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Abstract

Cement paste hydration is a complex physical-chemical process. The aim of this paper is to use three approaches to determine the degree of hydration: portlandite quantification, scanning electron microscopy and bound water quantification. In order to investigate the physical-chemical and mechanical properties, as well as the hydrates generated. Portland cement was synthesized and characterized in the laboratory. At all hydration durations, the portlandite quantification method and SEM-BSE image analysis show similar results. The method of SEM images analysis requires time to gather and process images, but is unaffected by the type of hydrates produced. The bound water quantification method gives a lower degree of hydration than two other methods at all hydration times. To test the reliability of these procedures, the compressive strength was calculated based on the degree of hydration. The results indicate that the portlandite quantification method and SEM-BSE image analysis are more accurate than the bound water quantification approach in terms of reproducing the experimental results.

Keywords: Cement, Hydration, Portlandite, Bound water, SEM-BSE, Compressive strength.

I. Introduction

Portland cement is a mixture of clinker and calcium sulfate in a ratio of approximately 95:5% [1]. Cement is one of the essential constituents in the manufacture of concrete; the most widely used building material in the world. The mineralogical composition of clinker consists of alite (C_3S: Ca_3SiO_5), belite (C_2S: Ca_2SiO_4), tricalcium aluminate (C_3A: $Ca_3Al_2O_6$) and tetra-calcium aluminoferrite (C_4AF: $Ca_4Al_2O_{10}Fe_2$). During hydration, the cement reacts with water resulting in the formation of different hydrates. Ettringite is formed from the reaction of calcium sulfate, tricalcium aluminate and water. The reaction of the silicates leads to the formation of portlandite (CH) and a Calcium Silicate Hydrate (C-S-H).

Previous studies [2, 3] have shown that C-S-H is the main hydrate of hydrated cement paste and contributes significantly to macro-properties of concrete such as strength and durability.

The composition of the C-S-H, depends on the water to cement ratio (w/c ratio), the temperature as well as the composition of the cement [4–6]. Indeed, in the literature, there are three distinct phases C-S-H depending on the C/S (CaO/SiO_2) ratio:

- C-S-H (α): 0.66 < C/S < 1 formed when the [Ca^{2+}] concentration is less than 2 mmol/l.
- C-S-H (β): 1 < C/S < 1.5 formed when the [Ca^{2+}] concentration is between 2 and 22 mmol/l.
- C-S-H (ϒ): C/S = 1.7 formed when the [Ca^{2+}] concentration is greater than 22 mmol/l.

In addition, Phung et al [7] have shown that the C/S molar ratio of the cement paste was critical in determining the microstructure of C-S-H and the decrease in the C/S ratio can alter the microstructure of C-S-H.

The amount of hydrates formed during hydration depends on the degree of hydration which is defined as a ratio of the amount of hydrated cement to that of the initial anhydrous cement. There are several experimental approaches to determine the degree of hydration of cement such as:

- Scanning electron microscopy (SEM-BSE) [8, 9].
- X-ray diffraction (XRD) [10].
- Thermogravimetric analysis (TGA) [11].
- Measurement of the heat of hydration by isothermal calorimetry [9, 12].
- Nuclear magnetic resonance (NMR) [3, 13].
- Compressive strength [14].

Several studies have employed the thermal analysis method (TGA) to determine the degree of hydration of cement. The basic idea is to use the following simplified equations ((Eq1) -> (Eq8)) to measure the portlandite amount (CH) [10, 11] and chemically bound water [12] generated during hydration [15–17].

$$C_3S + 5.3\ H \rightarrow C_{1.7}SH_4 + 1.3\ CH \quad (1)$$

$$C_2S + 4.3\ H \rightarrow C_{1.7}SH_4 + 0.3\ CH \quad (2)$$

$$C\bar{S} + 2\ H \rightarrow C\bar{S}H_2 \quad (3)$$

$$C_3A + 6\ H \rightarrow C_3AH_6 \quad (4)$$

$$C_3A + 3\ C\bar{S}H_2 + 26\ H \rightarrow C_6A\bar{S}_3H_{32}\ (\text{Ettringite}) \quad (5)$$

$$C_4AF + 3\ C\bar{S}H_2 + 30\ H \rightarrow C_6A\bar{S}_3H_{32} + CH + FH_3 \quad (6)$$

$$2\ C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3\ C_4A\bar{S}H_{12} \quad (7)$$

$$2\ C_4AF + C_6A\bar{S}_3H_{32} + 12\ H \rightarrow 3\ C_4A\bar{S}H_{12} + 2\ CH + 2\ FH_3 \quad (8)$$

In a recent study, Lei et al [3] used the $Ca(OH)_2$ quantification method measured by TGA analysis and the NMR method for the determination of the degree of hydration of cement paste (W/C = 0.3). The ^{29}Si NMR and ^{27}Al NMR is used to quantify the phases containing these element in a cementitious material. Good consistency between the two methods was observed (74.0% for the $Ca(OH)_2$ quantification method at 28 days and 78.4% for the NMR method at 28 days). However, in his study, the degree of hydration was calculated according to the equation (Eq9):

$$\alpha(t) = \frac{m\ Ca(OH)2}{25\ wt.\%} * 100 \quad (9)$$

Knowing that the 25% value is not always constant because the mineral composition of cement is always variable. In addition, the NMR method is a complicated method (long analysis time, 1 day for ^{29}Si NMR analysis), therefore, in this study, three methods used are: Method 1: Portlandite quantification method, Method 2: Bound water of quantification method, Method 3: SEM-BSE image analysis method.

