

C-A-S-H from hydration of limestone calcined-clay cements (LC³) observed by different electron microscopy techniques

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INTRODUCTION

Blended cements are widely used with the aim of reducing the CO₂ emissions associated to cement production. In this context, using both limestone and calcined clays is a good alternative to other supplementary cementitious materials (SCMs). Intermediate-grade clays, i.e. with intermediate kaolinite content, which are widely available on the earth crust and rarely used for other applications, can be used in limestone calcined clay cements (LC³): good performance was obtained for LC³ blends with kaolinite contents of 40-50%. To understand these excellent properties, the phase assemblage of LC³ blends with different grades of calcined-clays was characterized [1]. Among the phases forming during hydration, the calcium silicate hydrate (C-S-H phase) is of high interest. When using SCMs, C-S-H incorporates a low quantity of aluminum and is called C-A-S-H. The morphology of this hydrate is of particular interest since it can influence the macroscopic properties of concrete such as transport or strength properties. Nevertheless, it is impossible to observe on polished sections by conventional scanning electron microscopy (SEM) because of its size. For this purpose, high resolution SEM (HR-SEM) done on fractured surfaces is preferred. However, it is difficult to obtain high quality images of well hydrated samples because of charging effects. This charging comes from the rugosity of the observed surfaces.

Transmission Electron Microscopy (TEM), using TEM and/or scanning TEM (STEM) mode, is a powerful tool to study hydration of cementitious materials, especially with the goal of studying the microstructure and composition of hydrates [e.g. 2]. Contrary to HR-SEM analysis, high quality STEM images may be obtained at every stage of hydration, varying the sample preparation methods: milling by focused ion beam (FIB) at early ages or by precision ion polishing system (PIPS) for later ages. Nevertheless, the main drawback of this technique is the time-consuming preparation of the specimens (called TEM lamellas).

MATERIALS AND METHODS

LC3-50 blends, composed of 50 wt. % of PC, 15 wt. % of limestone, 30 wt. % of calcined clay and 5 wt. % of gypsum, were studied. Three different types of calcined clays were used, containing 17%, 50% and 95% of kaolinite. Portland cement was also used for comparison. Cement pastes were produced using a water to binder ratio of 0.4. The hydration was stopped by isopropanol exchange at 3 days and 14 days for HR-SEM observations and at 28 days for TEM.

Preparation of the samples for HR-SEM observations

Hardened cement pastes were fractured into pieces of approx. 2*2*1 mm, put onto a carbon conductive tape placed on top of an aluminum stub and finally covered by a layer of 5 nm of iridium to ensure electron conductivity using a Quorum coater Q150. A FEI XL-30 SFEG microscope was used with an accelerating voltage of 1.5 kV, a spot size of 3 and working distances of 1.4-1.7 mm, these parameters being required for high resolution images.

Preparation of the TEM lamellas

Similar pieces of hardened cement pastes were embedded in Sigma-Aldrich Epoxy Embedding Medium resin and then cut to approx. 2*2*0.7 mm size by diamond-wire saw. They were mechanically polished with Allied diamond lapping films. They were then transferred to a Gatan PIPS, operated at -110°C, where they were thinned by two argon guns down to electron transparency. It corresponds to a thickness of about 100 nm.

For STEM images, a FEI Tecnai Osiris TEM was operated at 80 kV with a small spot size, corresponding to a current of 0.15 nA. These parameters aimed at not degrading the hydrates which are well-known to be beam-sensitive [2,3].

RESULTS

HR-SEM images were recorded in areas where C-A-S-H was supposed to be present. Figures 1 and 2 show images of fractured pastes hydrated 3 days, for PC and LC3-50 blends. Figure 3 shows similar images after 14 days of hydration, for PC and the LC3-50 blend with 95% of kaolinite. At this stage of hydration, a lot of hydrates are present, and high quality pictures are difficult to obtain because of charging effects. It was not possible to record high quality pictures of LC3-50 systems with 17% and 95% of kaolinite.

C-A-S-H is indicated by white arrows on the pictures of Figures 1-3. The C-A-S-H morphology of the four samples looks like sheets or foils, not fibrils as it was expected for a blended cement at this stage of hydration [2, 4]. There seems to be no difference in C-A-S-H morphology between PC and LC3-50 systems. Moreover, there is no evidence of any morphology change with the calcined kaolinite content.

