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Influence of solution chemistry on the hydration of polished clinker surfaces—a study of different types of polycarboxylic acid-based admixtures

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Abstract

The influence of two different types of polycarboxylic acid-based superplasticizers (homo- [HP] and copolymer [CP]) on the early hydration of Portland cement clinker is investigated. Polished clinker surfaces are hydrated in aqueous phase extracted from cement paste with and without superplasticizers as well as in saturated $Ca(OH)_2/CaSO_4$ solution and in deionized water. Scanning electron microscopy (SEM) is used to characterize the early hydration products after 30 min and after 24 h of hydration. Contrary to the hydration reaction with deionized water, in the presence of ionic solutions, the texture and morphology of the clinker surface are significantly altered, and amorphous and crystalline hydration products, mainly ettringite, are formed. The amount and type of ettringite formed are strongly related to solution chemistry and type of superplasticizer. In the presence of superplasticizers, the formation of hydration products and ettringite is reduced and the hydration of the surface is suppressed. Furthermore, the rate of hydration in mortar is studied in the presence of the two admixtures by measuring the temperature evolution as a function of time. The concentration-dependent delay in temperature evolution correlates well with the microscopic observations of different amounts of ettringite formation.

Keywords: Clinker; Hydration products; Ettringite; Admixture; High-range water reducers; Polymers; SEM

1. Introduction

Cement clinker is composed of four main phases: two calcium silicate phases — alite (C_3S) and belite (C_2S), and two calcium aluminate phases namely C_3A and C_4AF.[1] The morphology and composition of the aforementioned phases can vary significantly depending on the manufacturing process and raw materials used. In general, C_3A and alite are more reactive than belite and C_4AF [1]. However, the reactivity of the different phases in clinker can be significantly altered due to the presence of impurities that can introduce foreign ions into the phases and thereby alter their structure and composition. Furthermore, gypsum is normally added to ordinary clinker in the range between 3% and 5% in order to control the rapid hydration of the aluminates. Cement hydration reactions are quite complex not solely due to compositional, morphological, and manufacturing variations, but also to other possible variables such as particle surface area, ambient conditions, and the presence of chemical additives or admixtures. The latter is a significant parameter to consider given that an increasing amount of chemical additives and admixtures are and will be used in order to achieve high-performance concrete exhibiting enhanced durability, strength, and toughness. Thus, understanding the mechanisms underlying cement–admixture interactions has gained significant importance. In fact, numerous cement hydration studies have been focused on the interactions between pure phases, mixtures of pure phases, real clinkers and different types of solutions with and without admixtures [2,3]. The microstructure and morphology of the hydration products have been commonly examined through fracture surfaces of paste and polished sections of clinker [4] and of sintered material [5,6].

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[1] Standard cement nomenclature is used: $C = CaO/S = SiO_2/H = H_2O/A = Al_2O_3/F = Fe_2O_3$.

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Table 1
Composition (%) of clinker (produced for ENV 197-1 Type I cement) measured with XRF

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	Mn_2O_3
21.2	4.3	2.3	65.7	1.9	0.71	0.11	1.5	0.27	0.33	0.02

Presently, one of the most widely used admixtures in the construction industry are *(super)plasticizers*. These admixtures improve the workability of concrete and reduce the amount of water required to achieve the required workability. Uchikawa et al. [7,8] have carried out extensive studies on the mechanisms of water-reducing and the fluidity-improving actions of organic admixtures in preparing fresh concrete. The whole range of admixtures (β-naphthalene sulfonic acid-, lignin sulfonic acid-, melamine sulfonic acid-, aminosulfonic acid-, and polycarboxylic acid-based organic admixtures) and available techniques for investigation were used. Polished clinker cross-sections were hydrated by dipping in water and aqueous solutions of organic admixtures for 30 s and investigated with in-lens type field emission scanning electron microscope (FESEM). Compared to the water experiment, where only little difference in the structure was observed (some tiny dissolution in alite phases), the presence of admixtures lead to the formation of particles in the nanometer range on alite and interstitial phases. In their environmental scanning electron microscope (ESEM) study on hydration of individual cement phases, Mehta et al. [9] have also investigated the influence of lignin sulfonic acid-based organic admixture (0.5% in aqueous solution) during early hydration (1 h) of (Class H cement) clinker thin sections. They found, compared to the pure water control experiment, that the hydration reactions — extensive dissolution of calcium silicate phases — were not impeded by the presence of the admixture but the presence of the admixture prevented any $Ca(OH)_2$ precipitation from the mix water. However, no extensive hydration studies have been performed specifically focusing on the latest type of superplasticizers based on polycarboxylic acid chemistry.

The aim of the present work is to investigate the influence of two types of polycarboxylic acid-based superplasticizers on the early hydration (between 30 min and 24 h) of the principal phases in cement. The testing conditions are designed to be simple and make use of the components actually existing in cement and not pure phases. Thus, polished surfaces of real OPC clinker were hydrated through their exposure to different types of solutions: aqueous phase extracted from cement paste (extracted solution) with and without the addition of superplasticizer, saturated solution of calcium sulfate/calcium hydroxide, and deionized water. Using polished samples, one can identify the different clinker phases and follow their specific interaction with the various solutions. The evolution of the microstructural and morphological changes on the clinker surfaces is characterized using conventional scanning electron microscopy (SEM). The changes observed on the polished clinker surfaces are correlated to the hydration behavior of mortar in the presence of different dosages of superplasticizer.

2. Materials and methods

2.1. Clinker

Crushed clinker (commercially produced for ENV 197-1 Type I cement/OPC, chemical composition given in Table 1) with a particle size of 0.16–0.32 mm is embedded in a polyacrylate matrix. The samples are ground and polished with diamond powder, using ethylene glycol in order to prevent hydration or dissolution of the clinker phases during sample preparation. The procedure resulted in a flat surface where the different clinker phases can easily be identified under a light microscope. Alite has an angular, often pseudo-hexagonal shape, whereas belite usually occurs as rounded, normally striated grains with lamellar structure [2,3]. The compositional homogeneity of the interstitial phase is known to be dependent on the conditions during the manufacturing process and the content of C_3A. Larger C_3A crystals can appear as a dendritic texture in C_4AF [3,10]. The reflected light micrograph presented in Fig. 1 shows a typical HF etched polished section used in this study. The alite and belite grains are embedded in an interstitial phase composed of a mixture of C_3A and C_4AF. Note that in the clinker used for this study, the predominant phases are alite and interstitial with only a small presence of belite and a few round-shaped inclusions of free CaO. In some areas, the interstitial phase is not homogeneous and small inclusions are observed which could be C_3A. Thus, in this investigation, no distinction is made between C_3A and C_4AF, and therefore hydration is compared only between the alite phase and the interstitial phase.

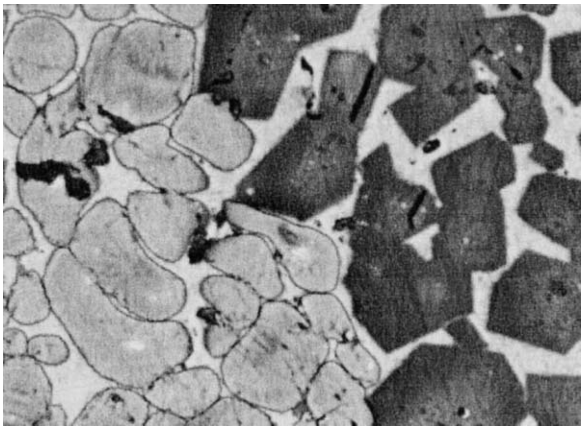


Fig. 1. Reflected light micrograph of polished clinker section (HF etched) with prismatic alite (right part, dark grey) and round belite (left part, grey) embedded in interstitial phase (bright).

