker cement to correctly understand, interpret, and predict the outcome of any plant production process. The cement industry's standard method (ASTM C 150) used in quantitative phase analysis of alite, belite, aluminate, and ferrite has long been known to provide approximate concentrations. The wet chemical and optical microscopy methods are too slow and too expensive to be used on a large scale. The X-ray diffraction-based Rietveld method features its own limitations and so far has been used in a very small number of industrial laboratories. This article describes original commercial software named  $C^{\text{em}}$ QUANT, employed for major and minor phase quantification in Portland cement.  $C^{\text{em}}$ QUANT's input data consists of up to 17 constituents, such as  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{SrO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{SO}_3$ , and loss of mass (LOM). Minor element oxides and LOM are essential if a full mineralogy is to be calculated and a high accuracy output data is to be obtained. Using a novel mathematical modeling approach, the input constituents are distributed among preselected mineral phases in such a way that the input and output mass balances are matched. The phases automatically quantified by  $C^{\text{em}}$ QUANT are: alite, belite, aluminate, ferrite, aphtialite, gypsum, bassanite, lime, calcite, periclase,  $\text{KC}_8\text{A}_3$ ,  $\text{NC}_8\text{A}_3$ , langbeinite, thenardite,  $\text{KC}_{23}\text{S}_{12}$ , arcanite,  $\text{C}_4\text{AMn}$ , and anhydrite. In comparison with Bogue calculation,  $C^{\text{em}}$ QUANT is much more accurate for major phases and provides concentrations of additional secondary phases. Fifteen international clinker cement reference materials were analyzed using  $C^{\text{em}}$ QUANT and obtained phase concentrations were compared with data from Bogue calculations. Main methods used in clinker cement phase quantification are discussed and compared with  $C^{\text{em}}$ QUANT. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Clinker; Portland cement; Phase composition determination; Mathematical modeling; X-ray diffraction; X-ray fluorescence

## 1. Introduction

Portland cement is the man-made material produced on the largest industrial scale. During the manufacturing process, the product's quality and kiln temperature must be controlled at regular intervals. One of the important quality parameters of Portland cement is its chemical and phase composition. Traditional methods employed in the composition determination involve wet chemistry (WCh), X-ray fluorescence (XRF), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and optical microscopy. XRF methods provide elemental concentrations, such as:  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{SO}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ , and  $\text{Fe}_2\text{O}_3$  [1–4]. Presently, even a direct carbon determination can be carried out by XRF to establish the  $\text{CaCO}_3$  content.

XRD methods supplement the elemental composition of cement with a free lime ( $\text{CaO}$ ). A dedicated diffractometer or a diffraction channel mounted inside an XRF spectrometer can be used for this purpose [5,6]. In the beginning of this decade initial efforts were made to estimate Portland cement's phase composition by XRD alone [7,8]. Phases such as alite, belite, aluminate, ferrite, bassanite, and gypsum were quantified using the Rietveld method incorporated in SIROQUANT software (Sietronics, Belconnen, Australia). Most of the time, the loss of mass (LOM) is also determined in an independent process.

In 1929, Bogue [9] put forth a method for estimating Portland cement's compound composition from its chemical analysis. The Bogue calculation has been the standard method used by the cement industry (ASTM C 150), although it has been clearly recognized as inaccurate. Given vigorous progress in mathematical modeling in recent years, a new attempt was made. The result, an ingenious algorithm and computer software called  $C^{\text{em}}$ QUANT, was created.

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The goal of the paper is to characterize the software and to present selected results.

## 2. The C<sup>em</sup>QUANT concept

It is generally known that elemental composition of materials can be very accurately determined using modern integrated coupled plasma-absorption emission spectrometry (ICP-AES), XRF, or gamma spectrometry, with water of hydration calculated by difference or through loss of mass on ignition measurements. XRF is widely used in the cement industry, requires limited sample preparation, and is very reliable and cost-effective. The C<sup>em</sup>QUANT concept is based on the assumption that the LOM and the elemental composition of a Portland cement sample would constitute sufficient input data for generation of phase content. The algorithm employs generally acknowledged but complex stoichiometry of phases in Portland cement and the mass balance [10].