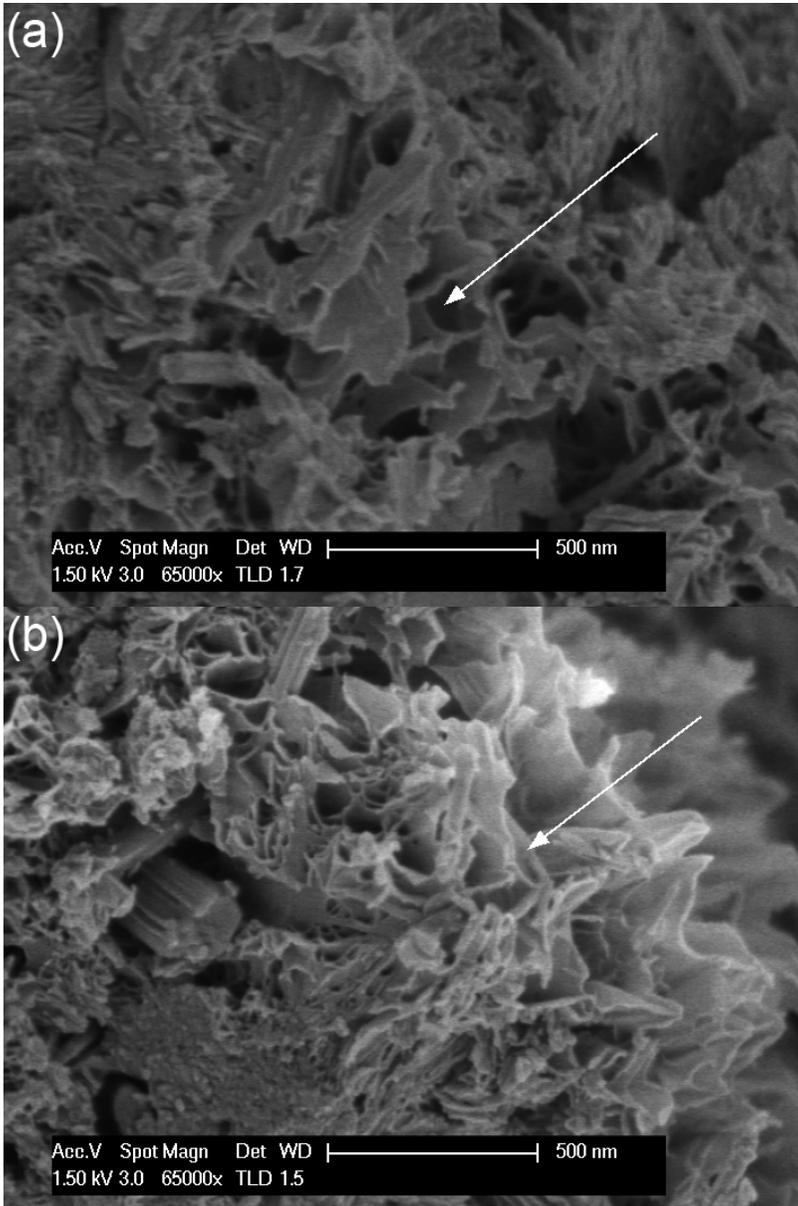


Figure 1: HR-SEM images of fractured surfaces of hardened cement pastes after 3 days of hydration, (a) PC, and (b) LC3-50 cement containing clay with 17% kaolinite content. White arrows indicate C-A-S-H.

