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Petrographic characterization of Portlandite crystal sizes in cement pastes affected by different hydration environments

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HIGHLIGHTS

- Crystals of Portlandite showed important variations in terms of age and curing conditions.
- Lognormal probability function fits the size distribution of the Portlandite crystals.
- Type and time of curing has an influence on the size of Portlandite crystals.

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ABSTRACT

Petrography is a valuable characterization method, which helps understand and determine whether any issue could affect the cement-based materials performance. This optical microscopy technique has multiple applications in the construction industry, such as the characterization of anhydrous or hydrated compounds, material durability and quality control. This paper presents the results of an experimental research program focused on characterizing the effect of humidity and dry conditions during the cement-paste curing, on the size characteristics of Portlandite crystals formed during hydration. Cement-paste thin sections with small variations in the water to cement ratio, divided into two groups, some of them continuously submerged in water while others left in the air under the environmental conditions of the laboratory, were prepared 7 and 28 days after mixing in order to observe them by using the petrographic microscope. From these observations, the variation of the different remnant anhydrous and hydrated minerals for each age and curing condition was evaluated, emphasizing in the characteristics of the Portlandite habits. Additionally, the statistical determination of the Portlandite crystal's sizes, whose average size for curing at room temperature at 7 was 11 μm and 28 days was 20 μ, while for wet curing at 7 days was 16.5 μm and 29 μm at 28 days. Results showed that for all anhydrous mineral phases, there were no statistical size differences, while the sizes of the crystals of the Portlandite phase showed important variations.

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1. Introduction

Petrography applied to concrete refers to the evaluation and description of cement-based mixtures by using conventional petrography techniques [1]. Since 1887, this has been a widely used tool for studying the components and microstructure of cement pastes, mortars and concrete mixtures. Nowadays, this optical microscopy technique has multiple applications in the construction industry, such as the characterization of anhydrous or hydrated compounds, material durability and quality control [2].

Petrographic analysis is widely used to estimate the reactivity potential of aggregates for concrete, noting that some authors place it as the first step for assessing the alkali-silica reaction [3]. Likewise, according to ASTM C295 [4] and ASTM C1778 [5] standards, this technique is used for the evaluation of said reaction. On the other hand, petrography has been used to assess, in tropical environments, the quality of hardened concrete bearing different water to cement ratios [6], and to evaluate the effect of the Interfacial Transition Zone (ITZ) of aggregates on the concrete strength [7]. Other authors refer to petrography as an auxiliary methodology for evaluating concrete exposed to fire [8], or as a tool to evaluate cracking, mineralogical changes and the level of damage due to fire [9].

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Although concrete petrography is a research field that allows a first approach to the microstructure, its application is determined by the material, the analyzing scale and the properties or characteristics that are to be observed. It is not the same to perform petrography on concretes with fine and thick aggregates than on mortars or cement pastes. The relationships and interactions among the components of the material vary according to the granulometry and size of aggregates. Additionally, the cement-hydration products change in the presence of aggregates due to the appearance of the interfacial transition zone (ITZ), and as a consequence, the cementitious matrix will not be the same in a cement paste sample than in one made out of mortar or concrete. Likewise, the mineralogical composition of the cement matrix will also vary depending on the presence of the aggregates.

The cement-paste characterization includes the description of the paste's physical properties (color, density, porosity, absorption), textural and mineralogical characteristics, air content, pore distribution, cracking patterns and crystalline arrangements of non-hydrated cement minerals and hydration products such as CSH gel and Portlandite [2]. During the cement hydration, the water molecules react with the calcium silicates: alite ($3CaO{\cdot}SiO_2$) and belite ($2CaO{\cdot}SiO_2$) present in the anhydrous cement. There, two alite molecules react with six of water forming three C-S-H-gel ($CaO.2SiO_2{\cdot}3H_2O$) and three Portlandite ($Ca(OH)_2$) molecules, as shown in Eq. (1). Additionally, two belite molecules react with four of water forming three C-S-H-gel and one portlandite molecules as shown in Eq. (2) [10].

$$2(3CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \quad (1)$$

$$2(2CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \quad (2)$$

The above equations show that the C-S-H gel is the main hydration product followed by the Portlandite. The methodologies used to characterize these two products by petrography are different: The C-S-H gel is crystallographically amorphous and therefore optically isotropic, which means that the refractive index is constant for any light transmission direction. In contrast, Portlandite belongs to the hexagonal crystallographic system and has different optical properties. The compositional percentage and distribution of the C-S-H gel can be estimated by means of point counts, while the size, distribution and crystalline habits of the Portlandite as well as its compositional percentage can be assessed in the cement paste. The formation of these products is related to the cement hydration and the water to cement ratio: the higher the hydration level, the higher the content of C-S-H gel and Portlandite.