The first approach for evaluating the degree of hydration is to use the following equations to calculate the $Ca(OH)_2$ amount estimated from the TGA analysis according to (Eq10):

$$m_{Ca(OH)2} = \frac{\Delta m\ 450°C-550°C(t).MCa(OH)2}{MH2O} \quad (10)$$

with:
$m_{Ca(OH)2}$: Amount of $Ca(OH)_2$.
$\Delta m\ 450°C - 550°C(t)$: The mass loss of the samples between 450 °C and 550 °C from the TGA analysis.
$M_{Ca(OH)2}$: Molar mass of $Ca(OH)_2$ equal to 74.09 g/mol.
M_{H2O}: Molar mass of water equal to 18 g/mol.
Then the degree of hydration of the cement can be calculated using the equation below (Eq11):

$$\alpha(t) = \frac{m\ Ca(OH)2}{mC\ .\ 0} \quad (11)$$

The mass of the sample can be calculated using the equation (Eq12):

$$m_c = \frac{m\ sample}{\left(1+\frac{w}{c}\right).(1+LOI)} \quad (12)$$

with:
α(t): Degree of hydration of the cement at time t.
m_{sample}: Mass of the samples.
m_c: Mass of the initial cement.
Υ_0: Amount of $Ca(OH)_2$ produced upon complete hydration of the cement. This value depends on the composition of the cement as well as the stoichiometry of the C-S-H gel of the cement hydration reactions (Eq(1) -> Eq(8)).
w/c: the water to cement ratio of the paste.
LOI: loss of cement on ignition.

The second experimental approach for determining the degree of hydration of cement recommended by the National Institute of Standards and Technology (NIST) consists in determining the amount of water chemically bound according to the following equation (Eq13):

$$\alpha(t) = \frac{Wn\ (t)}{Wn(\infty)} * 100 \quad (13)$$

with:
α(t): degree of hydration of the sample at time t.
$W_n(t)$: amount of bound water for a sample at time (in gram of water per 100 g of anhydrous cement).
$W_n(\infty)$: amount of water bound for a completely hydrated sample (in gram of water per 100 g of anhydrous cement).
The $W_n(t)$ value can be determined experimentally by (Eq14) if the two following conditions are met:

- No carbonation in the cement paste.
- Low weight loss of anhydrous cement before 1000° C

$$W_n(t) = \frac{\Delta m\ sample\ (105\ °C-1000\ °C)(t)}{m\ sample\ (1000°C)(t)} * 100 \quad (14)$$

In order to determine the $W_{n(\infty)}$ value, NIST provides an approximate theoretical estimation of the amount of bound water produced for the five main mineral phases of cement after hydration is complete [18].

The third method consists of the SEM-BSE image analysis technique to study the distribution of phases in the observation area. Indeed, this technique has been frequently applied to examine the cementitious material's microstructure [19]. In an SEM-BSE image, the backscatter coefficient increases monotonically with the average atomic number of each phase [20]. This allows differentiating and quantifying of each crystalline phases in the analysis area. However, in cement-based materials, the backscattering coefficients of numerous hydration products (C-S-H, Ettringite, etc.) are too similar to be separated individually on the histogram [19]. Because the epoxy backscatter coefficient is substantially lower than the other phases, the pores may be easier to segment [19].

The SEM-BSE image analysis has been used to quantify phases of hydrated cement paste [21], to study the phase distribution in the mortar interphase zone [22], and to estimate the reaction fraction of mineral additions in the cement matrix [9]. The three steps in this approach are as follows:

- Choice of magnification and resolution of the image.
- Phase segmentation by gray level thresholds.
- Quantification of phases in the analysis area.

Table 1 summarizes the advantages and disadvantages of the three methods of determining the degree of hydration used in this study.

Table 1
Advantages and disadvantages of the three methods (Method 1: $Ca(OH)_2$ quantification method, Method 2: Bound water of quantification method, Method 3: SEM-BSE image analysis method).

Method	Method 1	Method 2	Method 3

Advantages	• Ease of sample preparation. • Ease of processing the result.	• Ease of sample preparation. • Ease of processing the result.	• Apply cement containing a pozzolanic mineral addition, a slag.
Disadvantages	• Do not apply cement containing a pozzolanic mineral addition.	• An adequate analysis program to avoid the loss of bound water.	• Difficulty of sample preparation • Difficulty of processing the result.

