Porous structure and mechanical strength of cement-lime pastes during setting

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ABSTRACT

The acceleration of a cement paste setting as a result of lime addition may be shown from isothermal calorimetry measurements. We investigated the underlying mechanisms through two techniques that provide information on porous structure (using Nuclear Magnetic Resonance) and mechanical properties (elastic modulus measured by rheometry). The correlation of the two sets of results on a cement paste clearly reveals the successive steps of setting, and particularly highlights the so-called induction period. We show that this induction period disappears in the presence of lime, leading to an acceleration of the setting. We also show that beyond some critical concentration of added lime the acceleration of setting is negligible.

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1. Introduction

Current environmental problems constrain to a reduction of cement in the construction and to the use of more environmentally friendly materials. In this respect, binders consisting primarily of hydrated lime ($Ca(OH)_2$) and cement have undergone a renewed interest, in particular in the restoration of cultural heritage [1,2]. Indeed, hydrated lime is thought to be more environmentally friendly thanks to its ability to almost fully recarbonate in mortars, and is more respectful of old constructions. On the one hand, cement-lime binders are considered to combine strength at early age, thanks to the presence of cement, and porosity thanks to the presence of lime. On the other hand, this porosity lowers mechanical strength and can affect durability since it allows water to penetrate in the mortar instead of the blocks. In this context, many researches focused on the effect of lime on the porosity [3–6], and mechanical properties [1,2] of cement-lime mortars after hardening. It was in particular shown that the mechanical strength diminishes sharply when a small amount of lime is added to a cement paste and that blended mortars with a high percentage of lime present a large plastic zone [1]. Only few papers are related to the influence of lime on cement setting, although this could bring key information for understanding the impact of lime on the final structure of such systems.

Uchikawa [7] studied the effect of addition of few amounts of quicklime and hydrated lime on cement and showed that they both accelerate hydration reaction. This author also studied pure alite, which is the main phase in Portland cement, and showed that lime indeed acts as a set retarder on the hydration of this phase.

In this paper, we try to understand the role of hydrated lime in the setting of cement. It is generally admitted that hardening of a cement paste is due to the formation of calcium silicate hydrates (CSH) at contacts between cement grains by a dissolution precipitation mechanism.

From a physico-chemical point of view adding lime to a cement-water system can have several consequences. When lime is put in contact with water, it starts dissolving, producing OH⁻ and Ca^{2+} ions according to the following dissolution reaction:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2\,OH^-$$
$$solubility\ product\ =\ 7.9\ 10^{-6}$$
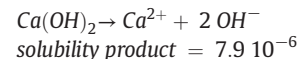
In our system, the saturation of the interstitial solution compared with CSH is necessary to lead to the precipitation of hydrates. When hydrated lime is suspended in pure water, it leads to a calcium concentration of 22 mmol/L; when cement is placed in pure water this calcium concentration is reached less than an hour after suspension [8]. In order to evaluate the role of hydrated lime on hydrate precipitation, the influence of various constant calcium hydroxide concentrations (from 6 to 33 mmol/L) on the nucleation and growth of CSH in a very dilute system containing calcium silicate grains was studied by Garrault et al. [9]. They showed that the quantity of CSH nuclei decreases with $[Ca(OH)_2]$

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and growth rate of CSH are modified. The initial calcium hydroxide concentration in the interstitial solution can have an effect on dissolution-precipitation processes and also on the CSH Ca to Si ratio [10].

At the same time, lime is composed of finer particles as cement (see Fig. 2) and has a high specific surface area as compared to cement (around ten times higher, see Table 2). Plus, it has been shown that CSH nucleation and growth on calcite crystals is possible [11], so we can imagine that a syntaxial growth of CSH on portlandite crystal can occur, and portlandite crystals of lime would then represent available surface to nucleation and growth of hydrates.

Nicoleau [12] studied the effect of an addition of hydrated lime on cement setting and showed that in the presence of lime, hydrates precipitate mainly in the pores of the cement paste. However, he did not study the effect of the amount of lime in the mix. In order to study the effect of additional surface available to CSH nucleation, Thomas et al. [13] studied the seeding effect of pure CSH particles introduced both in a C_3S paste and in a cement pastes. Their results showed a progressive shift of the exothermic peak of cement hydration towards shorter times as the amount of added CSH increases, meaning that the presence of additional available surface accelerates the hydration reaction. Plus, they showed that CSH seeds allowed precipitation to occur rapidly in the pores of the cement paste were the seeds are initially situated, leading to an increase of hydration rate when the C_3S grains are covered with hydrates and to more uniform porosity after 28 days. Modeling the system, the authors explained the double peak obtained in isothermal calorimetry by the occurrence of two phenomena, which are the "classical" precipitation of hydrates at the surface of anhydrous grains and the precipitation on CSH seeds in the pores. Kocaba et al. [14] studied the effects of a the substitution of cement by slag in a cement paste and showed that it accelerates cement setting, as the cumulative heat measured by isothermal calorimetry is greater in the presence of slag than in cement alone. This difference is attributed to the contribution of the reaction of the slag itself but also to the impact of the physical presence of slag on the rate of hydration of the clinker phases (filler effect). These two effects are separated.