French [1] established that Portlandite crystals tend to be large (up to 100 μm) and well defined in pastes holding high water to cement ratios, thus forming clusters, whereas small crystals uniformly distributed in the paste tend to occur in low water to cement ratios. A more recent study on the effect of the water ratio in the microstructure and composition of Portland-cement paste hydration products, shows that at a 0.25 water to cement ratio, Portlandite crystals appear in nanometric dimensions and dispersed in the C-S-H gel (amorphous in the XRD analyzes), whereas, the crystals size increases with a 0.4 water to cement ratio, featuring laminar habits [11].

The curing type and humidity conditions during the first days of hydration of pastes, influence the C-S-H gel formation, and the size, quantity and distribution of Portlandite crystals. Curing under dry conditions allows water loss, generating a decrease in the speeds and characteristics of the hydration processes, thus causing changes in the microstructure of the paste that directly affect its mechanical properties, especially regarding the compressive strength. Curing by immersion in water, substantially improves the formation of hydration products, thus causing important changes in the characteristics of the C-S-H gel and especially in those of the Portlandite, generating characteristics and particular features in the microstructure that promotes strength increases [12].

So far, the influence of humidity conditions (curing type) on the cement-paste hydration process has been mainly researched by mechanical and chemical tests, without assessing its effect on the mineralogical and textural characteristics of hydration products, specifically those of Portlandite. Likewise, optical petrography techniques applied to concrete have been mainly focused on the evaluation of several damage mechanisms associated with different durability issues, while the quantitative study of the features of Portlandite as a hydration product has been very limited. Although nowadays there are microscopy techniques more versatile and modern than optical petrography, such as scanning electron microscopy (SEM), the variability of cement-based materials makes it necessary to statistically quantify the features of the main hydration products, a condition that can be properly carried out by using optical petrography.

In accordance with the foregoing, this paper presents the results of an experimental research program focused on characterizing the effect of humidity conditions during the cement-paste curing on the textural characteristics of Portlandite crystals formed during hydration. As for cement-paste samples with small variations in the water to cement ratio (0.26, 0.27 and 0.29), divided into two groups, some of them continuously submerged in water while others left in the air under the environmental conditions of the laboratory, thin sections were prepared 7 and 28 days after mixing, in order to observe them by using the petrographic microscope. From these observations, the variation of the different remnant anhydrous and hydrated compounds for each age and curing condition was evaluated, emphasizing the characteristics of the Portlandite habits and mainly the statistical determination of the Portlandite crystals' size according to the curing time and type. This research is intended to contribute to the mineralogical characterization of cement pastes through the optical petrography technique.

2. Methodology

2.1. Materials

In this study, an experimental laboratory program was carried out using mixtures of Portland cement and water with no aggregate. Type I Portland cement according to ASTM C150 [13] was used to prepare all pastes. The cement density measured through the ASTM C188 [14] was around 3.2 g/cm^3 and the Fineness measured through the Blaine air-permeability apparatus [15] was around 3700 cm^2/g. Results for the composition of the oxides for the Portland cement used are shown in Table 1.

ASTM C150-18 states the procedure for calculating the approximate composition of cement phases according to the formulae of R. H. Bogue. Taking into account the results of the oxide

Table 1
Chemical composition of cement.

Constituent (wt%)	Portland Cement
SiO_2	20.47
Al_2O_3	5.09
Fe_2O_3	4.24
CaO	64.73
MgO	1.74
Na_2O	0.21
K_20	0.22
SO_3	2.22
P.I	0.77
Free Lime	0.97

composition showed in Table 1, the cement used was composed by 12.9% of Tetracalcium aluminoferrite (C_4AF), 6.3% of Tricalcium aluminate (C_3A), 12.4% of Dicalcium silicate (βC_2S) and 61.4% of Tricalcium silicate (C_3S). These results confirm that the cement used was Portland Type I. No chemical or mineral admixtures were used during mixing. Tap water was obtained from the water supply.