There have been no researches published to far that compare the various methods for determining the degree of hydration of CEM I cement. Therefore, the purpose of this study is to compare the feasibility and reliability of the SEM –BSE image analysis approach for estimating the degree of hydration of cement with two other methods using the thermogravimetric analysis (TGA).

II. Material and method

II.1. Method of characterization of the synthesized clinker and cement

The clinker cement (OPC 97TM) used in this study was synthesized in the laboratory by burning a mixture of limestone ($CaCO_3$), silica oxide (SiO_2), aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3). The proportion of components was calculated using the modulus usually used in the cement industry: the Lime Saturation Factor (LSF), the Silica Ratio (SR) and the Alumina Ratio (AR). The calculations of modulus (LSF, SR and AR) are presented by the equations below ((Eq15) -> (Eq17)):

$$LSF = \frac{100 * \%CaO}{2.8*\%SiO2+1.18*\%Al2O3+065*\%Fe2O3} \quad (15)$$

$$SR = \frac{\%SiO2}{\%Al2O3+\%Fe2O3} \quad (16)$$

$$AR = \frac{\%Al2O3}{\%Fe2O3} \quad (17)$$

In this study, the values LSF = 97, SR = 2.6 and AR = 1.45 were used for the formulation of mixture. Table 2 shows the composition of the components of the formulation.

Table 2
Mix design for the production of the clinker cement OPC 97TM.

Formula	Limestone (wt. %)	Alumina oxide (wt. %)	Iron oxide (wt. %)	Silica oxide (wt. %)
OPC 97TM	79.99	3.17	2.32	14.52

The raw materials were first mixed by adding water with a water/material ratio = 0.6 in order to have good homogeneity. After drying at 105°C, pellets (with a diameter of 40 mm and a height of 15 mm) are formed using a press and a force of 5 KN. The pellets were burned in a furnace at 200°C for 20 minutes, then the temperature increases to 1450°C with a heating rate of 7°C/minute, and kept at this temperature for 15 minutes. After clinkerization, the obtained clinkers were cooled in the furnace to reach the room temperature. Portland cement was produced by adding gypsum ($CaSO_4.2H_2O$) to ground clinker in order to have an SO_3/Al_2O_3 molar ratio of 0.6.

The content of free lime in the clinker was determined by the Schlafer-Bukokowski method. Indeed, cement manufacturers consider that a clinker, whose composition is perfectly dosed, has a CaO_{free} content of less than 2% wt. [23]. Therefore, in this study, the maximum acceptable CaO_{free} content is set at 2%.

The mineralogical composition of the clinker was identified by X-ray diffraction (XRD) and quantified according to the Bogue modified formula, which takes into account the presence of CaO_{free} [24].

The chemical composition of the clinker and hydrated cement paste phases was analyzed on the polished sections using a Hitachi S-4300 SE/N scanning electron microscope operating in backscattered electron mode (20 keV) and equipped with an energy dispersive X-ray spectrometer (EDS). For the measurement, the points were carried out on several zones.

The particle size distribution of the OPC 97TM cement was measured using the Beckman Coulter – LS13 320 type device after dispersing in an ethanol solution. The absolute density of the OPC 97TM cement was carried out

using an Accupyc 1330 helium pycnometer. The Blaine specific surface of the cement was measured according to standard NF EN 196-6 [25]. In this study, the Blaine surface of the cement is between 3500 and 4000 cm^2/g.

The chemical composition of the synthetized cement was verified by X-Ray fluorescence (XRF). The mineralogy of cement and hydrated cement paste was analyzed by X-ray diffraction (XRD) using a BRUKER D2 Advance device equipped with a Cu anticathode, $\lambda = 1.5406$ Å with the angle 2θ from 5° to 80° and a step of 0.02.

II.2. Method for determining the degree of hydration

In this study a cement pastes with a w/c ratio of 0.5 was used to determine the degree of hydration. After three minutes of mixing, the paste was introduced into the polytetrafluotethylene molds for measuring the degree of hydration, and into the 1x1x1 cm^3 size molds for the measurement of compressive strength. The cement pastes were demolded after 24 hours and stored in the saturated lime solution.

Based on previous studies [23, 26–29], the compressive strength of the cement paste was measured on the cube of dimension 1x1x1 cm^3 under a constant stress of 0.3 MPa/s using a uniaxial press at 2, 15 and 28 days of hydration. For each measurement, 6 samples were tested.

II.2.1. Determination of the degree of hydration by thermogravimetric analysis (TGA)

To prevent carbonation of the cement paste, in this study, no method of stopping hydration was used. The cement paste for the TGA analysis was analyzed immediately upon reaching the desired hydration time. The device used is the NETZSCH STA 409 type with the following experimental conditions:

- During the analysis the sample is kept under a flow of Argon at a flow rate of 75 ml/min.
- The temperature increases from 30 °C to 105 °Cat a rate of 2 °C/min, then maintained at 105 °C for 1 hour before increasing to 1100 °C at a rate of 3 °C/min.

