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## Scientific paper

# Early Hydration of Portland Cement Admixed with Polycarboxylates Studied Under Terrestrial and Microgravity Conditions

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## Abstract

The crystallization of ettringite at very early cement hydration (hydration period ~ 10 s) was studied under normal and zero gravity condition utilizing SEM microscopy. Furthermore, the impact of two polycarboxylate superplasticizers (one methacrylate ester-, one methallyl ether - based) on ettringite crystallization was investigated. It was found that under microgravity attained on parabolic flights, generally smaller, but a larger amount of ettringite crystals is formed resulting from the absence of convection and ion diffusion limited crystal growth. Furthermore, the PCE polymers were found to act as morphological catalysts for ettringite even under zero gravity condition.

## 1. Introduction

The process of nucleation and crystallization of minerals is described by two divergent theories – the “nucleation theory” and the more current “cluster theory” (Gibbs 1876; Frenkel 1939; Zeldovich 1943; Vekilov 2010a). Key parameter of the classical “nucleation theory” is the “critical radius” of an early metastable nucleus. This radius is reached when the volume energy of a nucleus becomes larger than its surface energy. Only nuclei possessing a radius larger than the critical radius can grow, whereas nuclei with a smaller radius dissolve again. The “cluster theory” postulates a mechanism involving “precritical clusters” or “pseudo phases” which act as a precursor. Contrary to the “nucleation theory”, these phases are assumed to be stable and already exhibit the final crystal structure. After additional aggregation “postcritical nuclei” are built which form the basis for further crystal growth (Galkin *et al.* 2007; Vekilov 2010b). Under normal gravity, the necessary transport of the building units (ions or molecules) occurs via diffusion and convection. In case of zero gravity, the convec-

tion phenomenon disappears and crystal growth becomes diffusion controlled only.

So far, surprisingly few experiments on crystallization under microgravity conditions have been performed, probably because of the high cost of such experiments. They were performed at the international space station (ISS) and include the crystallization of NaCl and of a large number of proteins and viruses (Fontana *et al.* 2011; McPherson 1993). For the latter, much more homogeneous and defect-free crystals were obtained. This was attributed to the absence of convection. Under zero gravity, crystal growth only relies on ion transport via diffusion and thus the growth becomes slower.

Ettringite presents the main anchoring site for superplasticizers (Plank *et al.* 2007). To understand its crystal growth and surface properties constitutes a key to clarify the interaction of such polymers with ettringite and to determine the factors influencing their performance more profoundly. Here, on parabolic flights which produce microgravity conditions for 22 s, the crystal growth and morphology of ettringite crystals were compared with those crystallized in the earth’s gravity field. Using ordinary Portland cement admixed with two different PCE superplasticizers based on methacrylate ester and methallyl ether macromonomers we hoped to produce more regular, defect-free ettringite crystals as a result of better controlled growth conditions instead of the flash precipitation which occurs under terrestrial conditions. Furthermore, from these experiments it was hoped to obtain a better understanding of cement-admixture interaction.

## 2. Methods and Materials

### 2.1 Materials

#### 2.1.1 Cement samples

The cement used in this study was an ordinary Portland

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cement CEM I 42.5 R provided by Schwenk Zement KG (Ulm, Germany) from their Allmendingen plant. Its phase composition as determined *via* Q-XRD using *Rietveld* refinement is exhibited in **Table 1**. In the experiments on cement hydration, a water-to-cement ratio of 1.0 was utilized.

### 2.1.2 Superplasticizer samples

In this study, two commercially available polycarboxylate (PCE) based superplasticizers (“Vivid<sup>®</sup> 500 A” and “Vivid<sup>®</sup> 500 C”, provided by Shanghai Sunrise Polymer Materials Co., Ltd.) were utilized. These samples were selected because they represent highly effective and commonly used PCE products.