Table 2
Composition (mg/l) of deionized water, artificial solution [saturated $Ca(OH)_2/CaSO_4$ solution], and extracted solution (aqueous phase extracted from ENV 197-1 Type I cement paste after 30 min hydration) measured with ICP-OES

	Al	Ba	Ca	Cr	Fe	K	Li	Mg	Na	S	Si	Sr
Deionized water	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.01	< 0.1	< 0.1	< 0.1	< 0.01
Artificial solution	< 0.1	< 0.1	1360	< 0.1	< 0.1	1	< 0.1	< 0.1	3	400	0.3	< 0.1
Extracted solution	< 0.1	0.5	770	22	0.2	14,000	4.2	< 0.1	720	5000	< 1	13

2.2. Solutions

Three basic solutions are selected for hydrating the polished clinker surface (Table 2): deionized water, artificial solution, and extracted solution (aqueous phase extracted from ENV 197-1 Type I cement/OPC paste). The experiments with the superplasticizers are exclusively performed with extracted solution.

The artificial solution is a simplified imitation of pore solution. 2.0 g $CaSO_4 \cdot 2H_2O$ and 1.7 g $Ca(OH)_2$ are mixed in 700 ml deionized water and left standing at room temperature over 1 week before use to ensure equilibrium conditions. The chemical analysis of this saturated solution with calcium, hydroxide, and sulfate ions is given in Table 2. The sulfate content is ~ 1.0 g/l (by ion chromatography) and the pH value is 12.5.

The extracted solution is obtained by filtering neat Type I cement paste ($W/C = 0.5$) after 30 min of hydration. The pH value of the extracted solution is larger than 13. The SO_4^{2-} content is ~ 14 g/l. The detailed ionic composition is presented in Table 2.

For experiments containing superplasticizers, the admixture is added to the extracted solution. Two different polycarboxylic acid-based superplasticizers are used: a homopolymer (HP) and a copolymer (CP), related to the backbone which consists for HP of one type of monomer and for CP of two types of monomer. Both are graft CPs, i.e., they consist of a backbone and side chains. The side chains are, in both cases, polyethers. The admixtures are used as pure compounds in a nonformulated and noncommercial form with higher solid content. They were added at two dosage levels: 0.4% (concentrate solution) and 0.004% (dilute solution) added by weight of active dry substance. 0.4% superplasticizer in relation to the water lies within the usual range for such products. 0.004% was chosen in order to imitate the decrease of the concentration in the aqueous phase, which can occur in real systems due to adsorption and incorporation.

2.3. Preparation and examination of the hydrated clinker surfaces

The embedded and polished clinker samples are hydrated by hanging them (polished side downwards) in excess amounts of the aqueous solutions described above. It was deliberately decided to hang the samples in solution instead of pouring solution onto the polished surface in order to avoid the deposition of free precipitates on the examined surface. An advantage of this experimental technique is that one has spatial control over the hydration products that selectively form in association to a particular phase.

For each experiment, samples are placed in freshly prepared solutions. The reactions are carried out in a closed container that include a reservoir of $Ca(OH)_2$ solution which acts as a trap for CO_2. When a specimen is removed from the liquid solution, it is first rinsed by dipping it in deionized water for a few seconds in order to

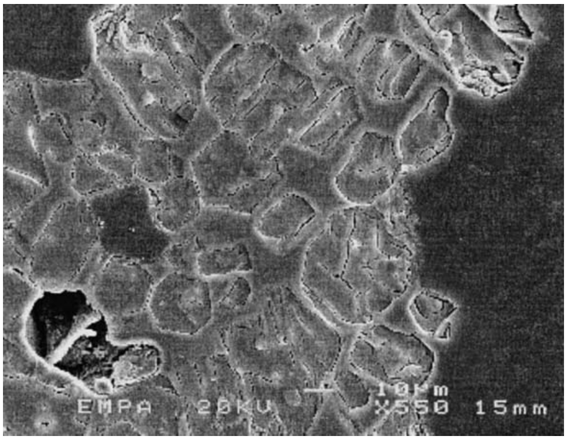


Fig. 2. SE micrograph of polished clinker surface after 30 min hydration in deionized water, relief structure, polyacrylate matrix (right side and top left, dark grey).

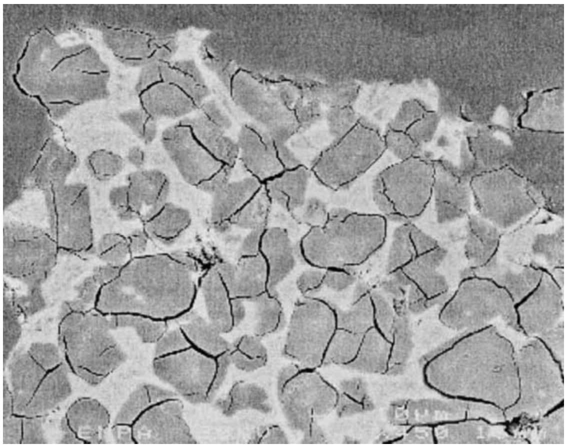


Fig. 3. BSE micrograph after 24 h hydration in deionized water, alite phases (dark) with cracks, interstitial phases (bright), and polyacrylate matrix (top, dark grey).

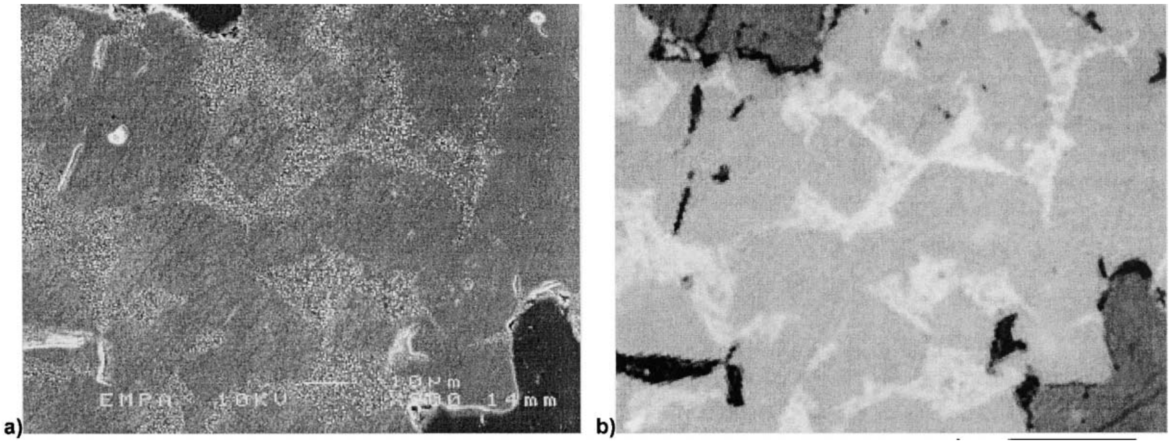


Fig. 4. (a) SE micrograph of polished clinker after 30 min hydration in artificial solution, phases are visible by the unequal formation of hydration products. (b) Reflected light micrograph of the same section before hydration, alite phases (dark), interstitial (bright), polyacrylate matrix (dark grey), and holes (black).

dilute the liquid film of concentrated solution reactants. Then the specimen is dipped twice in an ethanol solution for a few seconds to stop the hydration reaction. Finally, the sample is dried in vacuum (approx. 10^{-2} Torr) at room temperature for about 1.5 h. It is observed from preliminary tests that insufficient washing of the sample can lead to surface deposition of precipitates in the film of solution covering the clinker surface during removal (surface tension effects).