II.2.2. Determination of the degree of hydration by the SEM-BSE image analysis method

To stop the hydration, the samples for image analysis were submerged in an acetone solvent solution. Indeed, drying samples at 105 °C has the potential to alter the microstructure of the cement paste [30] and so impair image analysis results. A JEOL scanning electron microscope operating in backscattered electron mode (15 keV) with a magnification of 500 and a resolution of 1280 x 960 pixels was used to capture images of the sample. For the measurement, around 20 pictures were taken at various positions throughout the sample.

III. Results

This part presents, on the one hand, the result of characterization of the cement (OPC 97TM) and the cement paste in order to assess the quality of the cement synthesized in the laboratory, and on the other hand, the results of the degree of hydration of the paste determined by three different methods.

III.1. Characterization of clinker and synthesized cement

The CaO_{free} content of the clinker measured according to the Schlafer-Bukokowski method is 1.287%, which is less than the limit value (2%). This indicates that the clinker's composition is well dosed.

Table 3 and Table 4 show the chemical composition of the mineral phases of the clinker identified by SEM-EDS analysis. Approximately 30 points were measured for each phase in different areas.

Table 3
Results of the SEM-EDS analysis on the silicate phases of the synthesized clinker.

Mineral phase	Formula	CaO/SiO_2 (Theoretical ratio)	CaO/SiO_2 (SEM-EDS results)
Alite	Ca_3SiO_5	3	3.42
Belite	Ca_2SiO_4	2	2.44

Table 4
Results of the SEM-EDS analysis on the interstitial phases of the synthesized clinker.

Mineral phase	Formula	CaO/Al_2O_3 (Theoretical ratio)	CaO/Al_2O_3 (SEM-EDS results)
Tricalcium aluminate	$Ca_3Al_2O_6$	1.5	2.44
Calcium aluminoferrite	$Ca_4Al_2O_{10}Fe_2$	2	2.575

The results of SEM-EDS analysis showed that the ratio of the main oxides in the four phases was higher than the theoretical value. A similar result was found in Gineys's et al. research on clinker synthesized in the laboratory [23]. The difference between the theoretical and experimental values could be due to the presence of minor elements in the mineral phases, for example, Al and Fe in the C_3S and C_2S phases. This could influence the ratio of major elements in these phases. Table 5 show the physical characteristics of OPC 97TM cement. The Blaine surface of the cement reaches 3800 cm^2/g, which respects the values of the Blaine surface targeted between 3500 and 4500 cm^2/g.

Table 5
Physical characteristics of OPC 97TM cement synthesized in the laboratory.

Cement	Density (g/cm^3)	Blaine surface (cm^2/g)	BET surface (m^2/g)	d10 (µm)	d90 (µm)
OPC 97TM	3.15	3800	1.224	0.72	43.31

The chemical composition of OPC 97TM cement is also presented in Table 6.

Table 6
Chemical composition of OPC 97TM cement.

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	LOI at 950 °C	Total
(wt.%)	20.5	4.7	3.1	65.5	1.90	3.6	99.2

The chemical composition of the main elements of the hydrated calcium silicate by the SEM-EDS analysis measured on the sample of the hydrated cement paste at 2 days is presented in the Fig.1. Around 100 points were measured in four different areas. The $CaO\text{-}SiO_2\text{-}Al_2O_3$ ternary diagram is superimposed on the ternary diagram produced by Lothenbach [31]. This diagram shows the positions of the main cement hydrates: $Ca(OH)_2$, C-S-H (with two C/S ratios) or even C-A-S-H. The diagrams show that the hydrated calcium silicates are mainly concentrated in areas where the C/S ratio is greater than 1.7. A similar results have been found in previous studies on CEM I [11, 32]. Fig.2 illustrates the C/S and Al_2O_3/SiO_2 ratios of the different measured points.

The result show that:

- The C/S ratio (CaO/SiO_2) obtained in the C-S-H phase varies from 2.5 to 3.5 but is always higher than the value of 1.7 used in the equations for the description of cement hydration (Eq1), (Eq2). This difference can be due to the EDS points made and to the size of the diffusion bulb which analyzes an area and not a point. Typically, the diffusion bulb's size is 1 μm^3 and the resolution of a SEM 20 kV tungsten filament is 3 nm. Thus, other hydrates are analyzed and will have an influence on the C/S and Al_2O_3/SiO_2 ratios, in particular, the C/S ratio [32].
- The average value of the Al_2O_3/SiO_2 ratio of hydrates measured is equal to 0.14 and this value is very consistent with the initial value of the Al_2O_3/SiO_2 ratio in the anhydrous OPC 97TM cement (the Al_2O_3/SiO_2 ratio in the cement is equal to 0.137). This result means that all of the aluminum in the cement is found in the C-A-S-H and C-S-H phases. The incorporation of aluminum into the C-S-H phase has been demonstrated in research by Richardson et al [33]. This study showed an Al/Si ratio equal to 0.25, corresponding to the maximum aluminum that can be incorporated into C-S-H.

