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Analysis of C_3A hydration using soft X-rays transmission microscopy: Effect of EVA copolymer

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Abstract

The hydration of pure C_3A ($Ca_3Al_2O_6$) in calcium hydroxide–gypsum saturated solution was analyzed using soft X-ray microscopy. The images show the presence of at least two different types of ettringite crystals during the first 4 h of hydration. They differ in morphology and growing rate. When poly(ethylene-co-vinyl acetate) (EVA) is present, there is a significant change in the hydration kinetics and morphology of the hydration products. EVA particles inhibited or even prevented the formation of ettringite crystals during the early stage of hydration. A cloud of small, bright particles are observed concentrated around the hydrating C_3A grains. The particles are most likely to be a product of reaction between EVA and inorganic species in solution.

Keywords: $Ca_3Al_2O_6$; Hydration; Polymer; Microstructure; Soft X-ray transmission microscopy

1. Introduction

Poly(ethylene-co-vinyl acetate) (EVA) is a polymeric additive used to improve the mechanical properties of mortar and concrete, such as flexibility, toughness, impermeability, and adhesion. EVA is mainly used in adhesive mortars. In a previous paper, Silva and Monteiro discussed the influence of EVA on the hydration of C_3S [1]. Using soft X-ray transmission microscopy and infrared spectroscopy, they observed that EVA particles are adsorbed on hydrating C_3S grains starting from the very beginning of the hydration process, thereby decreasing the rate of hydration. Conversely, EVA particles seem to play a role as nucleation agents for hydrated crystals. The formation of a polymeric film was observed 4 h after the beginning of the reaction. The film entrapped and covered the hydrating C_3S particles and the hydrated products. The presence of thick C–S–H needles, the evidence of alkaline hydrolysis of EVA, and the presence of particles with mineral–polymer like morphology led the authors to the conclusion that the reactive groups of both compounds—EVA and C_3S—chemically interact in the aqueous dispersion.

This paper studies the effect of EVA on the hydration of C_3A. The effects of polymers containing acetate groups on the hydration of calcium aluminates have been studied previously, especially for macro-defect-free (MDF) cements. The comprehensive review by Comotti et al. [2] suggests that the acetate groups released by the polymers chemically and physically interact with Ca^{2+} and Al^{3+} ions, forming an amorphous, cross-linked polymer phase and aluminium and calcium acetates; however, MDFs chemistry and microstructure can be very different from regular concretes and mortars, because MDF samples are produced under heating, do not contain sulfates, and have a very low water/cement ratio (around 0.1).

Georgescu et al. [3] studied systems containing C_3A, gypsum, and poly(vinyl alcohol–acetate), with normal water/cement ratios (around 0.6). Using infrared spectroscopy and thermal analysis, the authors concluded that the polymers probably adsorb on the surface of ettringite crystals, retarding their conversion into monosulfate crystals. Furthermore, organic–inorganic compounds are formed due to chemical reactions.

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Table 1
Characteristics of redispersible EVA copolymer*

Ash content (30 min at 1000 °C)	13.0%
Apparent density of the powder (DIN 53189)	472 g/l
Particle size	75 μm > ϕ > 37 μm
Protective colloid	Poly(vinyl alcohol)
Minimum film forming temperature	Approx. 4 °C
pH of EVA dispersion in DI–water, 25 wt.%**	9.1

* Characteristics informed by the copolymer producer.
** Characteristic determined by pH meter.

Few studies deal with the morphology of hydrated phases in the C_3A–gypsum–polymer system. Afridi et al. [4] analyzed the microstructure of EVA-modified mortars through scanning electron microscopy and concluded that ettringite crystals are thicker when EVA is added to cement pastes. They opined that this was due to a decrease in the kinetics of hydration and a modified sulfate supply in the system, which was confirmed by Silva [5]. This finding is contradicted by Chandra and Ohama [6], who reported that the ettringite needles are thinner and smaller in cement pastes with organic admixtures. Clearly, this field requires further investigation.