The clinker surfaces are investigated in the unhydrated state and in the early stages of hydration (30 min and 24 h) using conventional SEM. Changes of specific details upon hydration are observed. For the SEM investigations, a conductive layer of gold or carbon was applied to the samples using standard SEM preparation procedures. Secondary electron (SE) mode was used for the observations, and occasionally, back-scattered electrons were employed to facilitate phase identification. In order to facilitate the text, often, "alite phase," "interstitial phase," and equivalent terms are used well knowing that actually the hydrated material existing at the surface of these phases is seen.

Energy dispersive X-ray analysis (EDX) was used to determine the composition of the hydration products. However, the nature of the information obtained is only qualitative because the hydrate layer or products are too thin, thus the hydrates cannot be analyzed exclusively without including chemical composition of the background.

2.4. Hydration: heat evolution in mortar

The hydration of mortars is investigated by monitoring the temperature change. The mortars are prepared according to European Norms (EN) 196-part 1 by mixing 225 g tab water, 450 g cement CEM I 42.5 (cement manufactured with the type of clinker used in this study), and 1350 g Norm sand. Four concentrations of admixtures (0.1%, 0.2%, 0.5%, and 1.0% dry substance based on cement mass) are evaluated besides the plain mortar. The hydration monitoring set-up consists of a thermocouple and an insulating

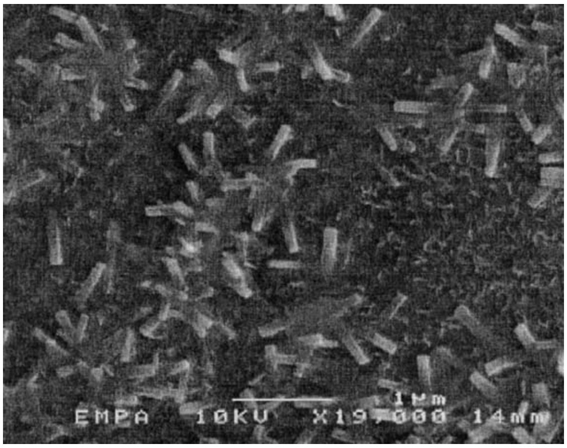


Fig. 5. SE micrograph of alite phase after 30 min hydration in artificial solution, prisms and tiny rod-like deposits.

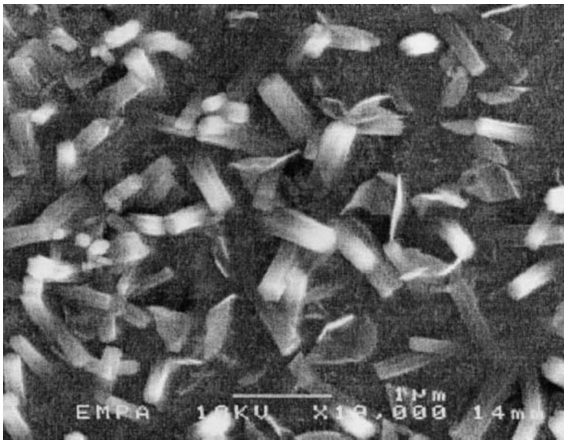


Fig. 6. SE micrograph of interstitial phase after 30 min hydration in artificial solution, hexagonal prisms and irregular-shaped sheet-like structures.

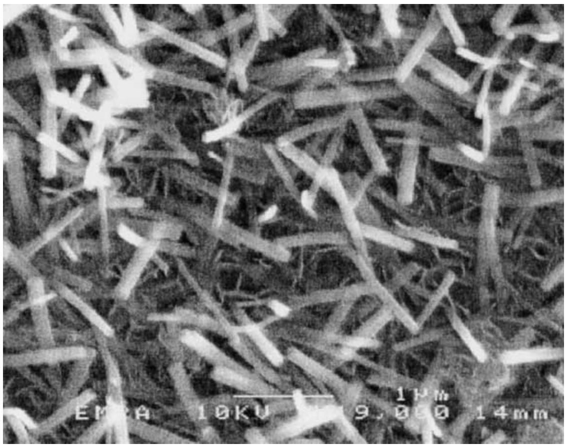


Fig. 7. SE micrograph of interstitial phase after 24 h hydration in artificial solution, needles and interlaced mesh-like structure underneath.

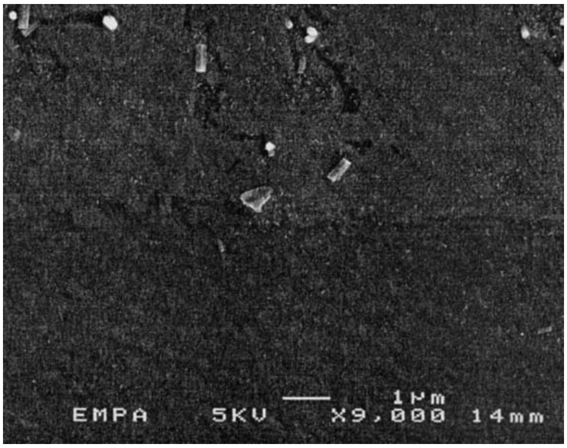


Fig. 9. SE micrograph of polished clinker after 30 min hydration in extracted solution, interstitial phase (upper part) and alite phase (lower part).

styrofoam box that proved to be effective in isolating the specimen from external conditions.

3. Results

3.1. Hydration of polished clinker surfaces in deionized water

After 30 min of hydration in excess deionized water (see Fig. 2), the polished clinker surface is covered by a uniform hydrate layer exhibiting a relief structure. As mentioned previously, the clinker sample is subjected to a vacuum during sample preparation, and therefore, drying shrinkage is inevitable. Interestingly, the SEM micrograph presented in Fig. 2 shows that cracks are predominant at the alite–interstitial phase interface as well as in the alite phase. Similar observations of the above cracking behavior can be made in micrographs presented by Mehta et al. [9]. These results indicate that the hydration products of the different clinker phases have different drying shrinkage behavior: alite is strongly affected and reduced in volume. Additionally, different thickness of the formed hydrate layer or different tensile strength may play a role.

After 24 h of hydration, the hydrate layer has undergone densification, rendering the distinction between alite and the interstitial phase in SE imaging difficult, if not impossible. Thus, back-scattered electron imaging (BSE) is used to reveal the phases (Fig. 3). Once again, no distinct morphological features are observed such as the formation of hexagonal-plate crystals of calcium aluminate hydrates [11] or calcium hydroxide. However, the images confirm the predominant formation of cracks in the alite phase.

