Confocal Raman Microscopy: new perspective on the weathering of anhydrous cement

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Abstract. Raman spectroscopy when is combined with Confocal microscopy is a non-destructive technique that allow us to obtain information in cementitious materials. In this study, we present non-destructive image and structural analysis of anhydrous cement with carbonation evidences by Confocal Raman Microscopy (CRM). The results obtained by CRM show a direct relationship between the presence of the weathering processes of an anhydrous cement with the presence of sulphates and surprisingly, with the existence of amorphous carbon in the medium.

1. Introduction
Raman spectroscopy is a vibrational spectroscopic technique complementary to the more widely used infrared spectroscopy. The use of Raman spectroscopy in the characterization of the various cements and supplementary cementitious materials (SCMs) has been investigated over the last four decades [1–4]. However, in 2013, Schmid et al. [5] published the first successful and to date only Raman imaging study on cementitious materials. In this study was possible to reveal the chemical heterogeneity of distinct clinker phases with different crystal orientations. Recent studies have evaluated the use of Confocal Raman Microscopy (CRM) as a non-destructive technique in the determination of the hydration process of the C₃S phase present in the clinker [6].

Raman spectroscopy when is combined with Confocal microscopy is a non-destructive technique that allows identifying the phase composition in inorganic [7] and carbon based materials [8] with high spatial resolution. Supporting us in Raman investigations of anhydrous and hydrated cementitious pastes, the use of CRM can give us excellent information about the properties of this material.

The aim of the present work is to study cement weathering features by CRM. Conventional techniques, such as FTIR and DTA/TG, are also applied on different cement samples in order to determine the degree of weathering. In addition of the good agreement between conventional techniques and CRM, a correlation between presences of amorphous carbon species is established with the extent of cement weathering. The present findings confirm CRM as a fast and reliable technique for the determination of weathering in cement and a key tool to understand the weathering mechanism.
2. Experimental procedure

2.1. Materials
Four types of Ordinary Portland cement (OPC, CEM I 52.5R) were used in this study. The chemical composition of these materials was measured with XRF and it is listed in Table 1. We have analyzed a recently produced cement without evidence of weathering (cement A), and with three kind of cements with evidences of weathering (B, C and D). The cements B, C and D were chosen after being exposed to the weather (poor storage) and under laboratory conditions (without temperature and humidity during storage) during 1 year, so they have different grades of weathering.

| Table 1. Chemical composition of different Portland cements studied (by XRF). |
|---------------------------|----------|----------|----------|---------|---------|---------|---------|---------|---------|----------|
| Cement | CaO | SiO₂ | Al₂O₃ | MgO | Fe₂O₃ | Na₂O | K₂O | TiO₂ | P₂O₅ | SO₃ | *LoI |
| A | 61.5 | 20.5 | 5.03 | 1.45 | 3.20 | 0.15 | 1.05 | 0.25 | 0.19 | 3.35 | 2.39 |
| B | 62.5 | 21.1 | 3.53 | 1.98 | 1.16 | 0.13 | 0.66 | 0.36 | 0.30 | 3.73 | 2.80 |
| C | 61.7 | 20.0 | 4.64 | 1.80 | 2.07 | 0.16 | 0.70 | 0.27 | 0.13 | 2.80 | 1.50 |
| D | 62.6 | 20.5 | 4.64 | 1.80 | 2.07 | 0.16 | 0.70 | 0.27 | 0.13 | 3.73 | 2.80 |

*LoI: loss on ignition

2.2. Characterization techniques
Chemical composition was determined by X-ray florescence analysis using a Magic X Phillips Spectrophotometer (Eindhoven, the Netherlands). Fourier Transform Infrared spectroscopy (FTIR) of samples was carried out by a FTIR spectrometer, Perkin Elmer, Spectrum 100. The FTIR spectra were obtained by analyzing KBr pellets containing 1.0 mg of sample in 300 mg of KBr. The DTA-TG test was performed by using an adaption of the ASTM E1131:2008 standard, on thermogravimetric and compositional analysis of solids and liquids. The equipment used was the simultaneous thermal analyser Setaram brand, model Labsys Evo with a balance accurate to 0.1 mg. The dynamic heating ramp varied between 40˚C and 1100˚C. The heating rate was 10˚C/min and the crucibles used were made of alumina. The reference material was α-alumina (α-\text{Al}_2\text{O}_3) previously calcined at 1500˚C. The test was conducted under N₂ atmosphere. All the tests were performed by using approximately 55 mg of sample. The distribution of phases at the Surface was performed by confocal Raman Microscopy (Witec alpha300R, Witec, Ulm, Germany). Raman spectra were recorded over a spectral range from 100 up to 3700 cm⁻¹. Confocal Raman measurements have been accomplished using a 532 nm excitation laser (green laser) and a 100X objective lens (N.A. 0.95) with an area of focus over the sample at a 5 mW laser power. The scan area was 25 x 25 μm, the parameter of the Raman image: 50 x 50 pixels, integration time per pixel was 1.2 s. Collected Raman spectra were analyzed by using Witec Control Plus Software (Witec, Ulm, Germany).