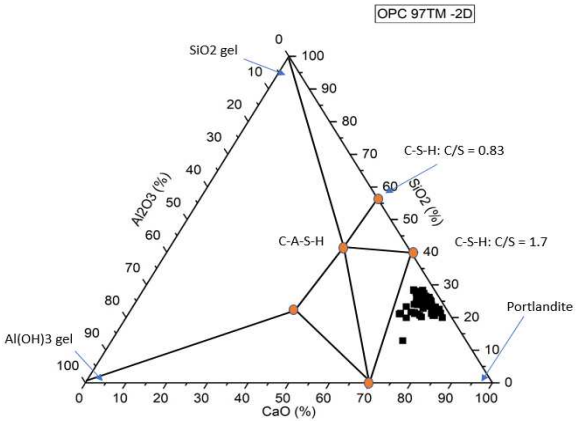

Fig. 1 $CaO\text{-}SiO_2\text{-}Al_2O_3$ ternary diagram obtained for the cement paste after 2 days of hydration.

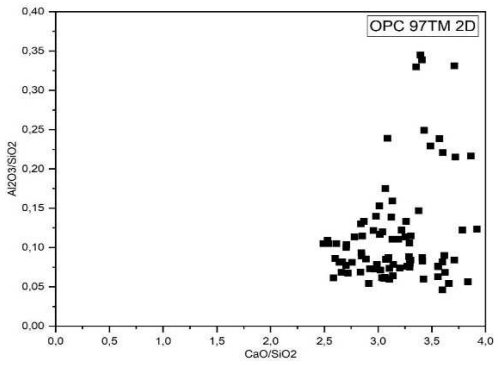

Fig. 2 Ratio of the principal elements of hydrated calcium silicate measured by SEM-EDS analysis on the sample of the cement paste after 2 days of hydration.

The evolution of the mineral phases over time of hydration identified by the XRD analysis is presented in Fig.3.

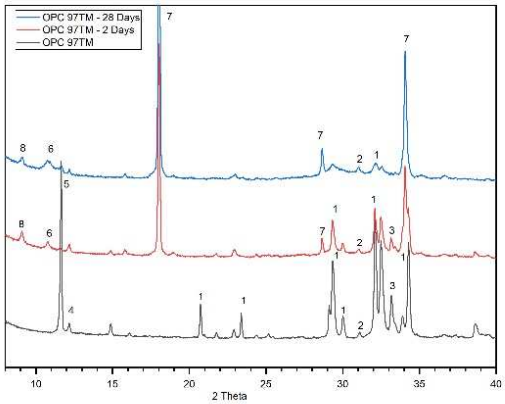

Fig. 3 X-Ray diffraction of OPC 97TM over time of hydration (1: C_3S, 2: C_2S, 3: C_3A, 4: C_4AF, 5: Gypsum, 6: Afm, 7: $Ca(OH)_2$), 8: Ettringite (Aft).

The formation of additional phases such as ettringite and portlandite in the hydrated cement paste has been observed. These hydrates formed correspond to the products described in equations (Eq 1) -> (Eq 8). However, the presence of hydrated calcium silicate (C-S-H) is difficult to detect due to its amorphous nature.

The compressive strength of the cement paste is presented in the Table 7. This result is consistent with the previous XRD result showing the transformation of anhydrous phases to hydrates in hydrated cement paste, which is the origin of resistance development.

Table 7
Compressive strength of the cement paste over the time of hydration.

Time (days)	Compressive strength (Mpa)	Deviation (%)
2 days	25.26	6.5
15 days	57.98	9.5
28 days	66.61	8.5

III.2. Degree of hydration of cement by portlandite quantification analysis by TGA analysis

The amount of portlandite produced during cement hydration was estimated by TGA analysis on cement pastes at 2 and 28 days of hydration. Table 8 shows the mineral composition of the cement and the $Ca(OH)_2$ amount produced during complete hydration, according to the calculation from the simplified equations (Eq1) -> (Eq8). Indeed, the results of the SEM-EDS analysis on the clinker and the cement paste showed a different element ratio than the theoretical ratios used in these equations.

Table 8
$Ca(OH)_2$ production for a complete hydration of cement of OPC 97TM cement.

Anhydrous phases	Mass content in cement (%)	CH mass for 1 g of anhydrous cement (g/g of cement)
C_3S	73.96	0.312
C_2S	4.77	0.0062
C_3A	5.93	0
C_4AF	9.77	0.0147
CaO_{free}	1.24	0
Gypsum	4.33	0
Total	100	0.3329

Fig.4 shows the TGA analysis curve of the cement paste after 2 days of hydration.