C<sup>em</sup>QUANT input data consists of constituents as follows: CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, SrO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>, and LOM. Among the input constituents, only the first four oxides are absolutely required to run the software. However, minor element oxides and LOM are essential if a full mineralogy is to be calculated and a high-accuracy output data is to be obtained. A sample mineralogical composition corresponding to Portland cement is calculated, provided that the input constituents fall within the concentration ranges listed in Table 1. Another condition that needs to be met is:  $97.5\% < \text{TOTAL} < 102.5\%$ , where TOTAL is the sum of the input concentrations.

In addition, the user may insert concentrations of certain compounds to enforce specific calculations. For example, concentrations of gypsum, bassanite, lime, and calcite can be entered if known. In this way the number of remaining unknown phases becomes smaller and LOM is no longer required. The input concentration ranges admitted by C<sup>em</sup>QUANT are relatively wide; however, the current C<sup>em</sup>QUANT program does not yet allow quantitative phase

analysis of materials such as high-alumina cements. The quality of the output data depends entirely on the quality of the input data. Thus, for high accuracy phase quantification, the reliability and integrity of input data must be ensured.

Input data may be entered for a small number of samples in a manual mode; larger sample sizes can conveniently be entered using a spreadsheet-type table. C<sup>em</sup>QUANT also accepts XRF output files.

Based on the input data presented in Table 1, finding a phase composition solution for a Portland cement specimen is a very unusual task. C<sup>em</sup>QUANT software uses a total mass balance of the input constituents to generate the phase composition. It is then assumed that the LOM and the elemental constituents are distributed among preselected mineral phases (see Sections 3 and 4) in such a way that the input and output mass balances are matched. Almost all major and minor input constituents naturally occur in several major phases. The problem with finding a solution for such a system was that the number of unknowns considerably exceeded the number of known input constituents. Such a system described in the form of a set of algebraic equations does not have a unique (nonzero) solution. Thus, the mass balance equations were solved with the help of mathematical modeling. In C<sup>em</sup>QUANT's case, the mathematical modeling is based on a Monte Carlo method [11–15]. The Monte Carlo method may briefly be described as a procedure that involves the use of sampling devices based on probabilities. These sampling devices generate random numbers employed to approximate a solution for a given mathematical problem. In C<sup>em</sup>QUANT, two independent Monte Carlo procedures are used simultaneously.

The occurrence of each  $X_i$  phase between its lower and upper limits is equiprobable. The probability density function  $f(X_i)$  for each estimated phase is shown in Eq. (1):

$$f(X_i) = \begin{cases} 1/(X_{iup} - X_{ilow}) & \text{if } X_{ilow} < X_i < X_{iup} \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

with the corresponding cumulative distribution function shown in Eq. (2):

$$f(X_i) = 0 \quad \text{if } X_i \leq X_{ilow}$$

$$f(X_i) = \begin{cases} (X_i - X_{ilow}) / (X_{iup} - X_{ilow}) & \text{if } X_{ilow} < X_i < X_{iup} \\ 1 & \text{if } X_i \geq X_{iup} \end{cases} \quad (2)$$

In the procedure, the uniformly distributed pseudorandom numbers are drawn from the corresponding probability density functions. The inverse transformation method and the rejection method [13] are employed to determine whether or not the numbers are acceptable for use. The arithmetic

Table 1  
C<sup>em</sup>QUANT input data: elemental composition (expressed as oxides)

Input data	Composition limit (%)	
	Low	High
CaO	50.0	75.0
SiO <sub>2</sub>	16.0	27.0
Al <sub>2</sub> O <sub>3</sub>	0.05	15.0
Fe <sub>2</sub> O <sub>3</sub>	0.05	20.0
TiO <sub>2</sub>	0	2.5
Mn <sub>2</sub> O <sub>3</sub>	0	1.0
SrO	0	0.5
MgO	0	7.0
Na <sub>2</sub> O	0	2.0
K <sub>2</sub> O	0	2.5
P <sub>2</sub> O <sub>5</sub>	0	3.0
SO <sub>3</sub>	0	7.0
LOM	0	8.5

means of all accepted phase concentrations give the estimate of the final concentrations. Phases quantified in the simulation process are described below.

Alite is triclinic when pure, but small amounts of solid solution cause it to become monoclinic or trigonal. Maximum substitutions of Mg and Al could be  $x = 0.025$  and  $y = 0.0075$ . In this work, it was assumed that  $0.01 < x < 0.025$  and  $0.002 < y < 0.0075$ . Solubility of Mg in alite was modeled using data by Möller [16].