The transmission soft X-ray microscopy is an important tool to fill this gap. The technique allows the observation of wet samples at atmospheric pressure, i.e., the hydration of cementitious phases can be followed in real time within 5 min after the contact with water. The interactions between the X-rays and the atoms in the sample produce a contrast that permits the formation of an image. The dissolution of particles and nucleation and growth of new phases can be visualized.

To better understand the influence of EVA on the hydration of portland cements, one of its main compounds—C_3A—was synthesized, ground, and analyzed pure or mixed with the copolymer. The development of the hydrated phases from the first moments of the hydration mechanism was followed by soft X-ray transmission microscopy of highly diluted dispersions. The morphology of the hydrated phases, the rate of particles dissolution and growing, and the overall particles distribution were studied during the early hydration.

2. Materials and methods

Pure C_3A was synthesized, ground, and sieved in order to study its early hydration and the effect of EVA copolymer. Particles with dimension smaller than 37 μm were selected for this study.

A commercial redispersible-powdered EVA was used and its characteristics are presented in Table 1. The inorganic part (ash content) of the commercial EVA contains the minerals magnesite (37 wt.% of the inorganic compounds), dolomite (13%), calcite (14%), talc (16%) and kaolinite (20%), identified and semi-quantified using XRD analysis. EVA redispersible-powder was sieved in an attempt to reduce the amount of inorganic phases in the mixtures and particles with diameter between 75 and 37 μm were selected for the analysis.

The soft X-ray transmission microscope used in the research is operated by the Center of X-rays Optics (Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA). Details about the optics features of the synchrotron radiation and the X-ray microscope are described elsewhere [7,8].

Due to the thickness restriction of the sample (up to 10 μm), the solid particles were dispersed in a liquid media and then centrifuged for the analysis. A saturated solution in respect to calcium hydroxide and gypsum (pH = 12.3) was prepared with fresh, boiled de-ionized water and to void carbonation was protected inside a glove bag filled with nitrogen gas.

Wet samples of C_3A with and without EVA were prepared. Two EVA/water ratios were studied (0.02 and 0.04 g/cm^3), and the water/C_3A ratios was 5 cm^3/g. After agitation for not more than one minute and immediate centrifugation for 10 s, a small droplet was taken from the supernatant solution and was assembled in the sample holder between two silicon nitride windows for the analysis (see Refs. [1] and [9] for details regarding this procedure). The samples were analyzed at high resolutions (up to 25 nm) right after the contact with such solution.

In the soft X-ray transmission microscopy, the incident X-rays that pass through the sample are partially absorbed with a spatial variation dependent on the atoms present, their distribution, and the wavelength of the incident rays (λ) [7]. Fig. 1 shows the attenuation length (or absorption) versus photon energy for water, carbon, calcium, sulphur, and aluminium, which are the atoms present in the samples. The photon energy used for the analysis was just below the oxygen edge (517 eV, 2.4 nm wavelength). Because it is above the K absorption edge for carbon (284.2 eV), the absorption of mostly carbon containing organic material at 517 eV is about an order of magnitude less than the