2.2. Specimen preparation

Based on preliminary results obtained from normal consistency tests [16], three water to cement ratios were used to prepare cement pastes: 0.26, 0.27 and 0.29. For each mixture, several samples were cast in pre-oiled 50 mm reusable cast iron molds, filled with two layers of paste and compacted to remove the air and reach the maximum density. After molding, the specimens were kept in a cool place, covered with a polyethylene sheet and demolded after 24 h. Half of the specimens was cured by water immersion, while the other half was cured by air in a standard curing room (20 °C ± 2°, RH 65%). The compressive strength was measured at 28 days by using a hydraulic testing machine in accordance with the ASTM C109 [17].

After a curing period of 7 days, a thin section was made for each mixture and curing condition. Although the analysis of these initial sections was only conceived as a control stage at early ages, its results and comments were included as part of the discussion of this paper. Again, after a curing period of 28 days, 3 thin sections were prepared for each water to cement ratio and each curing condition, for a total of 18 thin cement-paste sections. Each thin section, either from the ones at 7 or 28 days, was always obtained from the middle part of each specimen, which were prepared according to Nordtest method, NT Build 361 [18], using blue epoxy rather than fluorescent epoxy, and oil rather than water during the thin-section preparation, in order to prevent cement rehydration. All the sections were polished until 20 μm thickness was achieved. As the specimens of each mixture were cast in the same day, the samples were macroscopically homogeneous and showed similar colors, porosity and texture. More thin sections were made at 28 days in order to have a better understanding of the results of mature pastes and to reduce the uncertainty in the hydration of the cement pastes due to the curing condition. A total of 24 thin sections were analyzed. Table 2 summarizes the thin-section samples used.

Table 2
Summary of thin sections prepared.

Sample	Curing time (days)	Curing condition	Water to Cement Ratio		
			0.26	0.27	0.29
PA7	7	Air	1	1	1
PA28	28		3	3	3
PW7	7	Water Immersion	1	1	1
PW28	28		3	3	3

2.3. Petrography techniques

By means of optical petrography, the different minerals of the anhydrous cement, as well as the hydration products, were identified according to their optical properties. In order to achieve this, an Olympus CX-31P microscope and 100X and 50X lenses were used, traversing the sections by 2 mm-horizontal x 1.5 mm-vertical meshes. A total between 500 and 600 points were counted per section, for an overall total of 6103 data. Table 3 shows as an example the optical properties used for Portlandite in this research.

The cement pastes were characterized by using the following petrographic parameters:

a) Compositional: point counting of alite, belite, ferrite phase and aluminates phase (they were counted as a unit because it is not possible to differentiate them using petrographic scale), residual clinker grains (grains of two or more cement minerals), C-S-H gel and Portlandite.
b) Textural: measurement of the size of these components considering the larger diameter.

From the results obtained, the mineralogical composition of each mixture was calculated in percentage terms, and the size variation of the minerals was statistically evaluated according to the curing time and type. As for the Portlandite, the percentage for each of the habits found was additionally established, and the statistical variation in the crystal size of this mineral was determined.

Finally, additional observations were made using a backscattered electron imaging (BSE) by Scanning Electron Microscope (SEM) operating at 30.0keV accelerating voltage, where the Portlandite's crystalline features were corroborated. The observations were made from cube internal fragments upon having been subjected to compression and failed; these were coated using gold/palladium (Au/Pd). The SEM used corresponded to a FEI Quanta 200-r device.

3. Results and discussion

3.1. Mechanical properties

Upon having cured the cement-paste cubes for 28 days, three of them were tested for each mixture and for each curing condition, in order to obtain the compressive strength. A universal controlled-speed testing machine was used. As expected, Fig. 1 shows that the compressive strength is greater with the wet curing than with the room-temperature curing. The greatest difference occurs in the 0.26 ratio where the wet-curing average was 114 MPa, while in the case of the room-temperature curing the average was only 78 MPa. This result is consistent with the increase in C-S-H gel content observed through petrographic analyzes, where more gel was formed during the wet curing (32%) than during the room-temperature curing (26%). The results stated above were intended to quantify the curing type effect on the compressive

Table 3
Portlandite's optical properties. Adapted from Poole and Sims (2014) [18] and Campbell (1999) [19].

Portlandite – Calcium Hydroxide
Chemical composition: $Ca(OH)_2$
Crystal system: Hexagonal

COLOR	HABIT	RELIEF	BIREFRINGENCE	INTERFERENCE FIGURE
Colorless	Tiny euhedral sheets or strips in the hardened cement paste. It can also be found by filling in totally or partially empty spaces.	Low	Moderate: 0.028 Yellow, red, orange of first order	Uniaxial negative

Observations: In hardened cement paste, it is one of the few minerals that are not submicroscopic. It is possible to determine shape, size and distribution by petrography.