3.2. Hydration of polished clinker surfaces in artificial solution

After 30 min of hydration in a saturated $Ca(OH)_2/CaSO_4$ solution, the clinker surface is covered with several types of hydration products having a distinct morphology. In the SEM micrograph presented in Fig. 4 (before and after hydration), it is clearly seen that the hydration products

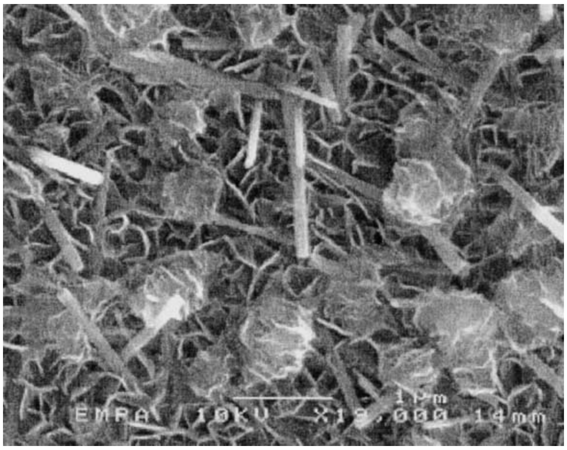


Fig. 8. SE micrograph of alite phase after 24 h hydration in artificial solution, needles and round particles in a scaly interlaced structured surface.

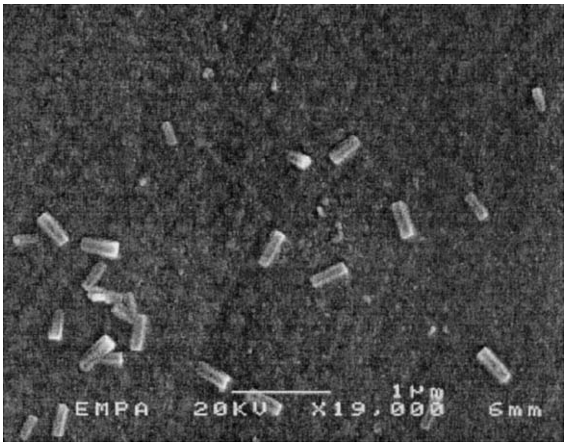


Fig. 10. SE micrograph of alite phase after 30 min hydration in extracted solution, hexagonal prisms and tiny spherical deposits.

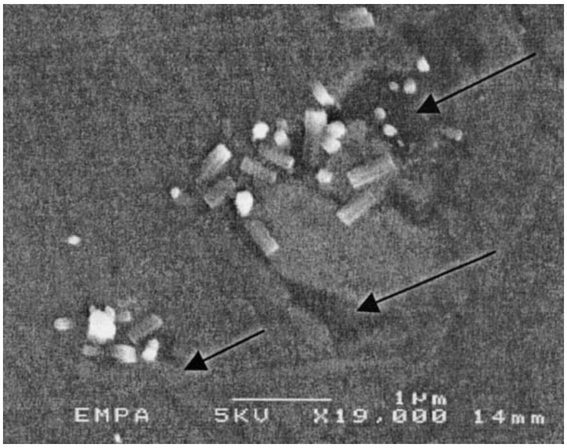


Fig. 11. SE micrograph of interstitial phase after 30 min hydration in extracted solution, hexagonal prisms and areas of lower depth (darker, marked by arrows).

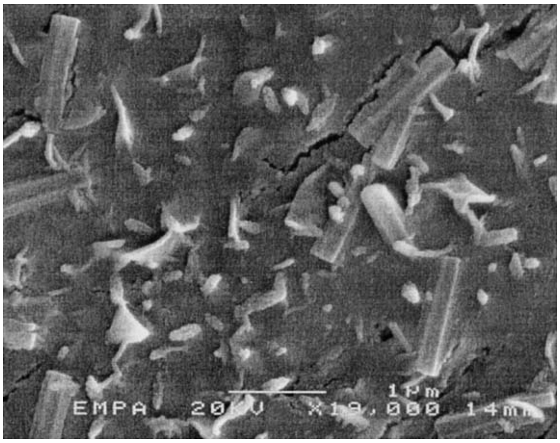


Fig. 13. SE micrograph of alite phase after 24 h hydration in extracted solution, prisms embedded in a layer with irregular-shaped structures and cracks.

formed on the alite surface are different from those formed on the interstitial phase. Ideomorph needles approximately 0.6 μm long (may be longer due to the fact that with SEM only the surface can be seen) and 0.1 μm thick (Fig. 5), and a lot of tiny rod-shaped particles (<0.1 μm) are formed on the alite phases. Whereas on the interstitial phases randomly oriented hexagonal prisms (<1.0 μm and <0.25 μm thick) (Fig. 6) and a few irregularly shaped thin, sheet-like structures are formed. Given that the latter morphology is formed on the aluminum-rich phases, it is likely that the sheet-like structures are comparable to the calcium aluminate hydrate crystals observed by Langenfeld and Stark [11] during hydration of C_3A in water or to small platelets of monosulfate shown in the study carried out by Odler and Shuming [5]. Interestingly, the hydration products observed after 30 min of hydration in the artificial solution are comparable to the 24-h hydration in pure extracted solution.

After 24 h of hydration in artificial solution, the interstitial phase is densely covered with ideomorph thin needles of ettringite, approximately 1.5 μm long. The surface underneath the needles shows a thin mesh-like interlaced structure (Fig. 7). The mesh-like structure resembles a morphology observed by Eckart and Stark [12] during the hydration of C_3A with sulfate solution. On the alite phases, there are only a few thin ettringite needles (1.5 μm long) and round particles of noticeable spherical morphology (diameter approximately 0.5 μm) that are present on a complex scaly interlaced structure (Fig. 8). The scaly interlaced structures look very similar to the C-S-H structures observed by Möser [15] during hydration of C_3S. Concerning the round particles, these resemble some C-S-H structures observed by Odler and Shuming [5].

3.3. Hydration of polished clinker surfaces in pure extracted solution

After 30 min of hydration in pure aqueous phase extracted from cement paste, a hydrate layer has formed

Fig. 12. SE micrograph of polished clinker surface after 24 h hydration in extracted solution, top: polyacrylate matrix (dark).

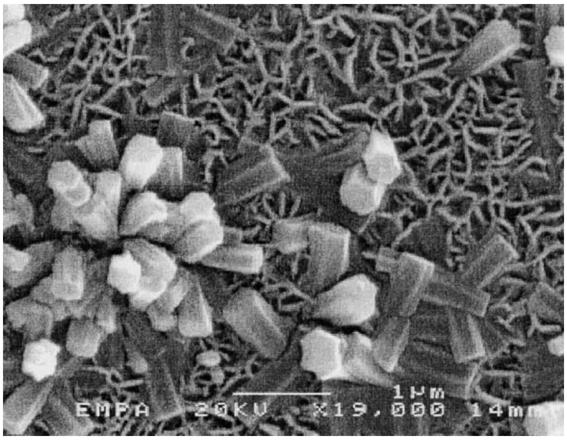


Fig. 14. SE micrograph of interstitial phase after 24 h hydration in extracted solution, clustered prisms and interlaced root-like structured surface.