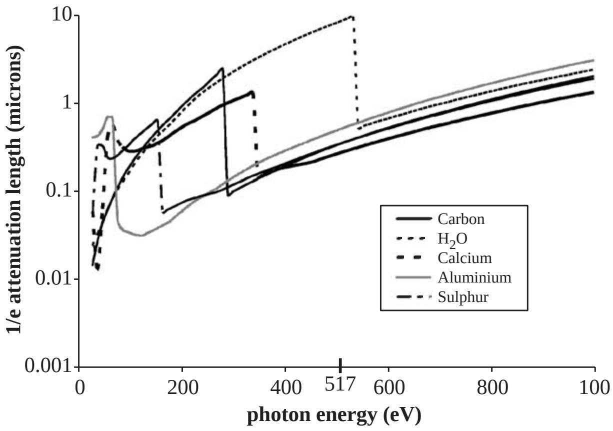
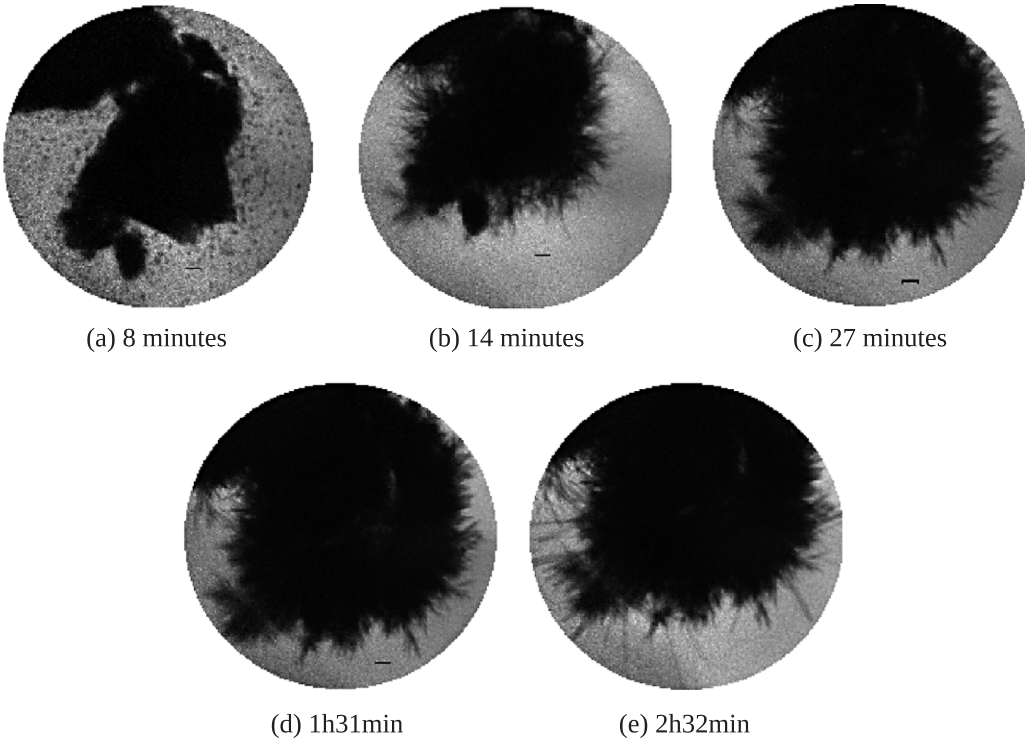


Fig. 1. Attenuation length versus photon energy for water, carbon, calcium, aluminium and sulphur.



(a) 8 minutes (b) 14 minutes (c) 27 minutes

(d) 1h31min (e) 2h32min

Fig. 2. Hydrating C_3A in CH–gypsum saturated solutions from 8 to 2 h and 32 min of hydration (scale bar is 700 nm).

absorption of water which means that a natural contrast is obtained between water and most carbon-bearing phases. i.e., polymer particles are not transparent to soft X-rays. At 517 eV, carbon, calcium, aluminium and sulphur absorb about the same radiation (see Fig. 1). Besides the influence of the characteristics of the incident rays, the contrast between different phases and the water depends on their composition and thickness. For the samples analyzed here, polymeric particles are semi-transparent to the X-rays compared to the metal-bearing phases.

3. Results

Fig. 2 shows some images of hydrating C_3A particles in CH–gypsum saturated solution from 8 min to 2 h and 32 min of hydration. Fig. 2a shows that the solution has many particles in suspension that disappear as soon as the hydrated needles start to grow from the surface of C_3A particle. The aspect of hydration is very similar to that observed when C_3S is hydrating under the same conditions [1]. After 14 min of hydration, the whole surface is covered with hydrated needles. At 27 min of hydration, the particle shows an increased volume (Fig. 2c). From this point to more than 1 h and 30 min of hydration (Fig. 2d), no changes were noticed; the particle seems to be resting in an “induction period.” However, at 2 h and 32 min of hydration (Fig. 2e), longer and thicker crystals grow from the surface of the hydrating C_3A particle. The same pattern was observed in most locations analyzed in the sample. Fig. 3 shows the last image taken during the analysis (at 3 h and 4 min after mixing), where two types of hydrated crystals are evident:

(i) A dense layer of thin needles covering the surface of the hydrating C_3A particle, which seems to fully be developed after 30 min of hydration. These crystals may be a little longer than 1 μm but not thicker than a few nanometers.