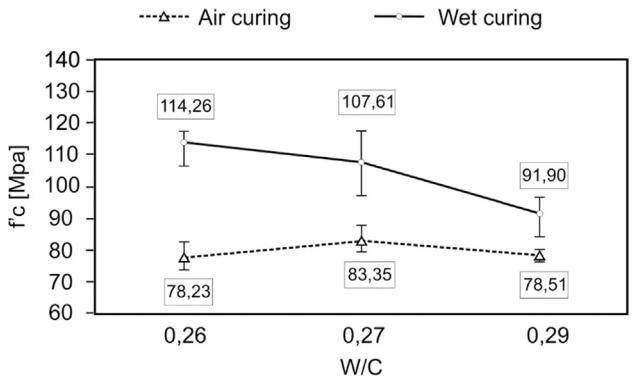

Fig. 1. Cement pastes compressive strength.

strength of cement pastes. To this end, the water saturation level of samples prior to tests was not considered as a study variable in this paper. In order to keep all the compressive strength tests under similar conditions, samples wet cured were removed from water 12 h before the test and were left to dry at the laboratory room-temperature. The above was considered as it has been reported by Chen et al. [20], the specimen saturation affects the compressive strength results.

3.2. Petrographic analysis

Regarding the composition of the cement paste, the alite, belite, ferrite, aluminate phases, and residual clinker showed a decrease in their content between 7th and 28th day, as a consequence of the continuous hydration process; however, in textural terms there were not observed significant variations.

Three mineral habits were identified in the Portlandite: massive, microcrystalline and crystalline, as described by Poole and Sims [21]. The Portlandite's optical properties shown in Table 3 are the same for each of the crystalline habits in which it occurs. The fundamental differences between them, established for their characterization, were the shape and size of the crystal, features that depend on the growth conditions of the mineral during the calcium silicates hydration. The crystalline habits of the portlandite corresponded to crystals with well-defined edges that allowed to measure the crystal's largest diameter (Fig. 2); the microcrystalline habit was observed as very thin crystal clusters with sizes less than 1 μm, (Fig. 3); and the massive habit is anhedral, that is, it does not have a particular shape (Fig. 4).

Fig. 5 compares the different habits identified during the determined curing times and types. It's worth noting that the massive portlandite predominates after 7 days in the room-temperature

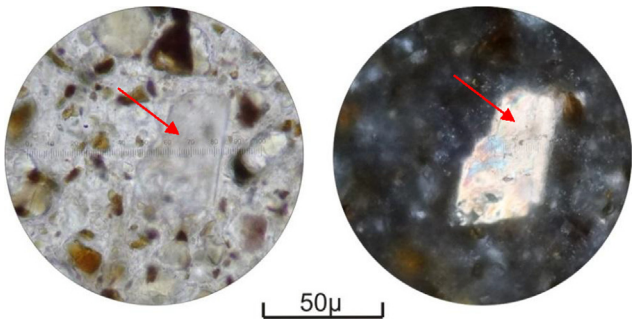

Fig. 2. PPL-XPL. Objective 100X. Thin section 0.29 WC 7 days. Well-formed crystalline Portlandite crystal (indicated by the red arrow), with moderate relief and fourth-order interference tones. Approximate size of crystal: 40 μ.

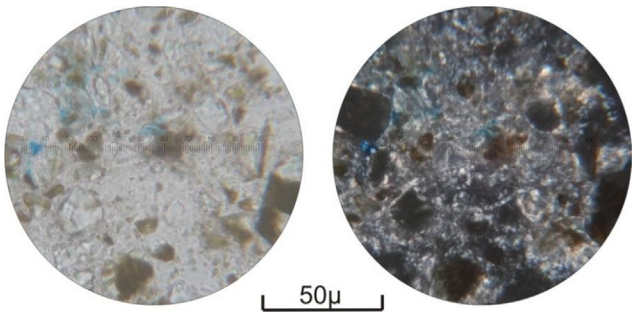

Fig. 3. PPL-XPL. Objective 100X. Thin section 0.27 AC 7 days. Remnants of anhydrous components are surrounded by a pearly matrix composed of Portlandite microcrystals (fourth-order interference tones).