- Zone (I): the temperature increases from 30 °C to 105 °C to remove evaporable water.
- Zone (II): the temperature is maintained at 105 °C for 1 hour to remove the rest of evaporable water.
- Zone (III): the temperature between 650 °C and 800 °C corresponds to the decomposition of calcite temperature. In this case, the loss of weight of the sample is very low, this means that the protocol allows avoiding the phenomenon of carbonation and the quantity of $Ca(OH)_2$ determined between 450 °C and 560 °C is the totality of the $Ca(OH)_2$ produced during the hydration of the cement.

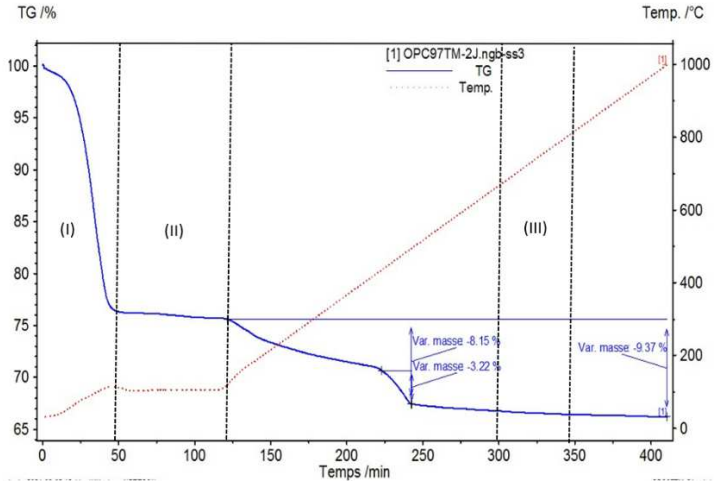

Fig. 4 TGA analysis of the cement paste (w/c = 0.5) after 2 days of hydration.

Table 9 shows the amount of portlandite as well as the degree of hydration calculated according to (Eq10), (Eq11) and (Eq12) taking the value Υ_0 (total amount of Portlandite produced when the hydration is completed) equal to 0.3329 (Table 8).

Table 9
Quantity of $Ca(OH)_2$ and the degree of hydration of the cement paste over the time of hydration.

Time (days)	Portlandite mass (g/100 g of pastes)	Degree of hydration (%)
2 days	13.24	60.09
28 days	20.44	92.16

III.3. Degree of hydration of cement by quantification of chemically bound water by TGA analysis

This approach determines the degree of hydration of the cement according to (Eq13) and (Eq14) using TGA analysis. The $W_n(\infty)$ value is calculated based on a theoretical approximation of the amount of chemically bound water for the five main phases of cement upon complete hydration. Table 10 shows the theoretical amount of water in the cement for complete hydration.

Table 10
Theoretical amount of water bound for complete hydration of OPC 97TM cement.

Anhydrous phases	Masse content in cement (wt.%)	Quantity of bound water produced in g of water/g of phase in the cement	Mass of water related to complete hydration (g)
C_3S	73.96	0.24	17.75
C_2S	4.77	0.21	1.00
C_3A	5.93	0.40	2.372
C_4AF	9.77	0.37	3.614
CaO_{free}	1.24	0.33	0.409
Gypsum	4.33	0	0
Total	100		25.145

From Table 10, we conclude that the $W_n(\infty)$ = 25.145 (g).
From the result of the TGA analysis (Fig.4), we then obtain:
$\Delta m\ sample\ (105\ °C - 1000\ °C)(2\ days)$ = 9.37 (g).
$m\ sample\ (1000°C)(2\ days)$ = 66.21 (g).

$$w_n(2\ \text{days}) = = \frac{\Delta m\ sample\ (105\ °C - 1000\ °C)(t)}{m\ sample\ (1000°C)(t)} * 100 = \frac{9.37}{66.21} * 100 = 14.152\ (\text{g}).$$

The degree of hydration of the cement within 2 days of hydration was calculated using (Eq13):

$$\alpha(t) = \frac{Wn\ (t)}{Wn(\infty)} = \frac{14.152}{25.145} * 100 = 56.28\ (\%).$$

Table 11 shows the degree of hydration of the cement paste calculated according to the method of quantification of water bound over time of hydration.

Table 11
Degree of hydration of OPC 97TM cement estimated by the bound water quantification method.

Time (days)	Degree of hydration (%)
2 days	56.28
28 days	80.85

III.4. Degree of hydration of cement by SEM-BSE image analysis method

Fig.5 shows the essential steps applied in this study to quantify the cement phases over time of hydration.

- Step 1: Acquisition of SEM-BSE images of the sample.
- Step 2: Acquisition of histogram of SEM-BSE images of the sample using Matlab software.
- Step 3: Quantification of phases on the diagram of histogram using Origin pro software.