Vivid<sup>®</sup> 500 A constitutes a MPEG type PCE based on  $\omega$ -methoxypoly(ethylene glycol) methacrylate ester possessing mixed side chains of MPEG - 1000 ( $n_{EO} = 23$ ) and MPEG - 2000 ( $n_{EO} = 45$ ). The molar ratio of MPEG - 1000 to MPEG - 2000 was 0.8:1 while the molar ratio of methacrylic acid to  $\omega$ -methoxypoly(ethylene oxide) methacrylate ester was 3.6:1. This sample was designated as S1.

Vivid<sup>®</sup> 500 C is a HPEG type PCE based on  $\alpha$ -methallyl- $\omega$ -methoxypoly(ethylene glycol) ether possessing a side chain of HPEG - 2400 ( $n_{EO} = 54$ ). The molar ratio of acrylic acid to the HPEG macromonomer was 3.2:1. Henceforth, this sample will be labelled as S2.

The molecular properties of the two polymers are presented in **Table 2** and the SEC spectra are shown in **Fig. 1**.

### 2.2 Experimental methods

The 0 g cement hydration experiments were conducted onboard a modified Airbus A 300 aircraft conducting parabolic flight maneuvers. The parabolic flight campaign was initiated by Deutsches Zentrum für Luft- und Raumfahrt (DLR, German Aerospace Center). For the

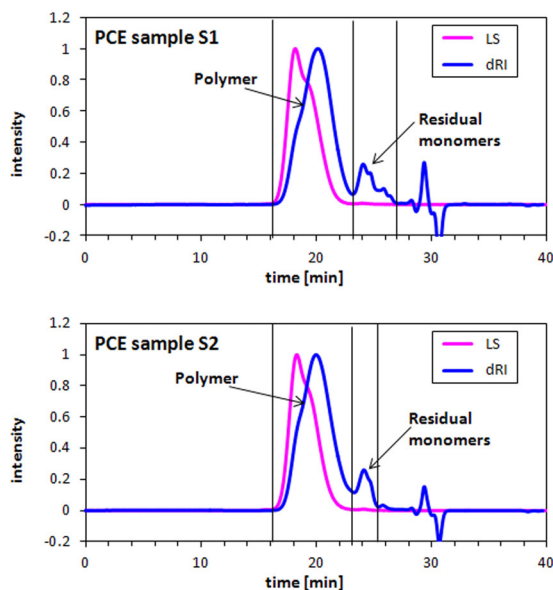


Fig. 1 SEC spectra of the PCE samples S1, S2.

Table 1 Phase composition of the CEM I 42.5 R sample as determined by Q-XRD analysis.

Phases	CEM I 42.5 R
C <sub>3</sub> S, m	58.83
C <sub>2</sub> S, m	17.01
C <sub>3</sub> A, c	3.61
C <sub>3</sub> A, o	1.60
C <sub>4</sub> AF, o	9.43
Free lime, <i>Rietveld</i>	0.09
Free lime, <i>Franke</i>	0.06
Periclase	0.66
Anhydrite	1.83
Hemihydrate (TG)	0.27
Dihydrate (TG)	2.42
Calcite	2.80
Quartz	0.36
Arcanite	1.04
Sum	100.02

experiments presented in this work, 15 parabolas were needed. The trajectory and the different gravity periods which occur during one parabola are illustrated in **Fig. 2**. The parabola starts with the plane ascending from an altitude of around 6,000 m to 8,500 m. During this period which last ~ 24 seconds hypergravity occurs in two phases. In the “pull - up” phase, gravity is 1.8 g until the airplane reaches an ascending angle of 30°. After this, gravity drops to 1.5 g. The hypergravity period ends when the plane achieves a gradient angle of 47°. At this angle (pilot audio command: “injection”), a transition period commences where the gravitational force drops from 1.5 g to 0 g within ~ 4 seconds. During the following 22 seconds microgravity conditions exist and the experiments were conducted. After the top of the parabola is reached, the aircraft descends and again accelerates strongly whereby hypergravity occurs again. At an inclination angle of 30°, the “pull-out” (pilot audio command) takes place until the plane is reaching a horizontal position. In this section which also lasts around 22 seconds, gravity again becomes ~ 1.8 g.