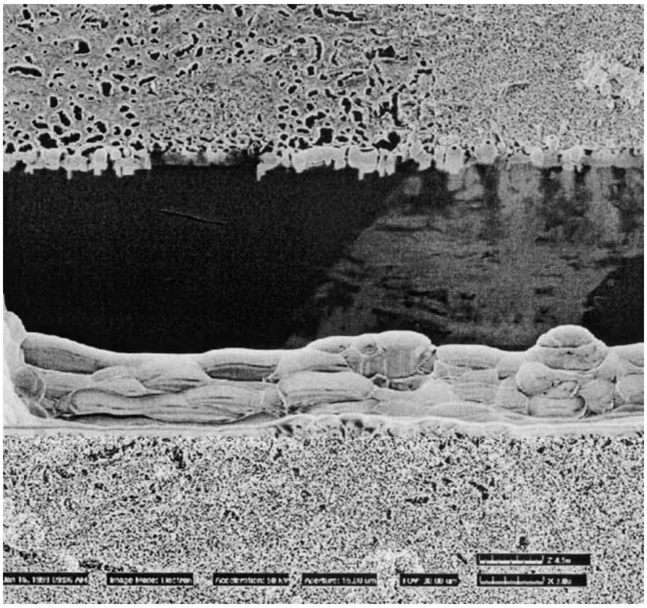


Fig. 15. SE micrograph of hydrated clinker surface after 24 h hydration in extracted solution (top), vertical cut (middle) by focused ion beam through alite phase (left side, dark) and interstitial phase (right side, bright spotted).

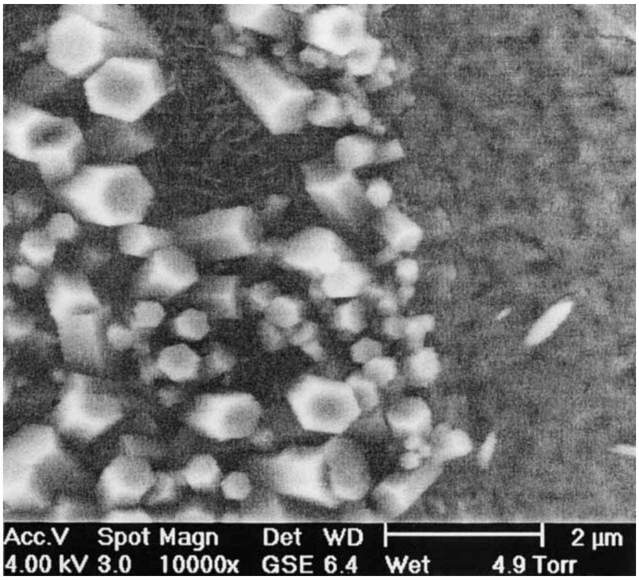


Fig. 16. ESEM micrograph of polished clinker after 19 h hydration in extracted solution, interstitial phase covered with hexagonal prisms and an interlaced mesh-like structured surface in between (left part), alite phase with a rough structured surface (right part).

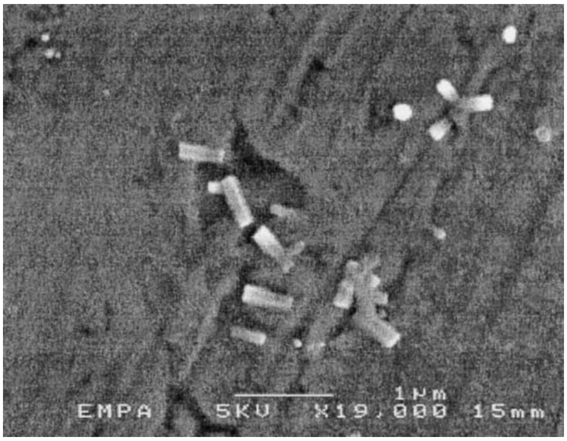


Fig. 17. SE micrograph of interstitial phase after 30 min hydration in extracted solution with 0.004% CP, prisms and areas of lower depth.

over the clinker phases (Fig. 9). However, the layer of hydration products covering the alite phase is rougher and characterized by a spherical morphology, whereas the interstitial phase is covered by a hydrate layer having a smoother surface. A few ideomorph prisms (0.4 μm long, Fig. 10) are also spread on the alite phases. However, these prisms lie parallel to the surface, and are most likely deposited on the alite phase during the rinsing process. On the interstitial phases, there are a few small spherical particles and hexagonal prisms (<0.5 μm long, ~ 0.1 μm thick) growing out of areas that are lower in depth (Fig. 11). These depressed regions could be a result of the rapid hydration of the C_3A of the interstitial phase in extracted solution and the succeeding formation of ettringite.

Following 24 h of hydration (Fig. 12), a distinct layer of hydration products covers the surface. The distinction between the alite phase and the interstitial phase is clear due to the formation of different hydration products. Similar to the above observations, on the alite phases there are deposits of ideomorph prisms of 1 μm in length that are engulfed by a hydrate layer. The formation of an irregular morphology and cracks also occurred (Fig. 13). The interstitial phase is covered by an abundance of hexagonal prisms, approximately 1 μm long and 0.2 μm thick, growing out of the surface in random directions (numerous clusters). In areas of the interstitial phase, not occupied by prisms, the

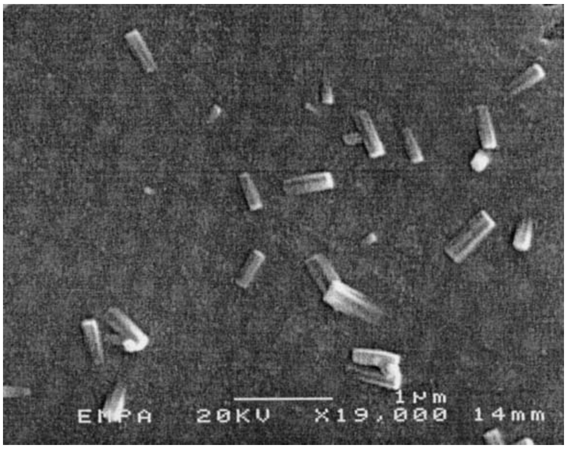


Fig. 18. SE micrograph of interstitial phase after 30 min hydration in extracted solution with 0.004% HP, prisms.

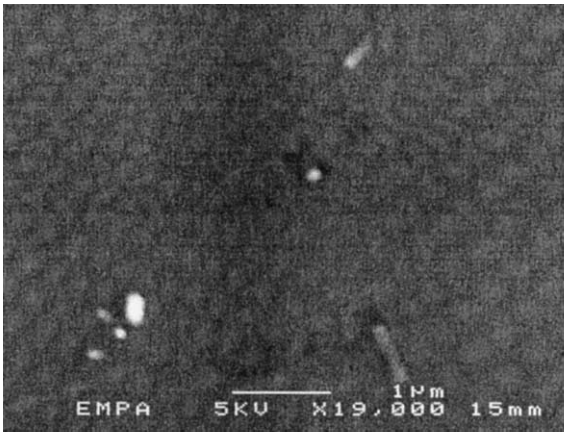


Fig. 19. SE micrograph of interstitial phase after 24 h hydration in extracted solution with 0.004% CP, prisms.

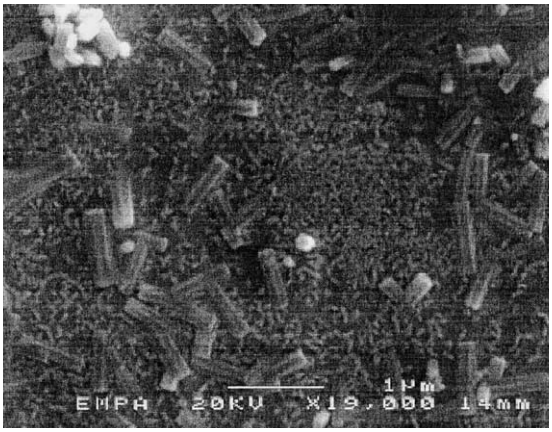


Fig. 21. SE micrograph of interstitial phase after 24 h hydration in extracted solution with 0.004% HP, prisms and rod-like deposits.

formation of a well-defined interlaced root-like structure is observed (Fig. 14). It has a certain similarity to structures described by Eckart and Stark [12] on hydration of C_3A with sulfate solution. This interlaced structure is thicker and different in morphology from the finer and thinner interlaced structure found on alite phases after hydration in artificial solution.