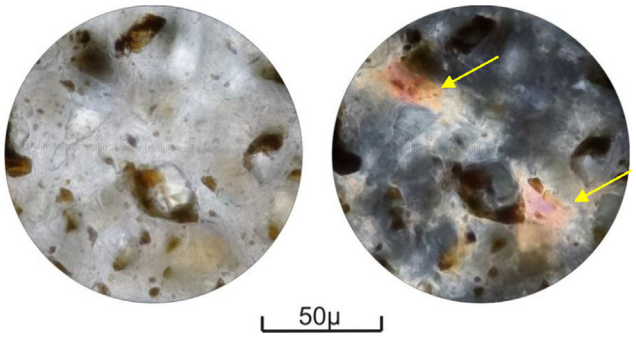

Fig. 4. PPL-XPL. Objective 100X. Thin section 0.29 AC 28 days. Massive portlandite is indicated.

curing, followed by the microcrystalline with little presence of massive portlandite, while regarding the wet curing, the identified portlandite corresponds in its great majority to the massive habit. At 28 days, regarding both types of curing and water to cement ratios, the massive habit is the main one, being slightly higher at the room-temperature curing with percentages between 21.7% (0.27 mixture ratio) and 26.1% (0.29 mixture ratio).

By means of Scanning Electron Microscopy (SEM), well-formed portlandite clusters and crystals were identified; it is worth noting that in these samples, the best formed crystals were filling pores as shown in Fig. 6. The foregoing may be due to the secondary hydration promoted by the water retained in these voids. Fig. 7 shows a well formed portlandite hexagonal crystal on a layer of C-S-H gel in formation, which confirms that this mineral turns into a more crystallized form during wet curing, which is increased by longer hydration times [22].

Fig. 8 shows the sizes of crystals from the remaining anhydrous cement-phases compared to Portlandite crystals. From there, it can be observed that regarding the size of these crystals, the alite and belite have sizes ranging from 12 μm to 30 μm, the ferrite phase with aluminates is slightly finer showing crystals sizes between 7 μm and 20 μm. However, these size ranges remain the same at both 7th and 28th day, with respect to both types of curing, for each mineral. The residual Clinker has a similar behavior, although with larger diameters that vary between 20 μm and 40 μm for all conditions. That is, none of these components shows a significant size change in time or between the two types of curing.

On the other hand, regarding the crystalline Portlandite, a clear influence of time and curing type on the crystal size was observed. After the 7-day curing period at room temperature, the sizes range between 5 μ and 14.2 μm, while with respect to the wet curing, they vary between 4.5 μm and 20 μm. The crystals are thicker at 28 days than at 7 days considering both curing types, also noting

