Comparison between Wet chemical Analysis and Rietveld Method Quantification in White Cement Samples

L.A. Gobbo[1,2], M.A. Cincotto[3], V.A. Quarcioni[3,4]
[1]*Instituto de Geociências – Universidade de São Paulo, Brazil;* [2]*Panalytical Brasil, São Paulo ;* [3]*Departamento de Engenharia de Construção Civil – Universidade de São Paulo, Brazil;* [4]*Instituto de Pesquisas Tecnológicas do Estado de São Paulo, Brazil*

Abstract: White Portland cement is composed of three basic oxides (CaO, Al_2O_3 and SiO_2) and minor components such as Na_2O, K_2O, SO_3, etc. The main and obvious difference with respect to grey cement is color, which represents a decisive criterion for evaluating the quality. The white cement clinker shows the interstitial phases composed almost only by C_3A. The wet chemical analysis was applied in this study to compare the results from X-ray diffraction (XRD). The main oxides results were applied to some Bogue modified equations to correlate results with those from mineralogical quantification. Phases quantification was done using the XRD and Rietveld analysis using the X´Pert High Score Plus software from Panalytical. The comparison of results showed good correlation for the main phases of clinker and also calcite from limestone. This research shows the Rietveld Method as an important tool for qualification and quantification of cement.

1. Introduction

With three basic oxides (CaO, Al_2O_3 and SiO_2) and minor components such as Na_2O, K_2O and SO_3, the obvious difference from white Portland clinker to grey cement is color, which represents an important and decisive criterion for evaluating the quality. To reach the required whiteness level, the coloring elements content (Fe, Mn, Cr, Ti, etc.) in raw mixes must be highly accurate. In white cement clinkering the appearance of the first liquid phase occurs from 1450-1470ºC, which represents an increase of at least 100ºC if compared with the grey cement process. The absence of Fe_2O_3 represents not only a higher temperature for liquid formation but also a higher viscosity and a lower liquid content (12-14%) than in grey cement. The addition materials as limestone and gypsum must have also the whiteness control.

White cement Portland is mainly composed by alite, belite and C_3A. In air of ordinary humidities, a phase of approximate composition $C_{12}A_7$ is formed during clinkerization. It reacts rapidly with water and occurs in some of the calcium aluminate cements [1]. The high AM in white cement raw mixes and also the rapid cooling rate in H_2O vapour can lead to the formation of $C_{12}A_7$. C_3A can occur as orthorhombic form when the Na_2O reach 3.7% in the phase [2]. Gobbo et. al [3] present an industrial example of the influence in white cement clinker, where the increase of Na_2O lead to the formation of orthorhombic C_3A. The C_4AF is not present due to the absence of Fe_2O_3 and possible minor compounds are free lime and periclase. Most common additions in the white cement production are calcite, gypsum and also blast furnace slags. The kind of fuel used is also highly well controlled due to their color influences.

The clinker phases quantification represents an important tool on quality control of Portland cement production. Until nowadays the most frequently applied method to estimate clinker phases composition is the Bogue procedure [4]. Bogue method gives theoretical (potential) composition based on calculation from elemental analysis. Microscopical techniques are well recognized not only on phases quantification, but also on clinker microstructure information. X-ray diffraction is recently applied in cement production control by clinker quantitative Rietveld analysis. Its not a technique used on cement analysis, but only in clinker analysis.

Phase composition of Portland cement is directly related to the physico-mechanical properties. Some examples are the high alite content cements used on high initial strength cements, the high belite content cement to the higher strengths at older ages; the setting time of cement that is related to the C_3A and gypsum contents. A Portland cement with higher C_3A content and lower gypsum will have a faster setting time.

In the Rietveld method [5] applied to XRD, a theoretical pattern is calculated and fitted to an observed powder diffractogram until the calculation describes the observed pattern as closely as possible. The calculation of a theoretical powder pattern requires crystal structure information about the phases to be quantified. The accuracy of the quantification is directly dependent upon the quality of the structural and instrumental parameters. Overviews concerning the application of the Rietveld method to clinker phase analysis have been more recently given [6,7,8,9,10,11]. Applications on the technique on white cement samples are also presented in some studies [12,13].

The aim of this research was to quantify all the cement phases present in a group of nine samples, produced without blastfurnace slags or also glassy materials.

2. Methods

Nine samples from nine different kilns were used in this research. Samples were already finely ground. Wet chemical analyses were performed in the Civil Construction Materials Laboratory of IPT (Institute for Technological Research). X-ray diffraction was held in the LCT (Technological Characterization Laboratory) from the University of São Paulo.

