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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.

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].

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

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

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