The segmentation of the pores from an image with gray levels (0-255), first requires the setting of a threshold value [34]. In the literature, many methods exist for determining this threshold value, which is very important for quantification with better precision, for example it corresponds to the point of intersection of the tangents to the peak curves of the pores and of the peaks of the hydrated phases (HP) (Fig.5). This threshold level of pore segmentation is around 50 for the cement paste in this study. After setting the threshold level, the deconvolution method was applied using the Origin Pro 8.5 software for phase quantification. The quantity of phases from the analysis of the images corresponds to the volume fraction of these phases in the cement paste and the degree of hydration of the cement is estimated according to the following equation (Eq18):

$$\alpha(t) = \frac{V\ anhydrous\ cement\ (t)}{V\ anhydrous\ cement\ (t=0)} * 100 \qquad (18)$$

The cement paste made with a W/C ratio equal to 0.5 corresponds to an initial volume fraction of the cement equal to 38.83%.

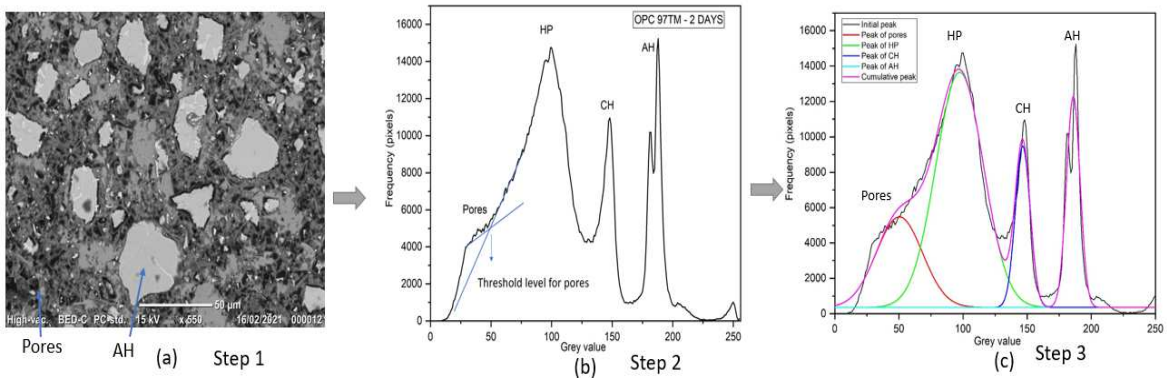

Fig. 5 Methodology of phase quantification using image analysis technique (cement paste after 2 days of hydration)

Several images were analyzed and the Table 12 shows the result of the degree of hydration of the cement over time of hydration by the method of SEM – BSE image analysis.

Table 12
Degree of hydration of cement estimated by the SEM – BSE image analysis method.

Time (days)	Amount of anhydrous cement (%)	Degree of hydration (%)	Deviation (%)
2 days	14.35	63.04	7.80
28 days	2.46	93.66	8.40

III.5. Assessment of the relevance of method for determining the degree of hydration

Table 13 shows the degree of the OPC 97TM cement paste determined by three different methods.

Table 13
Degree of hydration of the OPC 97TM cement paste determined by three different methods.

Method	Degree of hydration (%)	
	2 Days	28 Days
Method 1	60.09	92.16
Method 2	56.28	80.85
Method 3	63.04	93.66

The deviation of the degree of hydration estimated by different methods was observed. In order to assess the relevance of these methods, the Power's approach (Eq19) was used [35] which presents a model for estimating compressive strength as a function of the degree of hydration.

$$\sigma_c(t) = \sigma_0(X(t))^n \quad (19)$$

with:
$\sigma_c(t)$: Compressive strength at time t.
σ_0: Compressive strength when capillary porosity is zero. It is calibrated on the basis of determination of resistance at 2 days.
n: Value taken between 2.6 and 3.0. In general, a value equal to 2.6 is applied for CEM I.
X(t): Ratio of hydrate gel-space, is determined as following equation (Eq20):

$$X(t) = \frac{0.68\,\alpha(t)}{0.32\alpha(t)+\frac{W}{C}} \quad (20)$$

with:
α(t): Degree of hydration of sample at time t.
W/C: water/cement ratio.

From the relationship between the compressive strength and the degree of hydration (Eq19) and (Eq20), the experimental value of the compressive strength was used to assess the suitability of the three methods. The principle is to determine the degree of hydration at 28 days from the hydration at 2 days in order to achieve desired compressive strength. The degree of hydration at 28 days is calculated using the following equation (Eq21):

$$\alpha(28\ \text{days}) = \frac{0.5}{\left(\frac{0.32\alpha(2\text{days})/100+0.5}{\alpha(2\ \text{days})/100} * \sqrt[2.6]{\frac{\sigma c(2\ \text{days})}{\sigma c(28\ \text{days})}} - 0.32\right)} \quad (21)$$

with:
σ_c (2 days): Compressive strength at 2 days (Mpa).
σ_c (28 days): Compressive strength at 28 days (Mpa).
α (2 days): Degree of hydration at 2 days (%).
α (28 days): Degree of hydration at 28 days calculated from the degree of hydration at 2 days to reach the desired resistance value at 28 days (%).
Table 14 shows the value of the degree of hydration calculated according to (Eq21) from the degree of hydration at 2 days determined according to the three methods.