Belite can take several substances into solid solution. The substances that might most obviously occur in solid solution are MgO,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , CaO, and  $\text{K}_2\text{O}$ . In this program it was assumed that excess  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  substitutes in alite and belite. To satisfy various opinions, one of the software options allows the user to fix the ratio of the residual  $\text{K}_2\text{O}$  assigned to alite and belite.

Tricalcium aluminate has polymorphic modifications. Two compounds that are closely allied to  $\text{C}_3\text{A}$  are  $\text{NC}_8\text{A}_3$  and  $\text{KC}_8\text{A}_3$ . The solubility rates of  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  are set by default, although the user can also adjust them.  $\text{SiO}_2$  and MgO also enter into solid solution, but solubility of MgO in  $\text{C}_3\text{A}$  may not exceed 2.5%. In this work, it was assumed that  $\text{SiO}_2$  and MgO have 1% solubility in  $\text{C}_3\text{A}$ . It was also assumed that  $\text{NC}_8\text{A}_3$  and  $\text{KC}_8\text{A}_3$  are formed if certain conditions are met.

Ferrite is a solid solution, which usually belongs to the series  $\text{C}_2\text{A}-\text{C}_2\text{F}$ . It has been suggested that the limit may be  $\text{C}_4\text{AF}$ . In the presence of 3% MgO, the limit may extend approximately to  $\text{C}_6\text{A}_2\text{F}$ . Based on ASTM C 150-94 it was assumed that  $\text{C}_6\text{A}_2\text{F}$  is formed only when the alumina-ferric oxide ratio is less than 0.64. In all other cases  $\text{Ca}_2\text{Al}_x\text{Fe}_{1-x}\text{O}_5$  represents ferrite, where  $0 < x < 0.7$ . About 1.5% MgO may substitute for CaO in ferrite (0.5% in this work).

For most normal clinker compositions, the major sulphate phase will be aphtialite. If aphtialite is formed, it is assumed that a part of the remaining  $\text{K}_2\text{O}$  dissolves in aluminate, a part substitutes for CaO in belite, and that the  $\text{K}_2\text{O}$  balance dissolves in alite. Only with unusually low contents of  $\text{K}_2\text{O}$  in the clinker would one expect langbeinite and thenardite to be formed. The alkali oxides combine preferentially with  $\text{SO}_3$ . Alkali metals not present as sulphates occur mainly as  $\text{KC}_8\text{A}_3$ ,  $\text{KC}_{23}\text{S}_{12}$ , and  $\text{NC}_8\text{A}_3$ .

$\text{Mn}_2\text{O}_3$  probably substitutes for  $\text{Fe}_2\text{O}_3$  in Portland cement. A compound  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Mn}_2\text{O}_3$  is known to exist. Based on the recent work by Motzet and Poellman [17], it was also assumed that  $\text{TiO}_2$  forms  $4\text{CaO} \cdot 2\text{FeO} \cdot \text{TiO}_2$ . Following a work by Nurse [18],  $\text{P}_2\text{O}_5$  was assumed to be mostly present in solid solution as calcium phosphate in  $\text{C}_2\text{S}$ , thus markedly reducing the amount of alite.

Should phases such as calcite, gypsum, bassanite, and lime be known from other independent methods, the user may introduce their concentrations at the input level together with elemental concentrations (LOM is no longer required). This way the number of unknowns is reduced and the program carries out estimation of the remaining phase constituents.

### 3. Output data

The mineral phases of the Portland cement specimen are automatically saved as Worksheet 2 in the same spreadsheet file as the input data. Table 2 lists phases dealt with in the present version of C<sup>em</sup>QUANT and gives their description.

Phases described in Table 2 are automatically selected during simulation runs (by default). In the next software version, several user-selected secondary phases will be available to replace those that are currently employed by default. As such, C<sup>em</sup>QUANT will become more universal and will allow analysis of unusual phase composition associated with particular raw materials and process conditions.

### 4. Results

Fifteen international clinker cement reference materials were analyzed using C<sup>em</sup>QUANT. Their input concentration data is given in Table 3.