3. Results and discussion
- FTIR results
  Fig. 1a) shows the FTIR characteristics absorption bands of the main components forming the cement. All cements have a broad absorption band centered ca. 920 cm⁻¹ which is associated with the asymmetric tension of the Si-O bonds of the groups SiO₄ (ν₃) of the alite (C₃S) and the belite (C₂S). This absorption band correlated with the presence of the deformation bands of the O-Si-O (ν₄) bands at 460 cm⁻¹ and 520 cm⁻¹ and a shoulder at 847 cm⁻¹ corresponding to the symmetrical tension of the Si-O bonds of the SiO₄ groups. The characteristic absorption bands of the gypsum (\text{CaSO}_4·2\text{H}_2\text{O}) added as setting
regulator, are a strong and sharp absorption band at 1140 cm\(^{-1}\) (\(\nu_3\)) due to the SO\(_4^{2-}\) groups and another absorption band overlap with of the hemihydrate, CaSO\(_4\cdot\)1/2H\(_2\)O (or basanite) and anhydrite (CaSO\(_4\)) at 1124 cm\(^{-1}\) \[2\].

**Figure 1.** (a) FTIR spectra of the different cements used (A, B, C and D); (b) Area corresponding to the absorption band of the C-O bonds associated with the carbonates present in the cements.

If the different infrared spectra obtained for the weathered cements (B, C and D) are analyzed, very significant differences can be observed with respect to the A cement. Regarding the region between 1100-1200 cm\(^{-1}\) (region of sulphates), when a weathering process occurs, the calcium sulphate slightly decreases (cements B, C and D). The weathering of a cement is diminished when calcium sulphate reacts with the alumina phases before the cement hydration takes place that results in free lime elimination and ettringite formation. The intensity of the carbonate absorption band (C-O) increases as the weathering progresses, so that the formation of calcite-type calcium carbonates in cements B, C and D becomes more evident.

Focusing on the absorption band associated with the presence of carbonates, ca.1442 cm\(^{-1}\), the percentage of carbonate can be calculated by integrating their area. Fig. 1b shows that cement A possess the smallest area in the carbonate region, being the cement B with a greater presence of carbonates, and therefore, one that undergoes a greater weathering, followed by cement D and C, respectively.

By using infrared spectroscopy techniques, the higher intensity of the absorption bands associated to the vibration of the C-O bonds reveals the chemical evolution of weathered cements. In addition, there is also a change in the spectral region corresponding to continuous sulphate disappearering. As an advantage, FTIR allows the detect both crystalline and non-crystalline compounds. Moreover, as specific aspects of interest, the technique is highly sensitive for the determination of carbonate compounds but carbonates even in low amounts can overlap absorption bands corresponding to major compounds, making it difficult to discriminate between chemical species.

- **DTA/TG results**
The combined use of thermogravimetric (TG) and differential thermal analysis (DTA) techniques allows the study of the carbonation of samples of cement-based materials by analysis of the decomposition of calcium carbonate. The DTA makes it possible to determine the temperature range at which the transformation occurs and from the TG data it is possible to calculate the weight loss suffered by the sample during the transformation.

The decomposition of calcium carbonate occurs according to the following endothermic reaction:

$$\text{CaCO}_3 \rightarrow \text{CO}_2 + \text{CaO}$$

Table 2. % weight loss of CO$_2$ and CaCO$_3$ calculated in different regions of DTA/TG: 530-650°C region correspond to the decarbonation of different amorphous phases, like vaterite; 650-800°C region corresponds to the decomposition of CaCO$_3$; 800-900°C region corresponds to the decarbonation of calcite.

| Cement | 530-650°C | 650-800°C | 800-900°C | Total % weight loss of CO$_2$ | Total % of CaCO$_3$ |
|--------|-----------|-----------|-----------|-----------------------------|--------------------|
| A      | 0.33      | 0.39      | 0.04      | 0.76                        | 1.73               |
| B      | 0.73      | 0.88      | 0.05      | 1.66                        | 3.77               |
| C      | 0.43      | 0.84      | 0.03      | 1.30                        | 2.95               |
| D      | 0.34      | 1.13      | 0.06      | 1.53                        | 3.48               |

The weight loss corresponds to the CO$_2$ that is released as a gas. From these values the amount of CaCO$_3$ present in the sample can be calculated. Thus, when calculating the total percentage of carbonates present in the cements, the entire temperature range between 530-900°C must be taken into account. In Table 2 it can be seen how the cement B is the one that gave us a greater percentage of mass loss associated to the CO$_2$ loss of the present carbonates, indicative, therefore, of the greater presence of CaCO$_3$ in cement B, followed by the cement D and C, respectively.