The device developed for conducting the cement hydration experiments onboard consists of three syringes (BD Discardit II 20 mL, Becton Dickinson, Franklin Lakes, New Jersey, USA) connected with a three-way valve (**Fig. 3**). The dead volume was minimized (1 mL) by keeping the pipe lengths as short as possible. Syringe #1 was used as reactor holding the cement (5 g) whereas

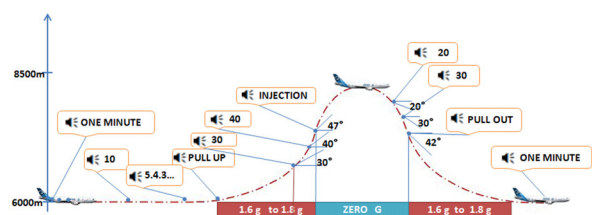


Fig. 2 Flight pattern performed by the air-craft during one parabola.

Table 2 Characteristic properties of the PCE samples S1, S2.

Sample	Yield [%]	M <sub>w</sub> [g mol <sup>-1</sup> ]	M <sub>n</sub> [g mol <sup>-1</sup> ]	PDI -	Anionic charge density [μeq g <sup>-1</sup> ]
S1 MPEG PCE	87	75,000	31,000	2.4	2,958
S2 HPEG PCE	90	75,000	30,000	2.5	2,024

Table 3 Average length, width and aspect ratio of ettringite crystals obtained from CEM I 42.5 R sample, hydrated for 10 s, 30 s and 60 s under terrestrial condition.

Hydration time	Gravity Condition	Length [nm]	Width [nm]	Aspect Ratio
10 s	1 g	676 ± 185	192 ± 42	3.6 ± 0.9
30 s	1 g	698 ± 144	191 ± 29	3.6 ± 0.9
60 s	1 g	758 ± 206	206 ± 67	3.8 ± 0.6

syringe #2 contained the mixing water including the PCE (6 mL, w/c = 1, 1 mL death volume). Syringe #3 contained acetone (10 mL) to stop the hydration reaction. All syringes were loaded at the ground laboratories prior to the flight. To separate the pore solution and retain the cement particles, syringe #1 was equipped with a filter paper (MN520, thickness 1.5 mm, Macherey-Nagel, Düren, Germany).

**Figure 4** shows how the experiments were conducted onboard the aircraft, with two experimenters operating the devices and the third one controlling the timing. As the experiments were performed manually it was expected that reaction times might vary at ± 1 sec between different samples. To ensure that such deviations did not impact the results, tests were performed in the laboratory including hydration times of 5 sec, 10 sec, 20 sec, 30 sec, 45 sec and 1 min. There it was found that between 5 sec and 1 min the crystal sizes were the same. There it was found that between 5 sec and 1 min the crystal sizes and amounts were comparable. As examples, **Table 3** presents the data on the crystal dimensions observed after 10 sec, 30 sec and 1 min reaction time. Apparently, ettringite crystallizes instantaneously because of its extreme low solubility (solubility product  $L = 10^{-44} \text{ g}^{-3} \text{ L}^{-3}$ ) and then enters a dormant period.

## 2.3 Analysis of samples

### 2.3.1 SEM imaging

This technique was applied to determine the amount of ettringite present on the surface of the cement particles and its morphology as well as crystal size of ettringite present on the surface of the cement particles. SEM images were recorded on a FEI 30 FEG environmental scanning electron microscope from FEI/ Philips, Eindhoven/NL. Each experiment was repeated three times (on parabolic flights) or six times (in the laboratory at 1 g) to ensure universality of the results. Furthermore, from every sample at least five different parts were looked at to ensure that only representative images were evaluated. All samples were fixed on the sample holder by using a carbon dispersion. Imaging was carried out at an accelerating voltage of 4 kV (spot size 2) and at working distances of 6 - 7 mm and a tilt angle of 20°. Generally, images were captured at 10,000 x, 20,000 x and 40,000 x

magnification.