C<sup>em</sup>QUANT's calculation results are presented in Table 4. For the first three samples in Table 4, the lime concentrations were known (Brammer catalogue) and entered with the input data. C<sup>em</sup>QUANT estimated the concentrations of free lime in the remaining samples. The phase concentrations given in Table 4 were estimated for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  solubility rates in aluminate ( $\text{KC}_8\text{A}_3$ ,  $\text{NC}_8\text{A}_3$ ) set at default levels (0.05). The user may select solubility rates (in aluminate and belite) that are different from default values. This choice affects concentrations of alite, belite, and aluminate. For example, selecting extreme allowable  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  solubility rates, concentrations of alite and belite in three reference materials (SRM 1881, SRM 1886, and SRM 1887) may move up or down by 1 to 3% (absolute).

C<sup>em</sup>QUANT-estimated concentrations of alite, belite, and aluminate were compared with those calculated using the ASTM C 150 method (Table 5). Figs. 1 and 2 present corre-

Table 2  
Phases and their description

Phase	Chemical formula	Maximum concentration (%)
Alite	$(\text{Ca}_{1-x-y}\text{Mg}_x\text{Al}_y)_3 \cdot (\text{Si}_{1-y}\text{Al}_y)\text{O}_5$	80
Belite	$\text{Ca}_2\text{SiO}_4$	45
Aluminate	$[\text{Ca}_{(1-x-y)}\text{K}_{(x)}\text{Na}_{(y)}]_3 \cdot \text{Al}_2\text{O}_6$	15
Ferrite	$\text{Ca}_2(\text{Al}_x\text{Fe}_{1-x})_2\text{O}_5$	20
Aphthialite	$\text{K}_3\text{Na}(\text{SO}_4)_2$	8
Gypsum	$\text{CaSH}_4\text{O}_6$	6
Bassanite	$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	5
Lime	CaO	5
Calcite	$\text{CaCO}_3$	5
Periclase	MgO	8
$\text{KC}_8\text{A}_3$	$[\text{CaO}_{(1-x)}\text{K}_2\text{O}_{(x)}]_3 \cdot \text{Al}_2\text{O}_3$	10
$\text{NC}_8\text{A}_3$	$[\text{CaO}_{(1-x)}\text{Na}_2\text{O}_{(x)}]_3 \cdot \text{Al}_2\text{O}_3$	
Langbeinite	$\text{Ca}_2\text{K}_2(\text{SO}_4)_3$	5
Thenardite	$\text{Na}_2\text{SO}_4$	5
$\text{KC}_{23}\text{S}_{12}$	$\text{K}_2\text{Ca}_{23}\text{Si}_{12}\text{O}_{48}$	15
Arcanite	$\text{K}_2\text{SO}_4$	5
$\text{C}_4\text{AMn}$	$\text{Ca}_4\text{Al}_2\text{Mn}_2\text{O}_{10}$	5
Anhydrite	$\text{CaSO}_4$	5

Table 3

Input composition data (%)

Sample	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	SrO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	LOM
RM8486	63.36	22.48	4.7	3.6	0.25	0.1	0.05	4.73	0.1	0.42	0.06	0.27	0.16
RM8487	67.2	21.43	5.53	1.98	0.27	0.04	0.11	1.48	0.14	0.72	0.29	0.83	0.17
RM8488	66.5	22.68	4.9	4.07	0.24	0.03	0.13	0.98	0.11	0.35	0.08	0.31	0.21
SRM1880	63.14	19.82	5.03	2.91	0.23	0.08	0.06	2.69	0.28	0.91	0.29	3.37	1.38
SRM1881	58.67	22.25	4.16	4.68	0.25	0.26	0.11	2.63	0.04	1.17	0.09	3.65	2.01
SRM1884	64.01	23.19	3.31	3.3	0.16	0.11	0.048	2.32	0.13	0.51	0.12	1.67	1.17
SRM1885	62.14	21.24	3.68	4.4	0.2	0.12	0.037	4.02	0.38	0.83	0.1	2.22	0.74
SRM1886	67.43	22.53	3.99	0.31	0.19	0.013	0.11	1.6	0.02	1.16	0.025	2.04	1.73
SRM1887	62.88	19.98	5.59	2.16	0.27	0.072	0.07	1.26	0.1	1.27	0.075	4.61	1.49
SRM1888	63.78	20.86	2.16	3.18	1.05	0.025	0.01	0.71	0.14	0.56	0.085	3.16	1.79
SRM1889	65.08	20.44	5.61	2.67	0.21	0.24	0.07	1.38	0.11	0.32	0.15	2.68	0.92
BCS353	64.8	20.5	3.77	4.82	0.16	0.23	0.23	2.42	0.1	0.49	0.077	2.25	0.13
BCS354	70	21.8	4.84	0.3	0.04	0.058	0.11	0.42	0.1	0.11	0.12	2.25	0.01
BCS372	65.3	20.3	5.37	3.42	0.29	0.074	0.05	1.31	0.1	0.76	0.07	2.95	0.01
GBW03201	63.45	21.17	5.26	3.2	0.23	0.01	0.01	1.17	0.2	1.18	0.12	2.13	1.82