The thickness of the hydration layer was investigated using focused ion beam (FIB), whereby a hole was cut perpendicular to the surface (Fig. 15). From the micrograph, the hydrate layer is estimated to have a thickness between 1 and 1.5 μm.

In order to ascertain that the microstructures observed in the SEM micrographs were products representative of actual hydration and not artifacts from sample preparation, a specimen dipped in extracted solution was investigated with an ESEM. Observations in the ESEM do not require a conductive material or a high vacuum. The ESEM micrograph presented in Fig. 16 is an image of a polished clinker surface hydrated in extracted solution. As one can see, the microstructure (hexagonal prisms and mesh-like structured surface) seen in the ESEM are comparable to those obtained by conventional SEM.

3.4. Hydration of polished clinker surfaces in extracted solutions with 0.004% polycarboxylic acid-based admixtures

An extracted solution containing 0.004% CP is reacted with the clinker surface. After 30 min of hydration, the alite and interstitial phases are weakly visible. On the alite phase, no distinct hydration products form except for a few spherical deposits. In the interstitial region, hexagonal prisms (< 0.5 μm long, Fig. 17) growing from areas with depth lower than the surface, and some spherical deposits are formed. However, in general, there is no significant change in the surface texture when the CP is added in this concentration.

After 30 min of reaction with the extracted solution and 0.004% HP, the clinker phases are clearly distinguishable due to the formation of hydration products on the interstitial

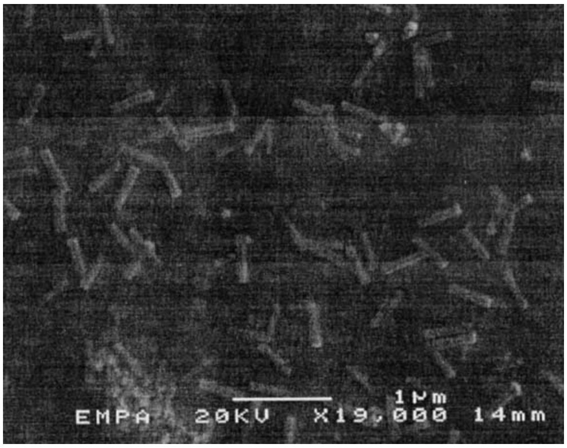


Fig. 20. SE micrograph of alite phase after 24 h hydration in extracted solution with 0.004% HP, prisms and spherical deposits.

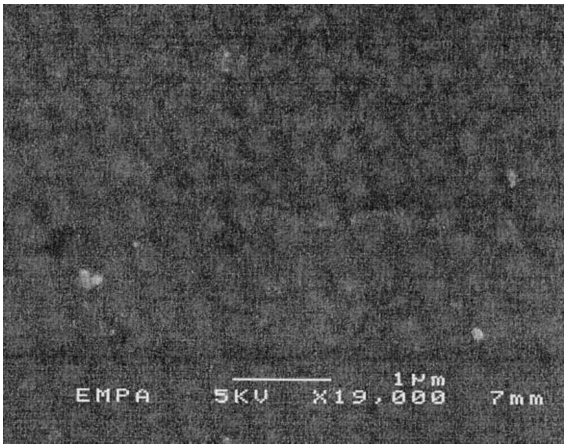


Fig. 22. SE micrograph of alite phase (upper part) and interstitial phase (lower part) after 30 min hydration in extracted solution with 0.4% CP.

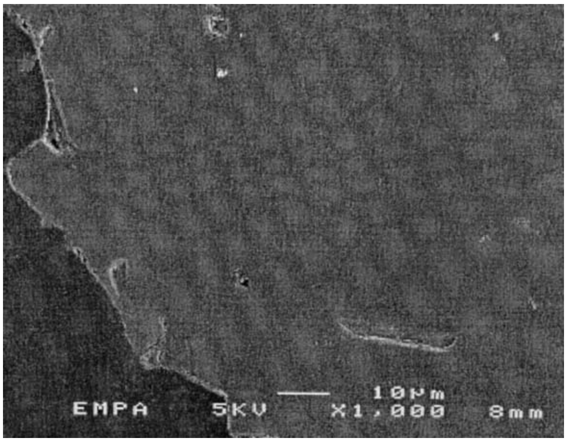


Fig. 23. SE micrograph of polished clinker after 24 h hydration in extracted solution with 0.4% CP, polyacrylate matrix (left side, dark grey).

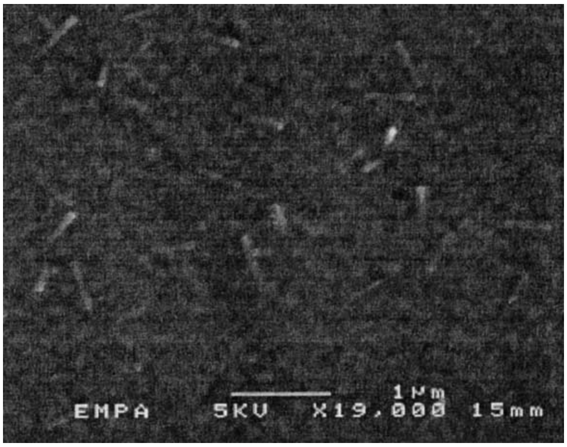


Fig. 25. SE micrograph of alite phase after 24 h hydration in extracted solution with 0.4% HP, fuzzy layer with tiny prisms.

phases. On alite there is no distinct morphology that forms on the surface. Whereas on the interstitial phases (Fig. 18), the abundant formation of hexagonal prisms and few spherical deposits (<0.1 µm) occurs. The texture of the surface has not changed. Unlike with CP, the presence of HP in the extracted solution leads to the formation of noticeable hydration products on the surface of the interstitial phase during the first 30 min of reaction.

After 24 h of hydration in the presence of CP, the clinker surface shows no evidence of hydration products on alite, whereas on the interstitial phase some randomly oriented hexagonal prisms (<1 µm long, Fig. 19) are present. On the other hand, the clinker surface hydrated in the presence of the HP shows the deposition of tiny spherical deposits (Fig. 20) as well as particles with a prismatic morphology (0.4 µm long) on the alite phase. Instead, on interstitial phases (Fig. 21), an abundance of hexagonal prisms (<0.9 µm long) and tiny particles is present.

3.5. Hydration of polished clinker surfaces in extracted solutions with 0.4% polycarboxylic acid-based admixtures

After 30 min hydration in extracted solution with 0.4% CP, the whole sample does not appear to have undergone any appreciable change (Fig. 22). Even after 24 h of hydration, the surface does not show any significant morphological change (Fig. 23). Only a few spherical deposits (<0.1 µm) are present.

On the other hand, a concentration of 0.4% HP in the extracted solution results in distinct changes in surface morphology after 30 min of hydration. Clinker phases are distinguishable due to the formation of distinct hydration products on the interstitial and alite phases. On the interstitial phase, one observes some spherical deposits as well as hexagonal prisms (<0.8 µm long) growing randomly in all directions. Only very few deposits (<0.2 µm) can be found in areas of alite phases.