(ii) Groups of large needles, which start to grow after more than 1 h and 30 min of hydration and continue growing both in length and thickness after 3 h of hydration. These needles may be longer than 4 μm and thicker than 300 nm, and show lower contrast to the water phase than the thin needles.

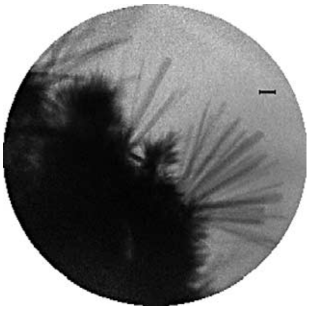


Fig. 3. Thin and thick hydrated needles growing from the surface of a hydrating C_3A particle, 3 h and 4 min after the mixture with calcium hydroxide–gypsum saturated solution (scale bar is 700 nm).

Note that some C_3A particles suffered substantial swelling during hydration. The particle shown in Fig. 2a

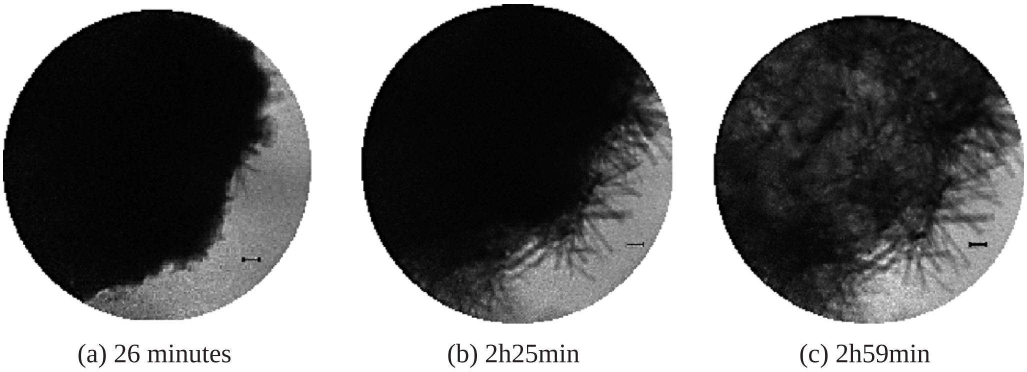

(a) 26 minutes (b) 2h25min (c) 2h59min

Fig. 4. Complete dissolution of a C_3A particle and formation of many hydrated needles inside the original boundaries of the particle (scale bar is 700 nm).

expanded more than 50% from the beginning of hydration to the end of observation. On the other hand, some particles completely hydrate inside their original boundaries after a few hours of reaction, showing no significant swelling. Fig. 4c shows a fully hydrated C_3A particle, semi-transparent to the soft X-rays, formed by many hydrated needles. The expansive characteristic of these crystals causes an 'explosion' later, releasing many of such crystals in the solution.

Contrary to that observed for C_3S [1], hydrated crystals grow and detach from the original C_3A particle, or they nucleate in solution spreading themselves to locations far away from the origin (see Fig. 5).

The presence of EVA copolymer significantly modified C_3A hydration. Fig. 6 shows images of C_3A particles hydrating in calcium hydroxide–gypsum saturated solution when EVA is present. Polymeric particles can be readily recognizable by their spherical shape and semi-transparency. Contrary to the observations made in the samples without EVA, no hydrated needles could be observed during almost 2 h of hydration. Over time, the concentration of polymer particles increased near cementitious grains. It is also possible that the numerous semi-transparent particles shown in Fig. 6c are a product of chemical interaction of C_3A and EVA in the alkaline solution. The hydration process was documented in six different locations of the sample; all of them showed the same aspect during the analysis.