lation graphs obtained for the considered series of reference materials. Microscopic data known for the first three reference materials (Brammer catalogue) are also presented in Figs. 1 and 2.

Comparison of data in Tables 4 and 5 as well as Figs. 1 and 2 indicates important differences for a number of concentration results obtained using C<sup>em</sup>QUANT and Bogue calculations. Almost all alite concentrations are higher in C<sup>em</sup>QUANT than in Bogue calculations. For belite and aluminate, the situation is just the opposite. Concentrations of ferrite in a few samples are appreciably different. It is clear that Bogue calculations are in error when the unaccounted secondary input constituents (MgO, K<sub>2</sub>O, Na<sub>2</sub>O, SO<sub>3</sub>, LOM) become non-negligible.

## 5. Key benefits

One of the most important benefits resulting from a general use of C<sup>em</sup>QUANT would be a simplification of the existing analytical structures. At present, it takes XRF, XRD, DSC, and also wet chemistry to carry the analytical load at various process stages. Using C<sup>em</sup>QUANT, it would no longer be necessary to utilize XRD, except to confirm the presence or absence of a few key phases when changing the raw materials. Also, use of wet chemistry could be greatly reduced. This means smaller laboratories, staff, investment, and operating costs. The obvious advantages involve gain in productivity and speed of phase analysis, efficiency (full analytical information), economy, uniformity (same results can be generated anywhere using the same input data), ac-

Table 4

Phase concentrations (%) obtained using C<sup>em</sup>QUANT

Sample	Alite	Belite	Alum	Ferrit	Aphth	Gyps	Bassan	Lime	Calcite	Pericl	Langb	Thena	Arcan	C4AMn	Anhy	KC23S12	INPUT	OUTPUT
RM8486	59.6	19.4	4.9	11.6	0.6	0.0	0.0	0.2	0.4	3.2	0.0	0.0	0.0	0.3	0.0	0.0	100.3	100.3
RM8487	70.0	8.9	10.5	5.8	1.5	0.1	0.1	2.5	0.3	0.1	0.0	0.0	0.0	0.1	0.0	0.0	100.2	100.2
RM8488	67.9	13.6	4.7	13.0	0.6	0.0	0.0	0.0	0.5	0.1	0.0	0.0	0.0	0.1	0.0	0.0	100.6	100.6
SRM1880	60.8	11.2	7.1	9.2	2.1	2.4	2.2	2.3	1.7	0.7	0.0	0.0	0.0	0.2	0.0	0.0	100.2	100.2
SRM1881	26.7	46.5	4.4	10.9	0.4	3.6	3.2	0.1	2.4	0.6	0.0	0.0	0.0	0.8	0.0	0.0	100.0	100.0
SRM1884	61.1	20.5	1.6	10.6	1.2	1.2	1.0	0.0	2.0	0.4	0.0	0.0	0.0	0.3	0.0	0.0	100.0	100.0
SRM1885	58.7	18.4	3.9	9.6	2.0	1.4	1.1	1.4	0.9	2.1	0.0	0.0	0.0	0.4	0.0	0.0	100.1	100.1
SRM1886	63.5	17.6	9.4	0.9	0.2	1.9	1.9	2.7	2.7	0.1	0.0	0.0	0.0	0.0	0.0	0.0	101.1	101.1
SRM1887	47.4	22.4	9.8	7.0	1.1	4.0	3.9	2.6	0.9	0.1	0.0	0.0	0.0	0.2	0.1	0.0	99.8	99.8
SRM1888	61.7	14.0	2.1	6.6	1.3	2.6	2.4	3.0	2.5	0.1	0.0	0.0	0.0	0.1	0.0	0.0	97.5	97.5
SRM1889	68.4	6.9	9.0	8.1	0.8	2.4	2.1	0.4	0.6	0.1	0.0	0.0	0.0	0.7	0.0	0.0	99.9	99.9
BCS353	77.4	2.4	4.0	10.0	1.1	0.5	0.6	0.7	0.0	0.5	0.0	0.0	0.0	0.7	2.0	0.0	100.0	100.0
BCS354	82.4	1.3	11.1	1.1	0.3	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.2	3.5	0.0	100.2	100.2
BCS372	67.3	7.1	7.3	10.7	1.1	0.0	0.0	1.7	0.0	0.1	0.0	0.0	0.0	0.2	4.1	0.0	100.0	100.0
GBW03201	44.9	27.1	6.9	10.6	2.1	1.2	1.0	2.5	3.4	0.1	0.0	0.0	0.0	0.0	0.0	0.0	100.0	99.9