To sum up, conventional techniques as FTIR and DTA-TG allow determining the cement weathering thorough the calculation of the CaCO$_3$ amount. However, these techniques fail to establish weathering mechanisms.

- Confocal Raman Microscopy results

A Confocal Raman Microscopy (CRM) study was performed on the four cements used in this study. In Fig. 2 the average Raman spectra of each cement can be observed. In cement A without weathering, the Raman spectrum of tricalcium silicate or alite (C$_3$S) is commonly dominated by the $\nu_1$ Raman band at ca. 839 cm$^{-1}$, a poorly resolved shoulder at ca. 890 cm$^{-1}$ and a weaker doublet at ca. 520-550 cm$^{-1}$. The main Raman bands are accompanied by additional vibrational (LV) modes at lower Raman shifts [1,2,6]. The Raman spectrum of dicalcium silicate or belite (C$_2$S) is dominated by a strong Raman band at ca. 860 cm$^{-1}$ and weaker Raman bands at ca. 900 cm$^{-1}$ and ca. 980 cm$^{-1}$. Additional Raman bands appear at ca. 520-550 cm$^{-1}$ as a triplet and at lower Raman shifts [6,9]. Some particles are also assigned to CaSO$_4$·H$_2$O (gypsum) with an intense and narrow Raman band at ca. 1022 cm$^{-1}$ having different Raman shift values. Moreover, the presence of minority phases as C$_3$A ($\nu_1$ AlO$_2$ vibration ranging from 756 to 760 cm$^{-1}$) and CaF are present in all cements studied, but its low presence gives us broad Raman bands having low intensity. Additionally, the presence of carbonate in cement A is scarce but their presence is determined by a narrow and intense Raman band at ca. 1095 cm$^{-1}$ assigned to CaCO$_3$ spectrum and another more intense Raman band located at ca. 992 cm$^{-1}$[4]. The Raman bands associated with CaCO$_3$
are not abundant and therefore their presence in the average Raman spectrum is low when compared with the main Raman bands. The presence of this type of carbonate is much more abundant in the three weathered cements than in cement A, especially in cement D. These carbonates correspond to the first stage of the CaCO$_3$ precipitation process from saturated solutions and carbonation of wet slurries as a well-described side effect when hydrating cementitious materials [10–12].

![Raman spectra](image)

**Figure 2.** (a) Average Raman spectra of the different cements obtained by CRM (100-2000 cm$^{-1}$ region). Presence of Raman bands associated to calcite at 180, 280, 711 and 1084 cm$^{-1}$; presence of Raman band attributed to sulphates at ca. 1022 cm$^{-1}$ and presence of two characteristics Raman modes of carbon as the D peak, at ca. 1365 cm$^{-1}$ and the G peak, ca. 1615 cm$^{-1}$; (b) Detail of the average Raman spectra of the different cements between 700-950 cm$^{-1}$. Raman bands associated to the main phases of clinker present in the cements are signaled C$_2$S (at ca. 860 cm$^{-1}$) and C$_3$S (at ca. 839 cm$^{-1}$).

The different weathered cements (cement B, C and D) were also analyzed by CRM (Fig. 2). As in cement A, weathered cements have C$_2$S (belite) and C$_3$S (alite) the major. In all samples, the presence of gypsum or other sulphates is identified with an intense and narrow band at 1022 cm$^{-1}$, although in very different proportions depending on the type of cement [2]. As can be observed in the average Raman spectra (see Fig. 2), the presence of gypsum is scarce in cement B, whereas in cement C it is even more abundant than in cement A (as reference).

Fig. 3 shows the different Surface Raman images by CRM for the different cements. The different main phases are represented by their color code. Among them, the C$_2$S and C$_3$S (signaled in pink and red, respectively) being the most abundant. In addition, the existence of minority mineralogical phases, such as, CaSO$_4$·2H$_2$O (signaled in blue) and Na$_2$Ca(SO$_4$)$_2$ (signaled in cyan) (Fig. 3b) added during the cement production process is observed. Moreover, the presence of CaCO$_3$ generated after the weathering process is marked (signaled in green, Fig. 3c). The formation of portlandite (signaled in yellow) can also be seen in some of the cements, especially in cements B, C and D. For shake of simplicity, main phases are shown individually in Fig. 3b, 3c and 3d in order to determine their spatial distribution and abundance.