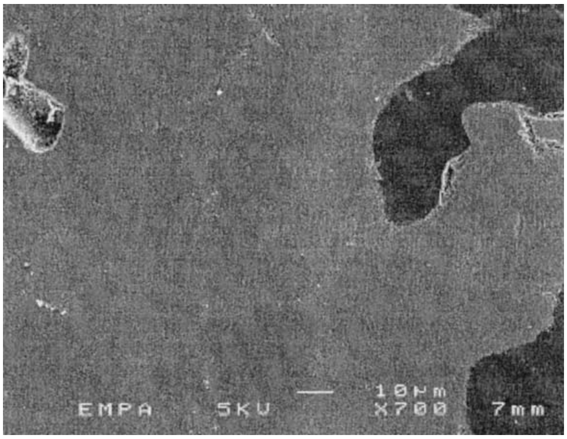


Fig. 24. SE micrograph of polished clinker after 24 h hydration in extracted solution with 0.4% HP, clinker phases weakly visible, polyacrylate matrix (right side, dark grey).

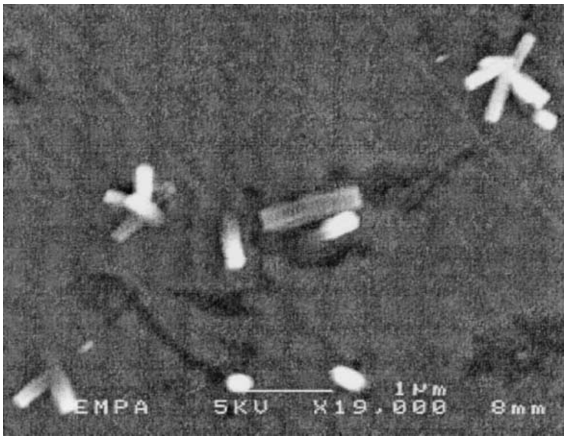
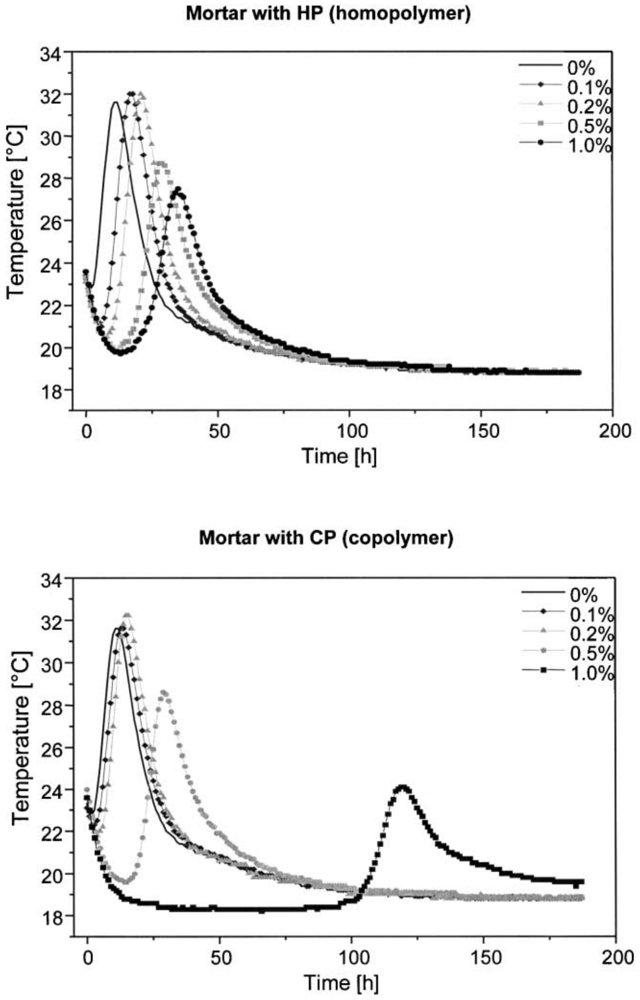


Fig. 26. SE micrograph of interstitial phase after 24 h hydration in extracted solution with 0.4% HP, hexagonal prisms in areas of lower depth (dark grey).

After 24 h of hydration in the concentrated HP solution, the clinker phases are weakly visible indicating growth of a hydration layer (Fig. 24). On the alite phases, some thin ideomorph prisms (0.5 μm long) stick in a fuzzy grained surface (Fig. 25). On interstitial phases, some hexagonal prisms are formed, particularly in areas of lower depth (Fig. 26), comparable to the short-term experiment with 0.004% CP. Nonetheless, the texture of the surface shows no distinct morphological change.

3.6. Hydration: heat evolution in mortar with various amounts of polycarboxylic admixtures

Both superplasticizers, the HP and the CP, significantly influence the setting behavior of mortar. The graphs presented in Fig. 27 show the temperature evolution in mortars containing different dosages of CP and HP. By increasing the dosage of both superplasticizers, the temperature evolution is delayed, and the maximums are shifted to longer hydration times resulting in retardation. At low dosages (0.1% and 0.2%), HP retards more; at high dosages (0.5% and 1.0%), CP retards more. 1.0% CP keeps the mortar even up to an age of 4 days in a plastic state.


Mortar with HP (homopolymer)

Mortar with CP (copolymer)

Fig. 27. Temperature evolution of norm mortars after mixing with water and HP or CP in various concentrations.

4. Discussion

Given the unique experimental set-up adopted in this study, the chemical interactions described are of the type solid-to-liquid phase. More specifically, the set-up basically consists of a two-dimensional multiphase surface exposed to solutions of varying chemistry. The nature of the solid–liquid interactions depends on factors such as the type of interface that exists between the two phases, mode of nucleation, diffusion rate of ionic species in solution (kinetics), precipitation, and growth. In general, there are two types of solid–liquid interfaces: atomically smooth/flat or diffuse/rough interfaces. In this study, the solid–liquid interface is considered to be predominantly of the smooth/flat type, therefore, it is important to note that the interactions between the two phases are most likely to take place in a narrow transition zone. Besides the interface, another important parameter governing the hydration reactions is the solution chemistry. Precipitation, diffusion, pH, nucleation, and growth strongly depend on the ionic concentration (saturated vs. supersaturated conditions) and species. Therefore, in this study, it is important to consider different types of solution chemistry (compositions) and document the range of hydration products that form as a result of the interactions with the clinker phases in order to understand how the polycarboxylic acid-based superplasticizers influence the hydration of the cement clinker.

A product of alite hydration is calcium hydroxide. However, no CH crystals are observed on the surfaces investigated in this study. There are several possible explanations: (1) the used solutions are not completely saturated; (2) they are partly saturated but no nucleation occurs; (3) nucleation occurs only in the liquid phase or on other hydrate precipitates that do not remain on the clinker surface. Since the amount of hydrated alite is small in relation to the solutions, (1) and (2) are more likely than (3).

A common microstructural feature observed in all of the experiments, except for the one with deionized water, is the formation of hexagonal prisms. The EDX microanalysis yields information that would indicate that the hexagonal crystals are ettringite, however, the obtained values are not conclusive since the X-ray results include information from underlying material. Nonetheless, the structure and morphology of the hexagonal crystals, their tendency to form on the aluminate-rich interstitial phases, and their absence in a sulfate-deficient solution are all indications that they are most likely ettringite crystals.