Alum = aluminat; Ferrit = ferrite; Aphth = aphtialite; Gyps = gypsum; Bassan = bassanite; Pericl = periclase; Langb = langbeinite; Thena = thenardite; Arcan = arcanite; Anhy = anhydrite.

Table 5  
Phase concentrations (%) calculated using ASTM C 150 method

Sample	Alite	Belite	Alum	Ferrite	Other <sup>a</sup>
RM8486	48	29	7	11	5.7
RM8487	65	13	13	6	3.5
RM8488	57	22	7	12	2.1
SRM1880	55	15	10	9	8.8
SRM1881	22	47	4	14	9.9
SRM1884	51	28	4	10	6.0
SRM1885	52	22	3	13	8.3
SRM1886	69	13	11	1	6.7
SRM1887	48	21	12	7	8.9
SRM1888	65	10	3	10	6.4
SRM1889	58	15	11	8	5.7
BCS353	68	8	2	15	5.9
BCS354	79	3	13	1	3.1
BCS372	60	13	9	10	5.3
GBW03201	49	24	9	10	6.5

<sup>a</sup>“Other” is the sum:  $\text{Mn}_2\text{O}_3 + \text{SrO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{SO}_3 + \text{LOM}$ . Titanium dioxide and phosphorus pentoxide were included with the  $\text{Al}_2\text{O}_3$  content (ASTM C-150).

curacy (approaches optical microscopy or XRD-Rietveld, and in many instances surpasses them), reliability and independence, ease of use, quality control, and possibility to calculate process parameters. The phase composition data corresponding to process parameters are: free lime (control of the kiln temperature), alite/belite ratio (cement hardness), aluminate (setting time), ferrite (consistency in color), gypsum (dehydration during milling), and  $\text{CaCO}_3$  (compliance with legal requirement for carbon content).

One of the most important operational advantages of  $\text{C}^{\text{em}}$ QUANT over other methods is its ease of use and high

speed of execution. For example, it takes mere seconds to execute calculations for 10 Portland cement samples using a typical Pentium PC computer, compared to hours with traditional methods. Only limited experience in chemistry or computer knowledge is required from an operator. The  $\text{C}^{\text{em}}$ QUANT software requires Microsoft Windows 95, Microsoft Excel 5 (or higher versions), and a standard computer configuration.

## 6. Discussion of other methods

It is necessary to determine a complete mineralogy of clinker cement (including minor constituents) to correctly understand, interpret, and predict the outcome of the plant production process. Three main methods (WCh, XRD, and microscopy) have been generally used by the industry for determination of the mineralogical composition of clinker cement.

Despite being costly and slow, wet chemical methods remain the major tool especially in process control and trade activities. Nevertheless, it has to be realized that WCh results often do not provide a true mineralogical description of clinker cement, but only approach it. The consecutive dissolution of phases with methanol and salicylic acid and saccharose was found to be cheap and reliable [19]. The same source claims that optical microscopy employing reflected light determines bi- and tricalcium silicates but the results are unreliable.

The XRD methods that are not based on the full diffraction pattern do not provide reliable or accurate results [19].