Fig. 7 shows images obtained from a sample left undisturbed in the test tube for 53 min, at which point a droplet was taken for the analysis. As can be seen, many hydrated needles developed from the surface of the C_3A hydrating particle, as well as needles formed in solution or detached from the original particle and dispersed in the solution, even though the concentration of EVA in this sample is twice the concentration used in the sample shown in Fig. 6. The difference between both samples is probably due to the conditions of hydration, i.e., the development of the hydrated needles could be the result of the sample resting in the test tube.

A further but discrete development and densification of the hydrated products can be observed in Fig. 7a and b. However, no large needles were observed in the samples with EVA, in comparison to the crystals detected in the sample without EVA as soon as 2 h after mixing (see Figs. 2–4).

Silva and Monteiro [1] reported the formation of a polymeric film in the C_3S–EVA systems, however no film

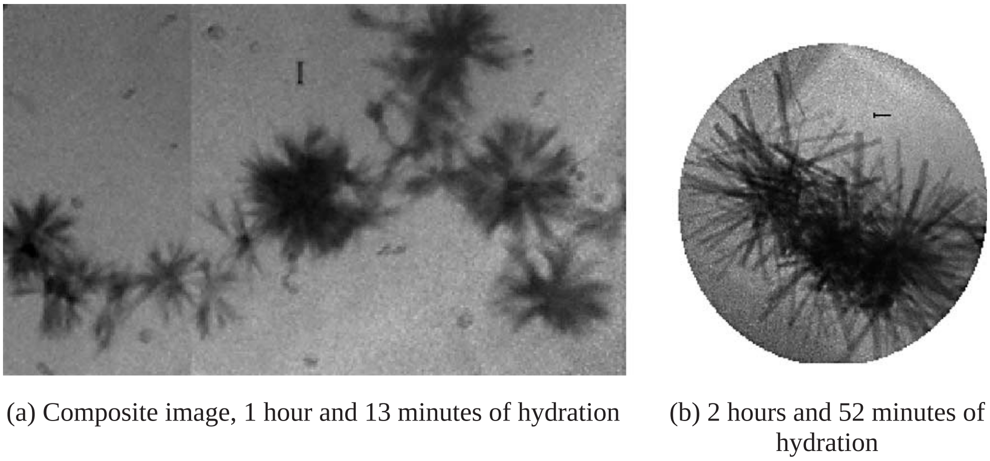
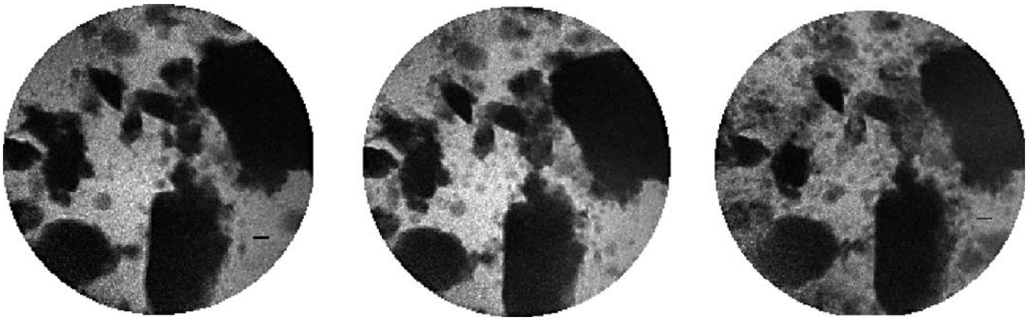

(a) Composite image, 1 hour and 13 minutes of hydration (b) 2 hours and 52 minutes of hydration

Fig. 5. Hydrated particles far away from the original C_3A grain. The images were obtained from two different samples (scale bar is 700 nm).