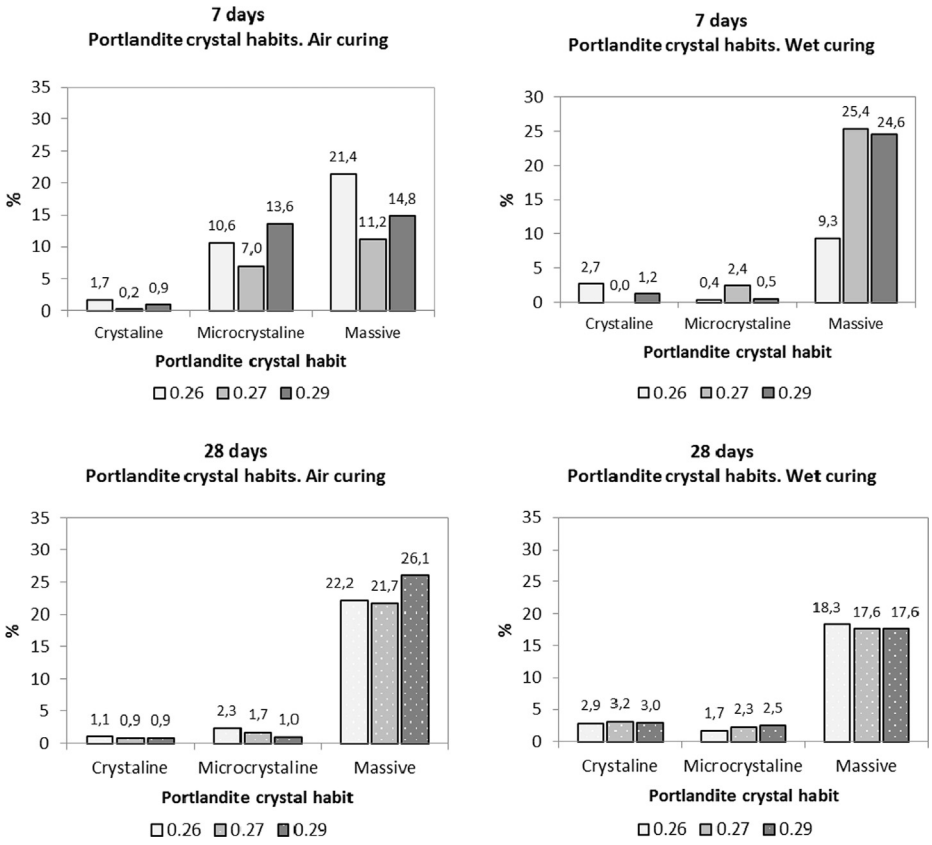

Fig. 5. Portlandite crystal habits.

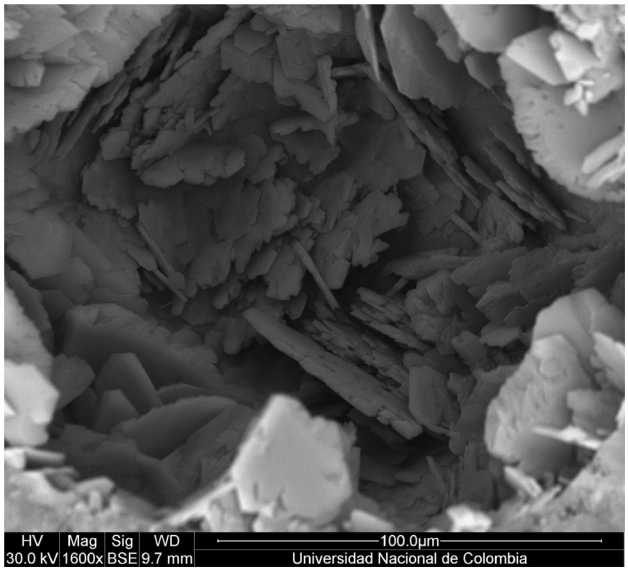

Fig. 6. SEM-BSE photomicrographs SEM –BSE. Accumulation of portlandite crystals. Sample with W/C: 0.27 Wet curing during 28 days.

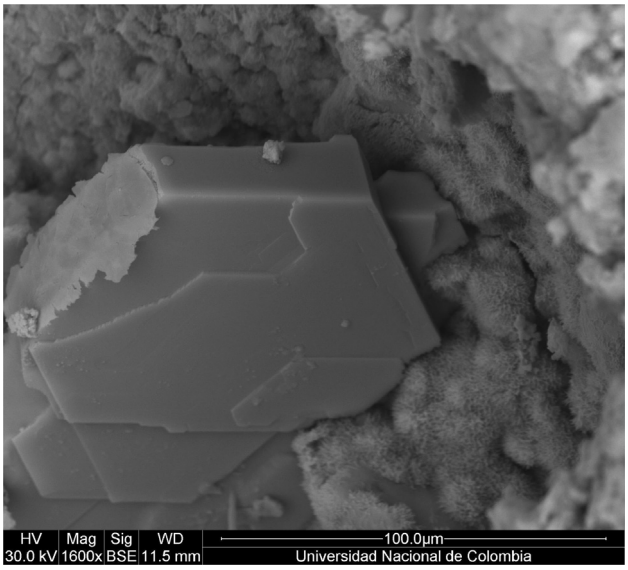

Fig. 7. SEM-BSE photomicrographs SEM –BSE. Portlandite crystal next to C-S-H gel in formation. Sample with W/C: 0.27 Wet curing during 28 days.

the larger sizes from the wet curing. When curing at room temperature, the sizes range between 10 µm and 25 µm, while in wet curing they are between 14.2 µm and 40 µm, as shown in Fig. 8. From all the anhydrous and hydrated mineral phases that were observed and quantified by means of the microscope, the greatest effect of moisture conditions during curing occurred on the Portlandite crystal size. Although a specific statistical analysis for this variable will be conducted later, it is important to note that Portlandite content was not analyzed in this paper, since it was similar for both curing conditions.

As it is well known in the cement chemistry, the calcium silicate hydration simultaneously allows the formation of C-S-H gel and Portlandite. Likewise, under normal humidity conditions during curing, in stoichiometric terms, the CaO/SiO_2 molar ratio in the C-S-H gel is always lower than that in the tricalcium silicate (alite), as reported by Hewlett [10]. Under dry conditions during curing, it