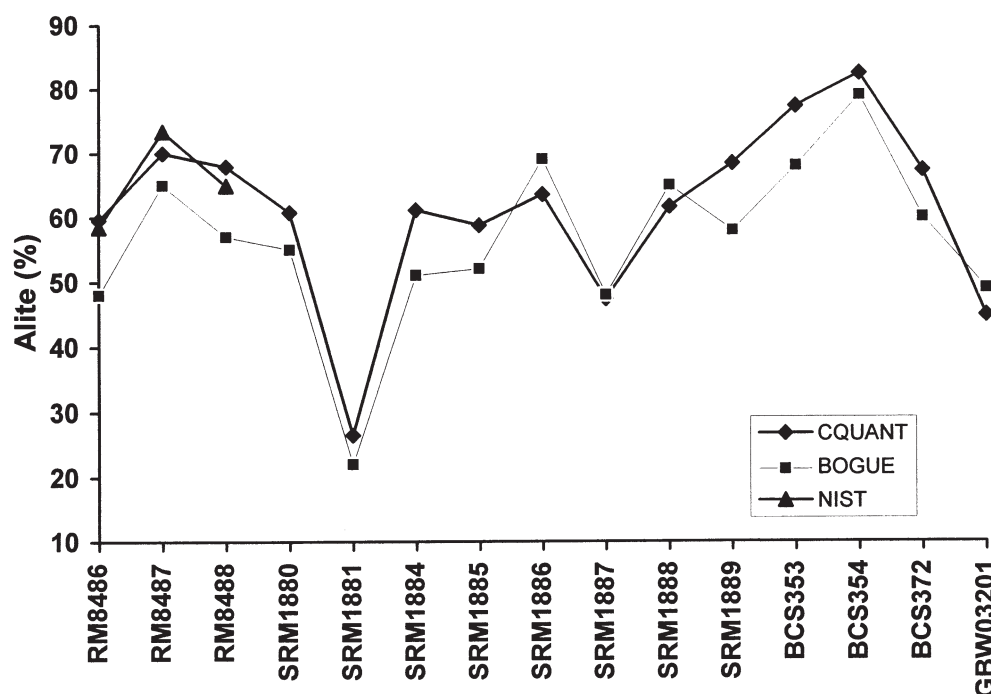


Fig. 1. Correlation graph obtained with  $\text{C}^{\text{em}}$ QUANT.

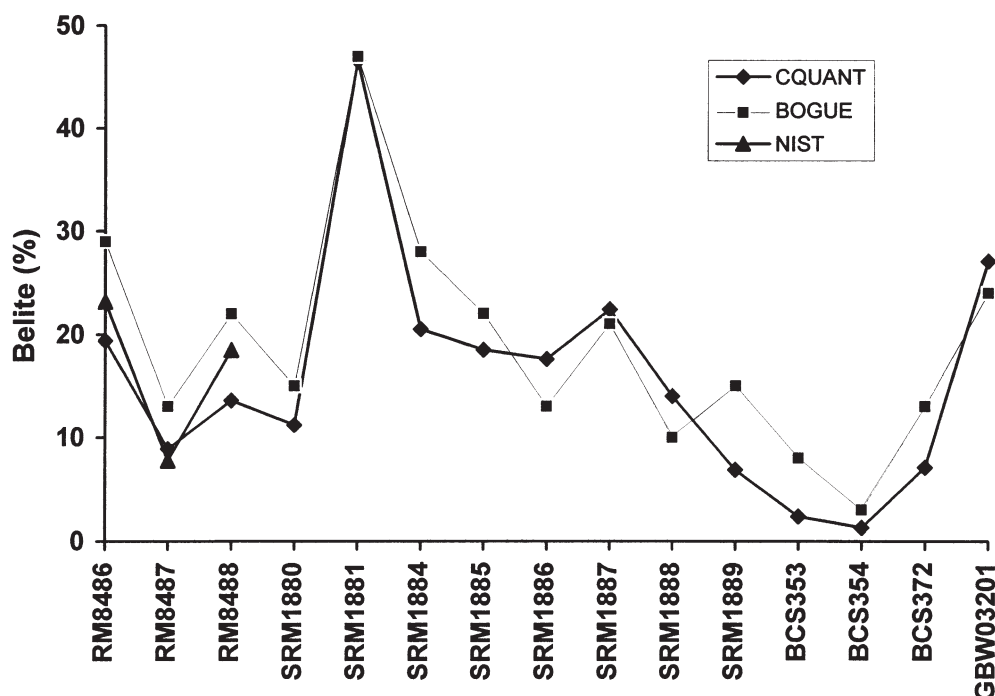


Fig. 2. Correlation graph obtained with C<sup>em</sup>QUANT.