2.1 Wet chemical analysis and Bogue determination

Chemical analyses were performed by wet chemical procedures commonly applied in the cement industry and in accordance with the Brazilian Standards, which can be summarized as:
- Loss on ignition: gravimetric method;
- Silicon dioxide (SiO_2): gravimetric method, after perchloric acid digestion;
- Aluminum oxide (Al_2O_3), ferric oxide (Fe_2O_3), calcium oxide (CaO), and magnesium oxide (MgO): complexometric titration with EDTA solution;
- Sulfur trioxide (SO_3): gravimetric method, after sulfate precipitation with $BaCl_2$ solution;
- Na_2O, K_2O, by flame photometry;
- Free lime content: titration, by ethylene glycol methodology;
-Insoluble residue: gravimetric method, after digestion in hydrochloric acid followed further digestion in sodium hydroxide solution;
- Carbon dioxide (CO_2): gasometric method, after thermal decomposition of the sample followed the gas absorption in the potassium hydroxide solution.

The potential phase composition of the white cement was calculated based on the results of chemical analysis, according to the Bogue method. The Bogue potential results were standardized to a total of 100% to enable the comparison with Rietveld analysis. The equations were transformed to use as a cement quantitative analysis and are presented below:

- Alite=(4,071*CaO)–(7,6*SiO_2)–(6,71*Al_2O_3)–(1,43*Fe_2O_3)–(2,85*SO_3)–(%free lime)
- Belite=(2,867*SiO_2)-(0,7544* %Alite)
- C_3A=(2,65*Al_2O_3)-(1,692*Fe_2O_3)
- Ferrite= 3,04*Fe_2O_3
- $CaSO_4$=1,7*SO_3
- $CaSO_3$=2,27*CO_2
- Periclase=%MgO-2,0 (if %MgO$\geq$2,0)

Due to the absence of ferrite in a white Portland cement, their results were not considered in the studied samples.

2.2 X-Ray diffraction

The powder diffraction analysis (XRD) were held in a Bragg-Brentano diffractometer (Panalytical X'Pert Pro) with a broad focus CuKα tube anode applying 40KV/40mA. The detector used was the X'Celerator, a multiple strip detector that allows a measurement in less time than a point detector.
The samples were mounted in a 27mm diameter holder by hydraulic pressing. The measurements were carried out in the range of 10 to 70 º2θ with a step size of 0.02 º2θ and a counting time of 3s/step, under configuration of ½º divergent slit, graphite monochromator and 0.2mm receiving slit. The recorded X-ray diffractograms are available in computer files and can be loaded directly into Rietveld program for further analysis.
Rietveld refinement is based on comparison of an observed X-ray pattern and a pattern calculated from structure data of one or more phases. Calculation is finished successfully when the residual error is minimized by the refinement of global and structural parameters.
The Rietveld refinement, based on comparison of an observed X-ray pattern and a pattern calculated from structure data of each phase, is successfully finished when the residual error is minimized by the refinement of global and structural parameters. Structural data of alite [14], belite [15], cubic C_3A [16], orthorhombic C_3A [17], $C_{12}A_7$, hemihydrate, gypsum, anhydrate, free lime, periclase, portlandite, calcite and dolomite were used for refinement and quantification.
Data sets were refined by the Rietveld method using the software X'Pert HighScore Plus, from Panalytical. The background was fitted with a Chebyshev function with 4 terms. The peak profiles were modeled using a pseudo-Voight function. The lattice constants, the phase fraction, and zero shift were also refined.

3. Results

3.1 Chemical Results

The oxides chemical composition by wet chemical analysis with free lime results and also loss on ignition (LOI), insoluble residue and CO_2 are presented on Table 1.

Table 1: Chemical composition of different studied cement samples.

Component	Sample								
	Cem1	Cem2	Cem3	Cem4	Cem5	Cem6	Cem7	Cem8	Cem9
LOI	5,1	5,5	11,7	2,6	4,1	7,9	2,7	1,7	10,6
SiO_2	22,5	20,5	17,9	22,2	20,4	19,7	22,2	24,7	18,2
Al_2O_3	3,3	4,0	2,1	4,2	4,3	4,0	4,3	2,1	4,0
Fe_2O_3	0,5	0,3	0,2	0,4	0,5	0,2	0,3	0,4	0,3
CaO	64,5	65,8	64,2	67,2	67,1	65,0	67,1	68,6	63,3
MgO	2,3	0,3	0,1	0,1	0,3	0,5	0,1	0,3	1,3
SO_3	1,5	3,0	3,0	3,0	3,2	2,4	3,1	1,9	2,3
Na_2O	0,0	0,1	0,1	0,0	0,0	0,0	0,0	0,1	0,0
K_2O	0,1	0,5	0,5	0,1	0,0	0,2	0,1	0,1	0,1
Free lime	1,72	1,7	1,8	2,0	4,8	1,9	2,0	2,3	1,6
IR	0,5	0,1	0,4	0,2	0,2	1,0	0,2	0,1	0,0
CO_2	3,3	3,4	9,4	0,9	0,6	5,6	0,9	0,3	8,5