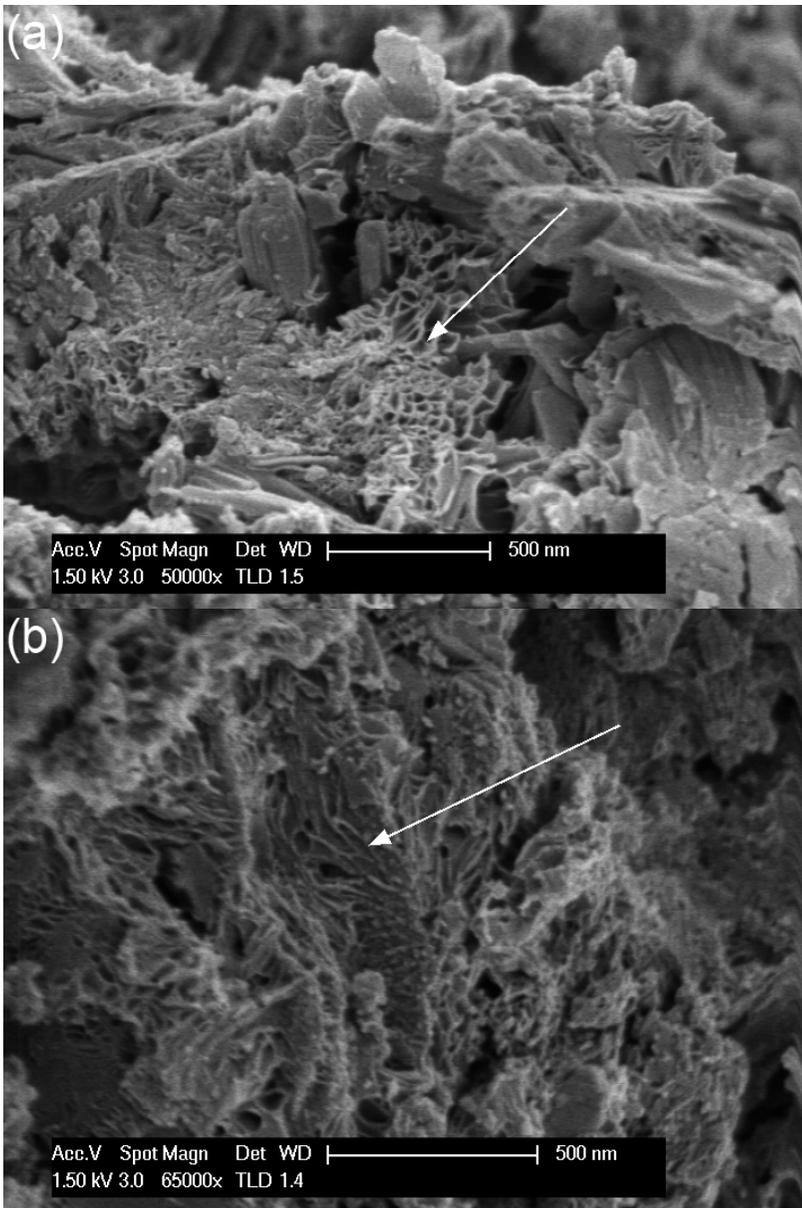


Figure 2: HR-SEM images of fractured surfaces of hardened cement pastes after 3 days of hydration, (a) LC3-50 cement containing clay with 50%, and (b) 95% kaolinite content. White arrows indicate C-A-S-H.