Most XRD methods of analysis involving standards are only quantitative when comparisons are made between samples of similar crystallinity. The mass balance supplementary information seems unavoidable [20]. Apparently, some hold a view that Rietveld software is the “black box” tool for cement quantitative phase analysis: it is not so. First, a diffractogram corresponding to the sample needs to be obtained (which takes some time). Second, using a standard software corresponding to the XRD instrument all major and minor phases need to be correctly identified (this is almost an impossible task given the number of polymorphic possibilities corresponding to cement major phases). Only then, one transfers the diffractogram to the Rietveld software and declares the phases that are intended for quantification. Rietveld modeling of industrial cements described in the open literature so far confirms a fixed (but not always constant) stoichiometry of compounds. For example, SIROQUANT software employs only one ferrite formula ( $C_2A_{1.75}F_{1.25}$ ). Accuracy of Rietveld results always needs to be compromised, because XRD misses some crucial secondary phases due to their relatively high limit of detection. For example, free lime content below 0.7% by mass lies below the limit of detection of the Rietveld determination [21]. The method is rather difficult to use for an average operator and the final result is operator-dependent. Fine grinding at the sample preparation stage and long counting times during measurement result in low sample throughput. In addition, quantification of solid solutions (all major phases) has always been problematic. Most Rietveld modeled results are normalized and consequently phase constituents tend to be overestimated [21]. In general, the industrial use

of a full-profile Rietveld quantitative XRD analysis of Portland cement has been limited to only a handful of top laboratories. Although the Rietveld method constitutes a genuine progress in cement phase quantification, it was too quickly promoted as a “black box” tool without recognizing and acknowledging its limitations.

Determination of the sulfate/sulfide ratio in clinker cement can also be accomplished by a direct XRF analysis as shown by Bonvin et al. [6]. In this case, the total sulfur concentration is known from the S K $\alpha$  intensity measurement, whereas the K $\beta$  line provides sulfate content.

It is possible to identify and quantify the  $C_3S$ ,  $C_2S$ , ferrite, and the  $C_3A$  phases on polished surfaces under the microscope, but this process is too slow to be meaningful for any purposes other than certification.

In future cement characterization activities and process control, one will certainly see more and more modern instrumental methods that are faster, easier to use, and more accurate. Given the current advent of computing potential and understanding of the mineralogical field, one can clearly foresee that involvement of chemical, XRD, and microscopic methods will be minimized in the near future. A very fast, cheap, and easy to use method for clinker cement phase quantification is clearly the next step. Most plants are already equipped with efficient and reliable X-ray fluorescence spectrometers capable of accurately analyzing all major and minor elemental constituents. Employing XRF, thermo-gravimetric analysis (TGA) (LOM), and C<sup>em</sup>QUANT would be the most attractive option in modern control of plant operating conditions. In comparison with Bogue calculation, C<sup>em</sup>QUANT is much more accurate for major

Table 6  
Methods of phase quantification

Method	Accuracy	No. of phase constituents	Speed	Economy	Usability	Availability
Wet chemistry	Accurate <sup>a</sup>	Limited	Very slow	Expensive	Difficult	Decades
Thermal analysis	Limited <sup>a</sup>	Limited	Moderate	Moderate	Moderate	Decades
Microscopy	Accurate	Limited	Very slow	Expensive	Difficult	Decades
Bogue	Limited	Limited	Very fast	Very cheap	Very easy	Decades
XRD calibration	Limited	Limited	Fast	Moderate	Moderate	1950s
XRD Rietveld	Accurate	Limited	Moderate	Moderate	Difficult	1980s
C <sup>em</sup> QUANT	Accurate	Numerous	Very fast	Very cheap	Very easy	1998

<sup>a</sup>For selected constituents and limited concentration ranges.

phases and provides concentrations of additional phases such as free lime, gypsum, bassanite, anhydrite, calcite, and alkali compounds. Another possibility would be to conserve the XRF-XRD system and with XRD continue determination of phases such as free lime, calcite, and gypsum. Then, output data from XRF-XRD would constitute input data for C<sup>em</sup>QUANT for possibly the most accurate and the fastest determination of major and secondary phases in clinker cement (no separate LOM determination required).

Table 6 gives a résumé of the discussed methods. They are compared in relative terms with respect to accuracy, speed, economy, usability, and availability.

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