A next step is to quantify and compare the carbonates amount found in the four analyzed cements (A, B, C and D). For this fact, we integrate the Raman band at 1084 cm$^{-1}$. The cement B presents a percentage of carbonation of the main phases of the clinker (C$_2$S and C$_3$S) of approximately 38.7%, being the cement A that presents a lower carbonation content of these phases (1.6%). In addition, the formation of carbonates has more affinity with the more basic species (C$_3$S), causing a hydrolysis reaction to
produce Ca(OH)_2 slowly \cite{13}. In this way, it can be seen quantitatively in Fig. 4a that the carbonates are between 4 and 8 times higher in the weathered cements (B, C and D) than in the reference cement A. Although carbonate regions with intense Raman signals exist in cement A, the area occupied by carbonates is qualitatively lower. Thus, as shown by FTIR and DTA/TG, cement B, C and D possesses a high degree of weathering, with cement B having the highest weathering. Thus, it can be attributed that the greater presence of the carbonates is mainly due to a surface weathering as demonstrated by CRM technique.

**Figure 3.** Surface Raman images by CRM of the different cements used in this study: cement A (as reference), B, C and D (weathered cements). (a) Surface Raman images of all main phases present in cements: C_2S, C_3S, CaCO_3, gypsum, glauberite, portlandite and carbon; (b) Surface Raman images of sulphates (gypsum, CaSO_4 signaled in dark blue and glauberite, Na_2Ca(SO_4)_2, signaled in cyan); (c) Surface Raman image of CaCO_3 (signaled in green) present in each type of cement due to the weathering; (d) surface Raman images of amorphous carbon (signaled in white) associated with the presence of CaCO_3.

CRM showed the presence of gypsum in each of the samples (see Fig. 3b). As already determined by infrared spectroscopy (FTIR), weathering in the cements tends to reduce the presence of sulphates. However, CRM allows observing that the appearance of calcium carbonates in the anhydrous cements after the weathering process does not cause a total disappearance of the sulphates species.

In all cements, two characteristic Raman modes of carbon are found. D peak, at ca. 1365 cm\(^{-1}\), which corresponds to a disordered state of carbon; and the G peak, ca. 1615 cm\(^{-1}\), which corresponds to the graphitic carbon (ordered state) \cite{8,14} (Fig. 5). The ratio I\(_D\)/I\(_G\) ≤ 1 indicates an amorphous state of the carbon. In all cements analyzed the ratio I\(_D\)/I\(_G\) is < 1, indicating a slight increase of the graphitic phase \cite{8}. It is important to note that in all the average Raman spectra the carbon coexists simultaneously with the carbonates. The presence of this carbon can be attributed to impurities in cements as consequence...
of their production process, either due to the use of fossil fuels or to the possible contamination by some type of fly ash addition. The use of CRM allows us to obtain more precise information about the weathering mechanism of commercial anhydrous cement. Firstly, the use of CRM can be directly correlated with the results obtained by conventional techniques as FTIR and DTA/TG, Fig. 4b. It can be observed that there is a fairly good linear correlation in the determination of carbonates between FTIR and DTA/TG techniques with CRM.

Figure 4. (a) area occupied by the presence of carbonates in the cements studied (in µm²); (b) lineal correlation in the quantitative determination of the presence of calcium carbonates between the FTIR and DTA-TG techniques with CRM in each of the studied cements.

Figure 5. Average Raman spectra of regions where carbon related Raman peaks are located for of all cements. The figure includes the calculated ratio ID/IG for the carbon phase.

4. Conclusions
The feasibility to use Confocal Raman Microscopy to determine the weathering of commercial cement has been proven. The results obtained by CRM have been corroborated by the techniques commonly used for this purpose as FTIR and DTA/TG, and a linear correlation between the different techniques is established. However, FTIR and DTA/TG possesses a limited resolution to point out the different phases contribution to the cement weathering. Raman spectroscopy is highly interesting as an analytical
technique since: it is a non-destructive technique that could be in-situ used, provides proportionate relevant data, requires short time of operation and gave a high degree of reliability. The use of advanced techniques of analysis applied to commercial cement opens new possibilities for combined chemical and spatial analysis. Thus, the authors believe that new insights related reactivity and kinetic of reactions in cement based material will bloom in the next years.

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