IR=Insoluble residue;LOI=Loss on ignition

3.2 Bogue equations results

The potential compositions based on Bogue equations are presented in the Table 2. The results reached to negative potential composition of belite in some samples. To obtain a total result of 100%, the negative belite results were settled to “zero” percent and the results were recalculated, as shown in the Table 3. The silicates and aluminates results were presented to the easily comparison with results from Rietveld refinement method.

Table 2: Chemical composition of different studied cement samples.

Component	Sample								
	Cem1	Cem2	Cem3	Cem4	Cem5	Cem6	Cem7	Cem8	Cem9
Alite	58,4	69,7	88,1	64,4	73,9	71,7	62,9	68,5	73,7
Belite	20,5	6,3	-15,0	15,	2,7	2,5	16,3	19,1	-3,5
C_3A	8,0	10,2	5,2	10,5	10,6	10,2	10,8	4,8	10,1
C_4AF	1,4	0,9	0,7	1,1	1,5	0,6	1,0	1,3	0,8
Free lime	1,7	1,6	1,8	2,0	4,8	1,9	2,0	2,3	1,6
MgO	0,3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
$CaSO_4$	2,5	5,1	5,0	5,2	5,4	4,1	5,2	3,3	3,9
$CaCO_3$	7,4	7,7	21,2	2,1	1,3	12,8	2,1	0,7	19,2
Total	100,3	101,6	107,1	100,3	100,2	103,7	100,4	100,1	105,8

Table 3: Recalculated potential composition of different studied cement samples, based on Bogue equations.

Component	Sample								
	Cem1	Cem2	Cem3	Cem4	Cem5	Cem6	Cem7	Cem8	Cem9
Alite	58,0	68,5	71,9	64,1	73,6	68,4	62,5	68,4	67,4
Belite	20,3	6,2	0,0	15,0	2,7	2,4	16,2	19,1	0,0
Silicate	78,3	74,7	71,9	79,1	76,3	70,8	78,7	87,5	67,4
C_3A	8,0	10,0	4,3	10,5	10,6	9,8	10,8	4,8	9,2
C_4AF	1,4	0,9	0,6	1,1	1,5	0,5	1,0	1,3	0,8
Aluminate	9,4	10,9	4,9	11,6	12,1	10,3	11,8	6,1	10,0
Free lime	1,7	1,6	1,5	1,9	4,8	1,8	2,0	2,3	1,4
Periclase	0,3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
$CaSO_4$*	2,5	5,0	4,1	5,1	5,4	4,0	5,2	3,3	3,6
$CaCO_3$	7,3	7,6	17,3	2,1	1,3	12,2	2,1	0,7	17,6
RI	0,5	0,1	0,3	0,2	0,2	0,9	0,2	0,1	0,0
Total	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0

3.3 Rietveld quantitative results

A scan with Rietveld refinement quantitative results is presented in the Figure 1. The difference plot graphic shows the fitting of the refinement. GOF (goodness of fitting) of all analyzed samples were below 3,0.