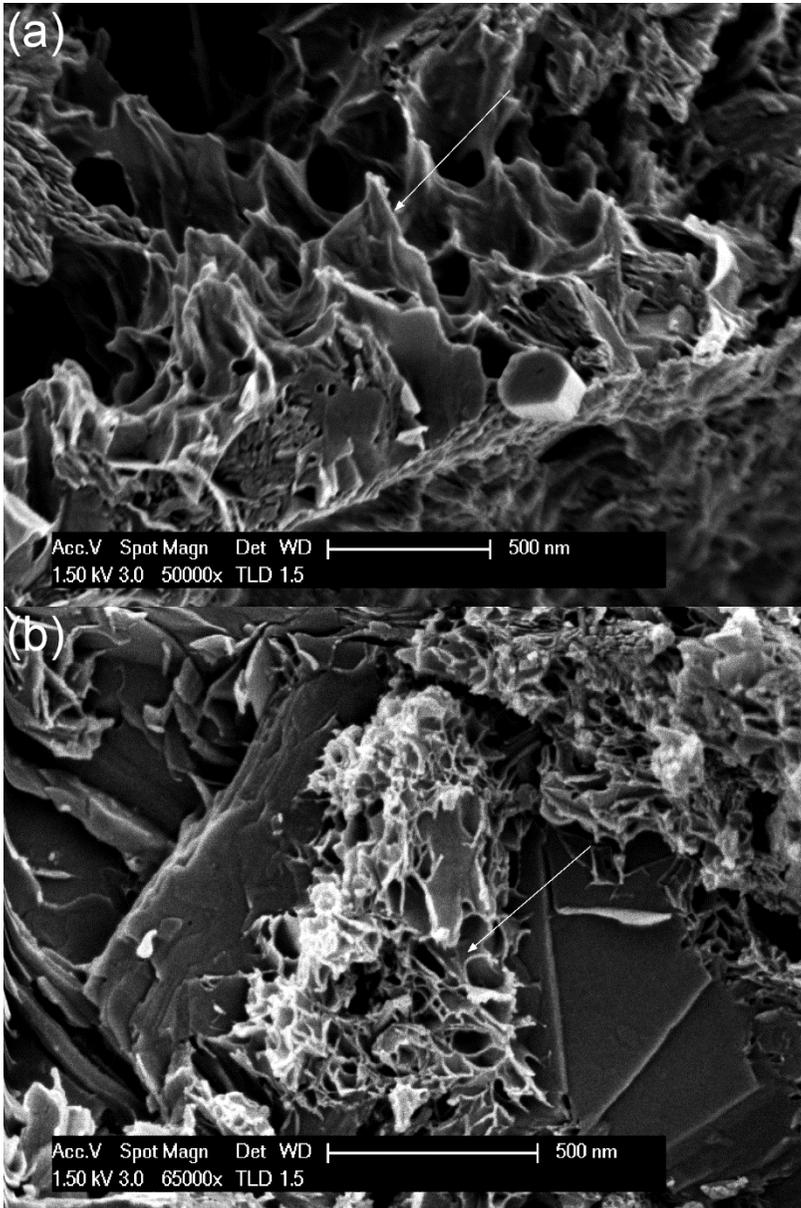


Figure 3: HR-SEM images of fractured surfaces of hardened cement pastes after 14 days of hydration: PC (a), LC3-50 cement containing clay with 95% kaolinite content (b). White arrows indicate C-A-S-H.

The thickness of the foils was estimated by image analysis and results are given in Table 1. It can be concluded from these results that the thickness of the foils is decreasing with increasing kaolinite content, and is decreasing as well with age for PC and LC3-50 (95% of kaolinite).

Figures 4 and 5 show the STEM bright field images obtained on the four systems after 28 days of hydration. Contrary to the images of Figures 1-3, these images show a fibrillar morphology for C-A-S-H for the four samples, as it was already stressed in [5].

The results of C-A-S-H morphology obtained with HR-SEM and STEM seem to be contradictory: they show a foil morphology of C-A-S-H at 3 and 14 days of hydration whereas fibrils are observed at 28 days. Nevertheless the observation technique was not the same. Although they both end up as two-dimensional (2D) images, HR-SEM show images of surfaces, which can be interpreted in term of 3D, whereas STEM gives images of polished sections, which give only 2D views.

Objects which look fibrillar in 2D could be sheets in 3D, depending on the direction of the sectioning.

Table 1: Thicknesses of the C-A-S-H foils for the studied samples. Thickness of the iridium coating (5 nm) was removed from the measured thicknesses.

Sample	PC		LC ³ -50	LC ³ -50	LC ³ -50	
			17% kaolinite	50% kaolinite	95% kaolinite	
Hydration time	3 days	14 days	3 days	3 days	3 days	14 days
Foil thickness (nm)	7.5 ± 2.5	3.3 ± 2.5	5.8 ± 2.1	5.3 ± 1.9	4.2 ± 2.1	2.1 ± 1.7