In the present work we wish to see if similar tendencies can be observed in the case of lime and to get more information on the impact of lime on the structure. In that aim we will follow the evolution of the porous structure through NMR relaxometry and the mechanical properties of the cement paste mixed with various lime quantities with the help of rheometrical tests. We start by describing the materials and methods (Section 2) then we analyze the structural evolutions of a cement paste (Section 3), a lime paste (Section 4) and a lime-cement paste (Section 5). In a last part, we look at the effect of lime concentration on cement setting (Section 6).
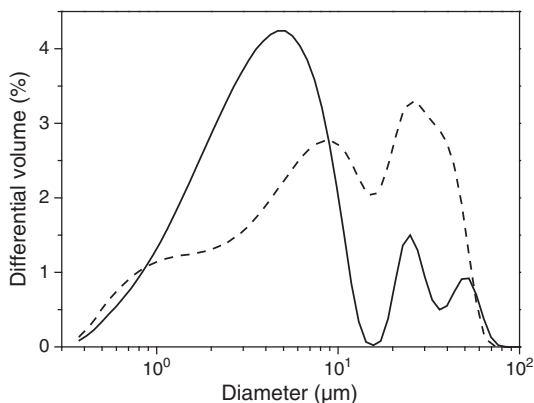

Fig. 1. Particle size distribution of raw materials: lime (continuous line) and cement (dashed line).
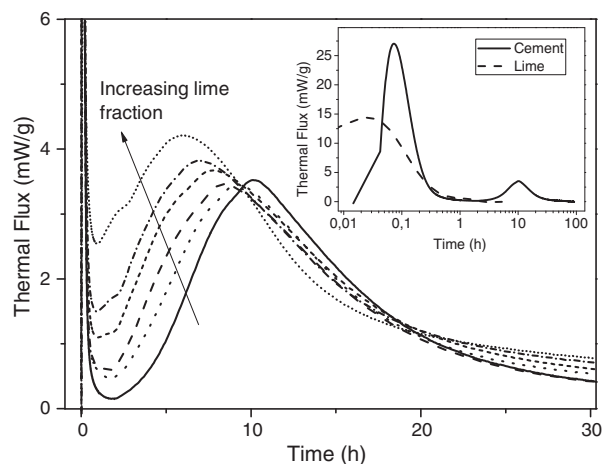

Fig. 2. Monitoring of setting followed by isothermal calorimetry of a cement paste and various lime-cement pastes containing 1 g of cement each. The lime to total solid (cement + lime) volume fractions are 0, 4, 11, 17, 26 and 50%; the water content was adjusted to reach a similar consistency. A comparison of thermal flux in the same cement paste and in a lime paste with a water to lime ratio of 1 is inserted.

2. Material and methods

2.1. Materials

We used a standard hydrated lime CL90 S (according to EN 459-1) provided by *Lhoist*, and a grey cement CEM I 52.5 N from *Vicat*. The composition of the hydrated lime was determined by thermogravimetric analysis (TGA) using a multiple sampling thermogravimetric analyzer TGA-2000 from Las Navas Instruments by a temperature ramp from 20 °C to 950 °C with a temperature increase of 5 °C per minute. The mineralogical composition of the cement was analyzed by Xray diffraction (XRD) performing Rietveld refinement. The compositions obtained using this methodology are presented in Table 1. Table 3 shows selected physical properties. The specific surface area was measured for both materials by N_2 adsorption according to the Brunauer–Emmett–Teller theory (BET) using a TriStar from Micrometrics. The powder density was determined according to EN 459-2 (loose bulk density). As expected, hydrated lime had a BET specific surface area more than ten times larger than that of cement, and a lower density.

The particle size distribution was measured by light scattering on a Coulter LS 13320 in methanol. Since hydrated lime has a tendency to agglomerate, which can lead to an overestimation of the particle size, the sample was first submitted to ultrasound during one minute (Sonics – 850 W). The cement exhibited a particle size distribution (see Fig. 1) spreading from 1 to 50 µm with a mean size around 10 µm while the hydrated lime contained particles in the range 1–10 µm with an average size around 4 µm. The particles above 15 µm correspond to agglomerates of lime particles which have not been disagglomerated by the US treatment.

Table 1
Main components of the studied cement, as determined by XRD.

Component [wt%]	Method	Cement
C_3S	XRD	56.9
C_2S	XRD	22.6
C_3A	XRD	0.6
C_4AF	XRD	14.8
$CaSO_4 \cdot 2H_2O$	XRD	1.7