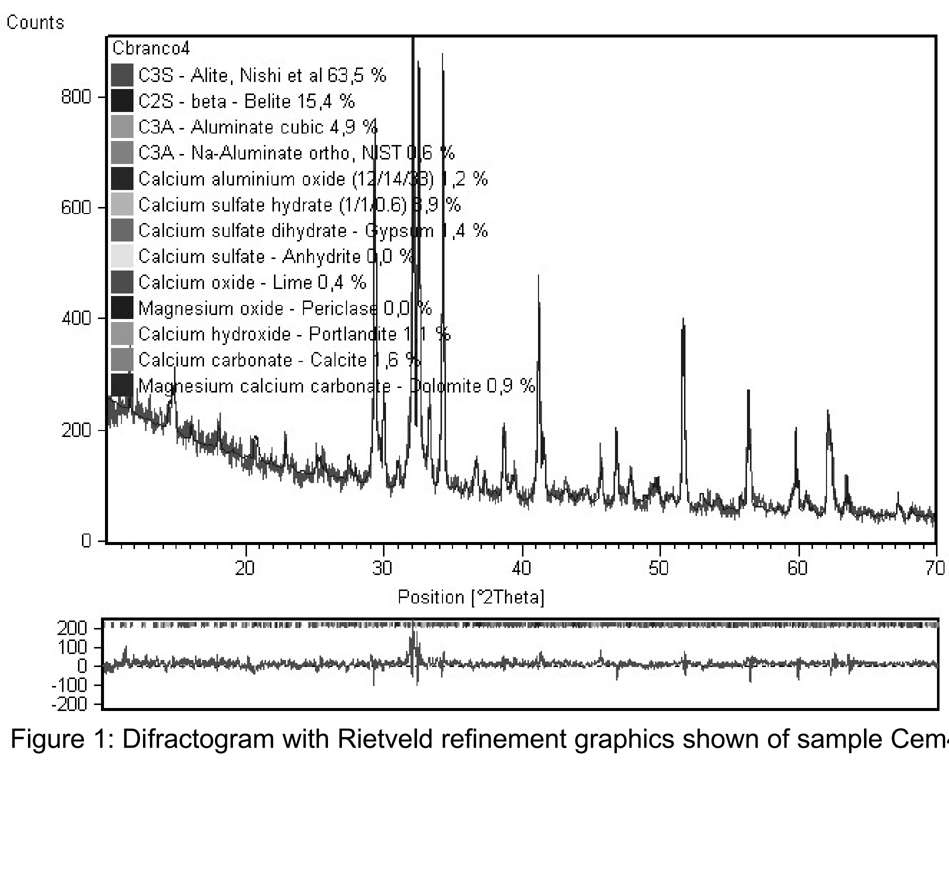


Figure 1: Difractogram with Rietveld refinement graphics shown of sample Cem4.

The Rietveld phase compositions are presented in the Table 4. The total of silicate and aluminate phases percentage are also presented.

Table 4: Phases composition based on Rietveld method.

Component	Sample								
	Cem1	Cem2	Cem3	Cem4	Cem5	Cem6	Cem7	Cem8	Cem9
Alita	61,5	70,9	52,1	63,5	72,0	54,5	67,7	70,1	48,7
Belita	11,2	8,8	9,7	15,4	6,3	9,6	14,9	16,6	7,3
Silicate (total)*	72,7	79,7	61,8	78,9	78,3	64,1	82,6	86,7	56,0
C_3A cubic	4,1	0,0	1,6	4,9	5,5	4,6	4,6	3,1	3,8
C_3A orthorhombic	0,0	2,9	0,0	0,6	0,0	0,1	2,6	0,0	0,6
Mayenite	1,0	0,4	0,9	1,2	1,4	2,7	1,9	0,0	2,3
Aluminate (total)**	5,1	3,3	2,5	6,7	6,9	7,4	9,1	3,1	6,7
Hemi-hydrate	0,0	5,5	4,2	8,9	3,4	4,8	0,0	4,1	5,2
Gypsum	8,5	1,7	0,0	1,4	7,7	4,1	2,0	0,0	1,8
Anhydrite	0,0	0,0	0,0	0,0	0,0	0,0	0,0	2,8	0,0
$CaSO_4$ phase***	8,5	7,2	4,2	10,3	11,1	8,9	2,0	6,9	7,0
Free lime	0,0	0,3	0,3	0,4	0,2	0,2	0,9	0,5	0,1
Periclase	0,0	0,0	0,1	0,0	0,0	0,0	0,3	0,7	0,3
Portlandite	0,0	0,0	0,0	1,1	3,6	0,0	0,0	1,2	0,0
Calcite	5,6	9,4	29,4	1,6	0,0	11,4	3,6	0,9	16,8
Dolomita	8,1	0,0	1,7	0,9	0,0	7,9	1,6	0,0	13,1
Calcite+dolomite	13,7	9,4	31,1	2,5	0,0	19,3	5,2	0,9	29,9
Total	100,0	100,1	100,0	99,9	100,0	100,1	100,0	100,0	100,0