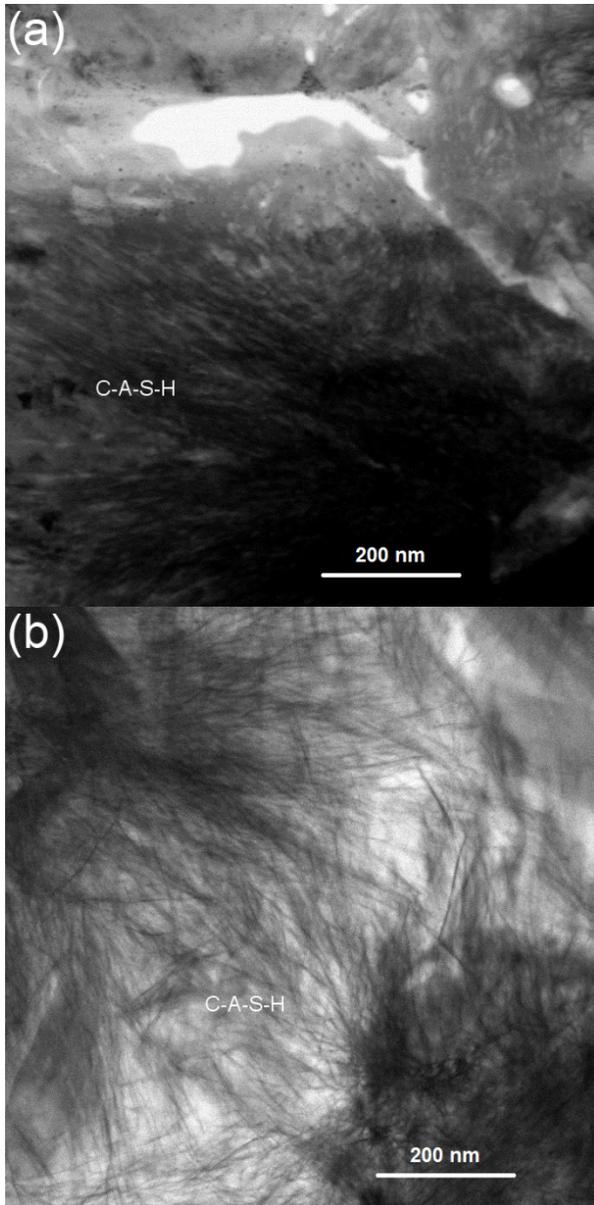


Figure 4: STEM images of cement pastes hydrated 28 days for (a) PC and (b) LC3-50 blend containing clay with 17% kaolinite content.

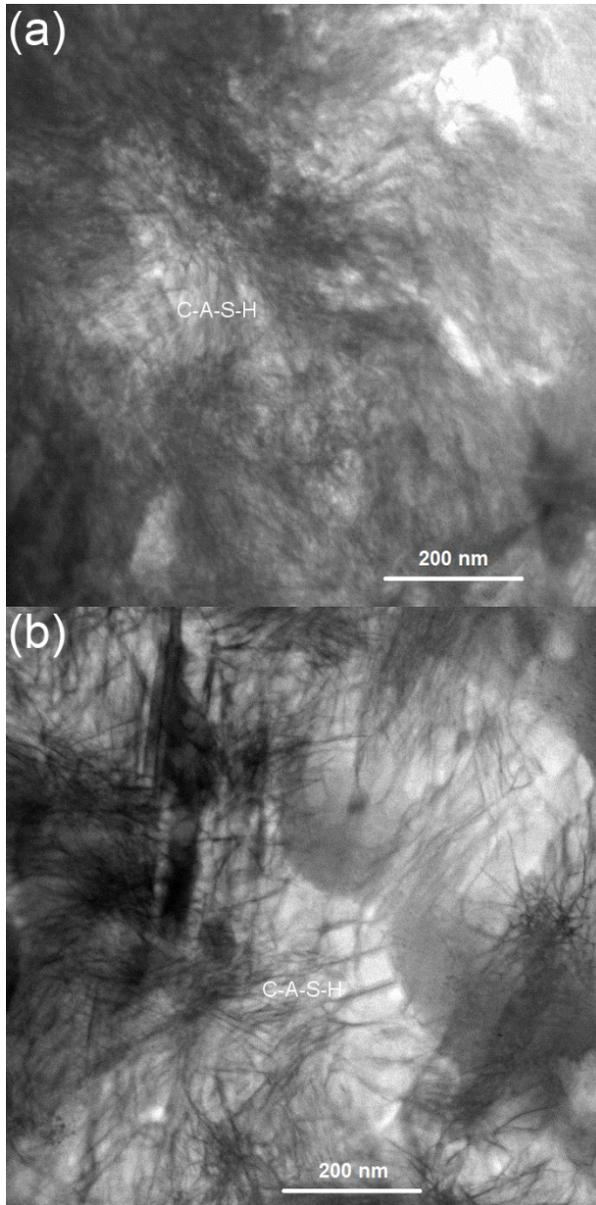


Figure 5: STEM images of cement pastes hydrated 28 days for (a) LC3-50 blends containing clay with 50% and (b) 95% kaolinite content.

CONCLUSIONS

- HR-SEM and STEM are complementary methods for observing the morphology of hydrates in cementitious materials at different ages.
- It has been shown that C-A-S-H morphology in PC and LC3-50 blends looks foil-like at 3 and 14 days, whereas it seems to be fibrillar at 28 days. The difference could come from the different observation methods used in both cases. In order to surely determine if the morphology is fibrillar or foil-like, TEM tomography could be used on the same TEM lamellas than those prepared for STEM observations.
- Moreover, the morphology has been shown to be the same for PC and LC3-50 blends independently of the kaolinite content of the clay.
- The thickness of the C-A-S-H foils was measured and it has been shown to be higher in the case of PC, and to decrease with increasing kaolinite content as well as with age.

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