(a) 7 min (b) 30 min (c) 1h52 min

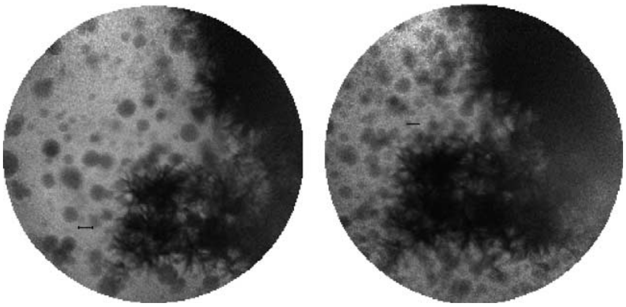
Fig. 6. Hydration of C_3A particles from 7 min to 1 h and 52 min after mixing with EVA and CH–gypsum saturated solution. EVA/water ratio is 0.02 g/cm^3 (scale bar is 700 nm).

was observed in the C_3A–EVA systems even after more than 4 h of hydration.

4. Discussion

Many features of C_3A hydration in a solution saturated with calcium hydroxide and gypsum were observed during the analysis performed by soft X-ray transmission microscopy. The images show that at least two different hydrated products are observed to grow outwards from the surface of C_3A particles. A layer of thin and short hydrated needles covers the surfaces of C_3A particles after few minutes of hydration. Brown and Taylor [10] suggest this layer is formed by ettringite crystals and is probably responsible for determining the setting of cement because its impermeability would decrease the dissolution rate of the anhydrous particles.

The reaction of C_3A with water in the presence of calcium sulfate and calcium hydroxide leads to the formation of ettringite, monosulfate, and C_4AH_{13}, but the extent of the formation of such phases depends on the ratio of gypsum to C_3A [11]. Based on scanning electron microscopy, Amathieu et al. [12] stated that C_4AH_{13} or ettringite form almost instantaneously at the surface of the grains when alumina is available, forming a layer that slows down the dissolution of the grains and the release of aluminium ions to solution. This phenomenon occurs when the concentration of lime in the solution is high, as is the case in the present study. Brown and Taylor [10] however, hypothesized the presence of a layer formed by hydrous alumina underlying the layer of ettringite on the surface of C_3A particles.



(a) 1h20 min (b) 4h30 min

Fig. 7. Hydration of C_3A from 1 h and 20 min until 4 h and 30 min of reaction. EVA/water ratio is 0.04 g/cm^3 (scale bar is 700 nm).

After at least 2 h of hydration, many hydrated needles, much bigger than the previously observed needles, formed mostly at the surface of hydrating particles (see Figs. 2e and 3) but also in the liquid phase (Fig. 5). The size, shape, and the growth geometry (similar to a fan) seem to confirm that the crystals are ettringite as well; they are bright, i.e., they have low contrast to the aqueous phase. The difference between the two types of ettringite crystals is probably due to their different thickness and arrangement. The thicker the needles and the higher the number of needles arranged parallel to the X-ray beam, the darker they look when imaged by soft X-rays.

The availability of Ca^{2+} ions in solution has been reported to influence the morphology of ettringite needles. Even though no analysis of the ionic concentration of the solution was performed, the concentration of calcium ions in the solution is highest at the moment of mixing and is expected to decrease over time with the continuous formation of ettringite crystals. According to Mehta [13], ettringite crystals are smaller and more numerous in the presence of lime, which is in accordance with the images observed in this work. Amathieu et al. [12] stated, however, that the morphology of ettringite needles strongly depends on the alumina concentration of the solution relative to the calcium and sulfate concentrations. Lower alumina concentration would lead to the formation of short, stubby crystals of ettringite. When the alumina concentration is higher, there would be a tendency to form long thin needles of ettringite. Thus, the different morphology of the ettringite needles is probably due to the changes in the ionic concentration or in the CaO/Al_2O_3 ratio of the solution during the course of hydration.