In the deionized water experiments, due to the large volume of water compared to the small surface area of the clinker material, the concentrations of ionic species in solution (Ca^{2+}, OH^-, $SO_4{}^{2-}$, $SiO_4{}^{4-}$, $Al(OH)_4{}^-$) change very slowly, and are too low for a through-solution reaction due to the narrow transition zone between the solid and liquid phases. During the hydration experiment, the ionic species show a rise in concentration, but do not achieve levels required for the formation of new hydration products on the clinker surface.

The formation of gaps in the alite phase subjected to hydration (see Fig. 3) is evidence that more material of the alite phase than of the interstitial phase dissolves. A possible explanation of this behavior is the better solubility of silicon compounds compared to aluminum compounds at a slightly or moderately alkaline pH. A related explanation would be the formation of an insoluble aluminum hydroxide layer on the interstitial phase, which hinders aluminum, iron, and calcium from further dissolution.

On the other hand, in the artificial solution, the pH value and the concentrations of the ions (Ca^{2+}, OH^-, $SO_4{}^{2-}$) apparently do attain a level necessary for the formation of new products. The conditions in the artificial solution lead to the formation of well-defined hexagonal ettringite crystals having a low length-to-thickness ratio. This observation corresponds to the investigations of Chartschenko at al. [13] and Mehta [14] where the length-to-thickness ratio of synthesized ettringite is extremely dependent on the pH value of the solution. Given the higher concentration of Ca^{2+} in artificial solution compared to extracted solution, the formation of more hydration products results. This indicates that the concentration of Ca^{2+} plays a decisive role in hydration.

The higher sulfate concentration in extracted solution (14 g/l), in comparison to the artificial solution (1.0 g/l), does not lead to an increased formation of hexagonal ettringite, but to an alteration in the size of ettringite. Once again, well-defined hexagonal prisms are formed, however, the length-to-thickness ratio is lower compared to the crystals found in artificial solution. These geometrical differences are likely to be a result of differences in pH values between the two solutions.

With extracted solution, well-defined hydration products form and the interstitial phase is more affected than the C_3S phase. This is opposite to the behavior in deionized water and could be explained as follows. The concentrations of the relevant species of the extracted solution (free ions, complexes, clusters, oligomers) are close or even above saturation. Therefore, no phase can significantly dissolve without causing precipitation more or less locally. The higher reactivity of aluminate (C_3A) compared to ferrite ($C_2A_xF_{1-x}$) [2] correlates with the good solubility of aluminum and the bad solubility of iron at pH 13. Of course, the presence of calcium or calcium and sulfate lowers the solubility of aluminum due to the low solubility products of the CAH and $CA\bar{S}H$ phases. However, Fig. 11 is evidence that the compounds of the extracted solution do not prevent the interstitial phase from reacting, but are at least partly incorporated into distinct crystals which are most likely ettringite.

The presence of 0.004% and 0.4% admixtures in extracted solution decreases or retards the ettringite formation significantly. The surface is only slightly affected and no products are formed which are susceptible to cracks as shown in experiments with pure water. Dissolution processes are most likely retarded due to polymer–clinker surface interactions. Thus, adsorption of the admixtures on the clinker surface as observed by Uchikawa [7] could cover reactive sites and retard the hydration. Specifically, as seen in this study, retardation in hydration is linked to the absence of ettringite crystals. The differences in the effect of the two polycarboxylic acid-based admixtures are remarkable and show the sensitivity of the experimental set-up to changes arising from solution–clinker surface interactions. Results would indicate that CP is more effective in reducing the clinker surface–solution interactions than HP. Less ettringite is formed in the presence of CP than in the presence of HP. This effect is more pronounced when the admixtures are present in higher concentrations. At the highest concentration, CP suppresses the formation of ettringite completely in first 24 h of hydration.

The different influence of the two superplasticizers on the hydration is also clearly visible in the setting behavior of mortar. The general experience of retardation, which increases with increasing dosage, is confirmed. Amazing is the opposite effect of the dosage to the extent of the retardation of the two admixtures. At low dosages (0.1% and 0.2%), HP retards more; at high dosages (0.5% and 1.0%), CP retards more. At 1.0%, HP delays the initial set by 1 day, CP by 4 days. This is evidence that not only the strength but also the mode of interaction with the cement is different.

The microstructural observations made in this study seem to reflect the hydration behavior of mortar with higher dosages of superplasticizers. More importantly, besides impeding the solution–clinker surface interactions, polycarboxylic acid-based superplasticizers influence the formation of ettringite, and this has an impact on the hydration behavior. In addition, the structural differences between polycarboxylic acid-based polymers (CP vs. HP) can significantly alter the hydration of cement-based materials and have long-term influence on the properties of the material.

5. Conclusions

- This study documents the microstructural features and their evolution resulting from the interaction between polished clinker and different types of aqueous liquids: deionized water, artificial solution (saturated $Ca(OH)_2$/$CaSO_4$ solution), extracted solution (aqueous phase extracted from cement paste), and extracted solutions containing different dosages of two different types of polycarboxylic acid-based superplasticizers: CP and HP.

- Results obtained in this study indicate that the hydration products of the major phases in clinker strongly depend on the solution chemistry and associated pH of the solution with which they interact.
- One predominant microstructural feature found in the hydration of the clinker are equal hexagonal prisms having a morphology that is commonly attributed to ettringite in cement-based systems. Hydration of the polished clinker surfaces with extracted solution and artificial solution result in two different types of ettringite microstructures that grow on the interstitial phase after 24 h of reaction. In the extracted solution (pH >13, sulfate ions 14 g/l, Ca^{2+} ions 0.77 g/l), the formation of ettringite with a low length-to-thickness ratio occurs, whereas in the artificial solution (pH 12.5, sulfate ions 1 g/l, Ca^{2+} ions 1.36 g/l), the ettringite crystals are more slender.
- The influence of the different types of solution chemistry is not solely restricted to inducing changes in ettringite. In fact, hydration products on alite and on the interstitial phases show variations as a result of the different types of solutions. The morphology varies from rod-like structures to scaly interlaced, and spherical.
- In the presence of polycarboxylic acid-based admixtures, the hydration reactions are significantly altered, and no distinct or prevalent microstructural feature occurred in the first 30 min of reaction. SEM observations show that at a dosage of 0.004% CP severely slows down the hydration reaction, and very few hexagonal ettringite crystals are formed even after 24 h of reaction. The aforementioned effect is more pronounced at higher dosages. Temperature measurements in mortar containing CP support the microstructural findings, and in fact at the highest dosage (1.0% CP) the mortar remains in a plastic state up to 4 days.
- However, in the presence of HP, a featureless hydrate layer forms on the clinker surface during the first 30 min of reaction. After 24 h of hydration and an admixture dosage of 0.004%, the formation of hexagonal prisms on the interstitial phase and of tiny spherical particles deposited on the alite phases occurs. Unlike with CP, after 24 h of hydration the clinker surface shows the formation of some hexagonal prisms on the interstitial phase in the presence of the higher concentration (0.4%). Results from the temperature measurements in mortar show that at a high dosage (1.0%) of HP, the mortar is retarded for approximately 16 h, but then initial set occurs with a decrease in peak temperature.
- The results from this study show that the hydration of cement-based systems is intimately related to the formation of ettringite. More importantly, the polycarboxylic acid-based superplasticizers investigated demonstrate a strong influence on the development and formation of ettringite. This finding is important because changes in rheological behavior as a result of the presence of a superplasticizer are linked to hydration reactions of the major clinker phases.

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