Table 14
Degree of hydration at 28 days calculated from (Eq21) according to three methods, Method 1: Portlandite quantification method, Method 2: Bound water of quantification method, Method 3: SEM-BSE image analysis method.

Degree of hydration	Method 1	Method 2	Method 3
α (28 days) (%) (Eq21)	102.9	97.6	111.9
α (28 days) (%) (Experimental)	92.16	80.85	93.66
Deviation (%)	11.65	20.71	19.47

The result shows that:
- $Ca(OH)_2$ quantification method seems to give a better result compared to two other methods with the smallest deviation. However, the degree of hydration at 28 days calculated from method 1 and method 3 exceeds 100%. In addition, Zhang et al [36] found that the degree of hydration of CEM I cement paste varies between 55 and 80 % at 28 days depending on the W/C ration (W/C ration between 0.3 and 0.7).
- Comparing with Zhang's result, method 2 seems to present a reasonable result. However, it should be noted that some phases (Ettringite, C-S-H) start dehydroxylation at a lower temperature than 105 °C [11].

In addition, we chose to compare the experimental quantities of $Ca(OH)_2$ to evaluate the methods' relevance in our study because $Ca(OH)_2$ is a relatively easy data set to determine thanks to TGA analysis. The SEM-BSE image analysis presents the volume of $Ca(OH)_2$ over time of hydration. We convert from volume fraction to mass fraction using a $CaOH)_2$ density of 2.24 (g/cm^3). The $Ca(OH)_2$/initial cement mass ratio measured by the SEM-BSE images analysis method is calculated according to the following equation (Eq22):

$$\frac{Ca(OH)2\ (t)\ mass}{initial\ cement\ mass} = \frac{V\ Ca(OH)2\ (t)}{V\ anhydrous\ cement\ (t=0)} * \frac{2.24}{3.15} * 100 \quad (22)$$

With:
$Ca(OH)_2$(t) mass: Masse of $Ca(OH)_2$ at time t.
$V_{Ca(OH)2}$ (t) : Volume of $Ca(OH)_2$ at time t.
$V_{anhydrous\ cement\ (t=0)}$: Initial volume of anhydrous cement.
$Ca(OH)_2$ density : 2.24 g/cm^3.
Cement density: 3.15 g/cm^3 (Table 5).
The result of three methods is presented in the Table 15.

Table 15
$Ca(OH)_2$/initial cement mass ratio measured by three methods.

$\frac{Ca(OH)2\ (t)\ mass}{initial\ cement\ mass}$ (%)	Method 1	Method 2	Method 3
2 Days	20.27	20.15	21.25
28 Days	30.68	29.03	31.18

The result shows that:
- Method 1 and method 3 seem to present the result consistent with method 2 by presenting a higher ration. But the deviation is small.

IV. Conclusion

The objective of this study is to estimate the degree of hydration of cement synthesized in the laboratory by three different approaches: method of quantification of portlandite, method of quantification of chemically bound water and method of image analysis. The results showed that:

- The C/S ratio in the alite and the belite in the clinker measured by the SEM-EDS analysis are higher than the theoretical ratio equal to 3 and 2 respectively. The CaO/Al_2O_3 and CaO/Fe_2O_3 ratios in C_3A and C_4AF are also higher than the theoretical value of 1.5 and 2 respectively. The difference between the theoretical and experimental values could be due to the presence of minor elements in the mineral phases, for example, Al and Fe in the C_3S and C_2S phases. This could influence the ratio of major elements in these phases.
- The C/S ratio in the hydrated calcium silicate (C-S-H) phase measured by the SEM-EDS analysis on the hydrated cement paste at 2 days is also higher than the theoretical value of 1.7 used in the equations of cement hydration. This difference can be due to the EDS points made and to the size of the diffusion bulb which analyzes an area and not a point. In addition, the incorporation of aluminum in this phase has been detected. This could have an influence on the C/S ratio.
- The bound water quantification method seems to present a reasonable result using the Power's approach and using the result in the literature.
- The $Ca(OH)_2$ quantification method seems to overestimate the degree of hydration. The result also depends on the temperature range of $Ca(OH)_2$ quantification on the TGA curve.
- The SEM – BSE image analysis method presents relatively similar results with the results by the $Ca(OH)_2$ quantification method. This method demonstrates the feasibility used as a reliable method to determine the degree of hydration, the amount of hydrates in a cementitious material. However, it is necessary to improve the number of images and the resolution to increase the precision.

Declaration of competing interest:

The authors declare that they no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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