When EVA is present, different features are observed, as reported by Ref. [1], such as the adsorption of EVA particles on the surface of hydrating cement phases, the nucleation of hydrated phases on EVA particles, and the altered morphol-

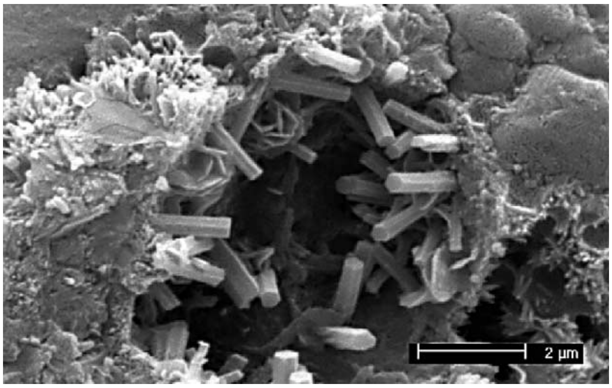


Fig. 8. Ettringite crystals inside a Hadley grain in an EVA-modified, 21-day old cement paste [5].

ogy of the hydrated products compared to pure systems. However, many other features are unique to the hydrating C_3A system.

EVA has an important effect on C_3A hydration, as demonstrated by the aspect of the particles in hydrating C_3A solution. The effect is even stronger than in C_3S systems, studied by Ref. [1]. When EVA is present, no hydrated needles were observed for almost 2 h of hydration in samples. A cloud of small, bright particles around the very dark, hydrating C_3A particles occurs. It is possible they are products of interaction of groups released by the copolymer and inorganic species in solution.

The alkaline hydrolysis of EVA is expected in the high pH (around 12.3) of the saturated solution used in the microscopic analysis, and the bond between the acetate group (CH_3COO^-) and metal ions is also expected. Using X-ray diffraction and electron probe microanalysis, Edmonds and Majumdar [14] observed that acetate polymers complex more readily with aluminium than with calcium ions, possibly through cross-linking of the polymer chains. This could explain the apparent higher reactivity of EVA with C_3A than with C_3S.

Because of the consumption of aluminium rather than calcium ions in C_3A–EVA–gypsum systems, the formation of large ettringite crystals is likely to be inhibited. Assuming that EVA particles act as nucleation sites for hydrated crystals [1], a higher number of small ettringite crystals would exist in cement-based materials containing EVA; Afridi et al. [4] and Silva [5] observed the opposite in cement pastes and mortars. Silva observed very well formed ettringite crystals in EVA-modified cement pastes (Fig. 8) and thin needles of ettringite in pure pastes.

Note that Portland cement-based materials are much more complex systems than the C_3A–EVA–gypsum solutions analyzed here. Others factors can also influence on the crystal nucleation and growth, such as the type and concentration of ionic species in solution and the water/cement ratio. Furthermore, Silva et al. [15] demonstrated that EVA retards the overall hydration of the cement. The large ettringite crystals shown in Fig. 8 could then be due to a slower hydration rate. Indeed, besides the chemical effects of EVA, its adsorption on the surface of hydrating C_3A grains and on the surface of hydrated products, as observed in Figs. 6 and 7, inhibits even more the hydration process.

No EVA film formation was observed in C_3A–EVA–gypsum systems, in contrast to EVA–C_3S systems, where the presence of the film was noticed 4 h after mixing. It is possible that the relationship between the copolymer and the aluminium atoms affects the ability of EVA to form film.

5. Conclusions

The hydration of C_3A in a calcium hydroxide–gypsum saturated solution analyzed by soft X-ray transmission microscopy forms at least two hydrated products with different shape. One is a layer of short, thin ettringite needles that covers the surface of the hydrating C_3A after few minutes of hydration. It is possible that this layer retards the hydration due to its physical effect. The other is observed to exist after at least 2 h of hydration. These long, thick ettringite crystals are arranged in a fanlike shape in solution or grow outward from the hydrating particle. Their distinct morphologies are probably due to a different ionic concentration in the solution over time.

EVA significantly changes the morphology and kinetics of the hydrating system. Its effects are even stronger in C_3A systems compared to C_3S systems (see Ref. [1]). A cloud of small particles forms around hydrating C_3A grains, slowing down the hydration rate and the overall reaction. It is possible the small particles are a polymeric phase or a composite phase formed by the interaction of organic and inorganic species.

Contrary to the observations made in C_3S systems, no film formation was noticed during the analysis, and it is assumed that the interactions of EVA and hydrating C_3A hinder the film-forming ability of the copolymer.

Acknowledgments

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