*alite+belite;**C_3A+mayenite;***hemihydrate+gypsum+anhydrite

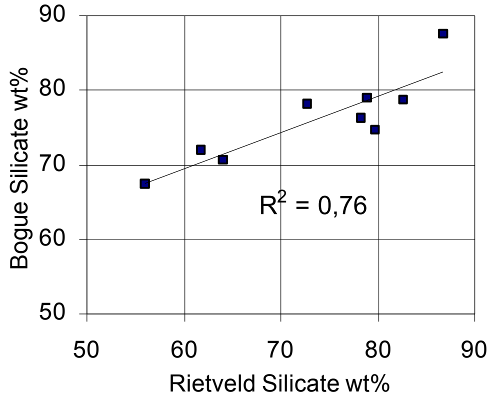
4. Discussion

The comparison of results showed good correlation for the silicates (R^2=0,76) and short for aluminates (R^2=0,59 and R^2=0,86 excluding one sample). A good correlation was found for the calcite (R^2=0,90) and very good for the sum of calcite and dolomite versus the CO_2 content by chemical analysis (R^2=0,98). The correlations are shown in the Figures 2a to 2e.

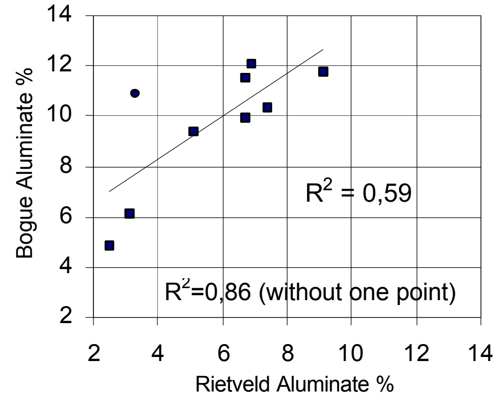
The best correlation was observed on phases without substitution ions in the unit cell, as observed in the calcite, dolomite and also free lime and portlandite. The good performance of calcite and dolomite on the refinement is also due to the higher crystallinity and also the presence of isolated high intensity peaks (example of the 29,4°2θ of calcite without overlapped peaks from other phases).

Composition of real clinker crystals are not chemically pure as required by the Bogue method, limitating the correlation for its phases. Significant Mg, Al and also other elements may be incorporated in alite and also belite.

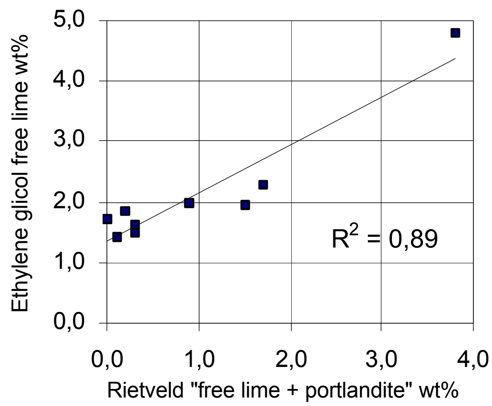
This research shows the Rietveld Method as an important tool for qualification and quantification of cement. In this way, the method can be very useful to study the mechanical properties of cement.



2a



2b



2c

Figure 2: Correlation between Rietveld method wt% and Bogue potential wt%:

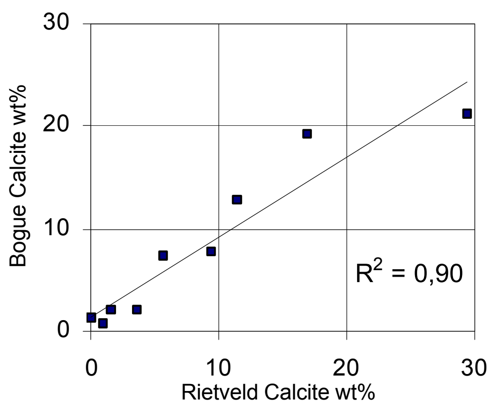
2a-Silicates (alite+belite);

2b-Aluminates (Cub.C_3A+ort.C_3A+$C_{12}A_7$);

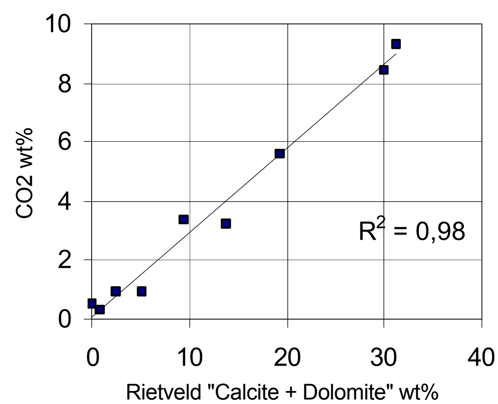
2c-Rietveld Free lime+Ca(OH)2 x Rietveld free lime;

2d-Calcite; and,

2e-Calcite + Dolomite x CO_2.



2d



2e

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