For quantification of the amount of ettringite formed, images from representative surface areas of cement ( $12 \times 9 \mu\text{m}$ ) at a magnification of  $10,000 \times$  were taken, and the amount of ettringite formed from the neat cement at 1 g was set as 100 % (reference).

### 2.3.2 X-ray diffraction

Samples were analyzed in the range of  $5 - 70^\circ 2\theta$  using a Bruker AXS D8 Advance instrument (Bruker, Karlsruhe, Germany) with *Bragg-Brentano* geometry and Cu K $\alpha$  source (30 kV, 35 mA).

For quantification of the amount of ettringite formed, a

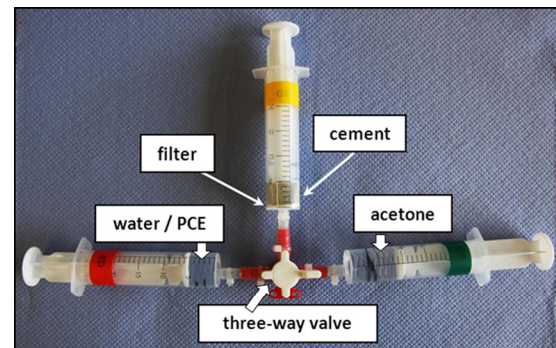


Fig. 3 Experimental device used to perform the cement hydration experiments.

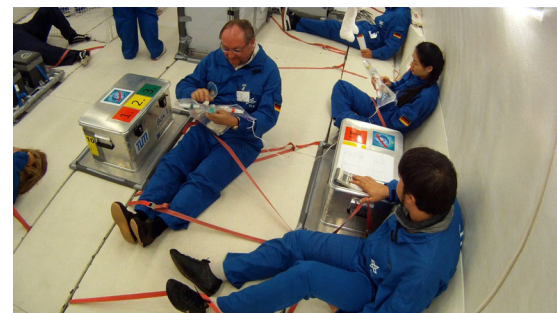


Fig. 4 Conducting the experiment on early ettringite crystallization onboard the zero g airplane. Note that all experimenters are fixed to avoid free floating during the zero gravity period.



method described in the literature for clay minerals was adopted (Bhaskar *et al.* 1994). Here, the characteristic ettringite reflection at  $9^\circ 2\theta$  was analyzed with a polynomial of 2nd order and smoothed using a 15 point Savitzky-Golay filter. The data were then subjected to an impulse analysis. The average intensity from three independent measurements was reported as final value.

### 3. Results and discussion

#### 3.1 Cement hydrated without PCE

Evaluation of the SEM images revealed that on the surface of the cement sample, even after the very short hydration period of 10 seconds, numerous nano-sized ettringite crystals had formed (Fig. 5). The crystals showed the typical hexagonal prismatic shape and were statistically distributed across the surface of the cement particles. XRD analysis (Fig. 6) revealed that at 1 g and 0 g conditions, no other crystalline cement hydrate has been formed apart from ettringite.

Furthermore, by integrating the peak areas in the XRD spectra as described in section 2.3.2, the amount of ettringite produced at 1 g and 0 g condition revealed that under microgravity, ~ 15 % more crystals were

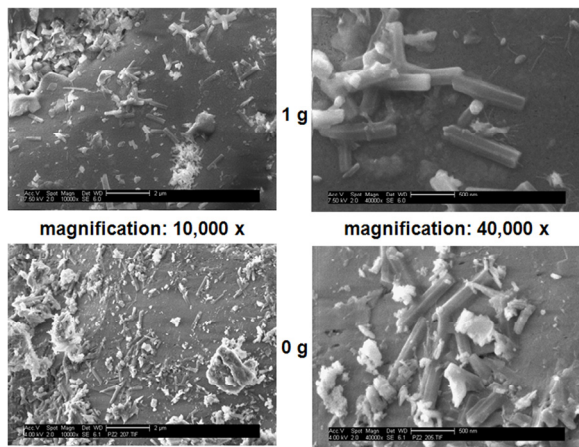


Fig. 5 SEM images of CEM I 42.5 R sample hydrated for 10 s under terrestrial (top) and zero gravity (bottom) conditions.

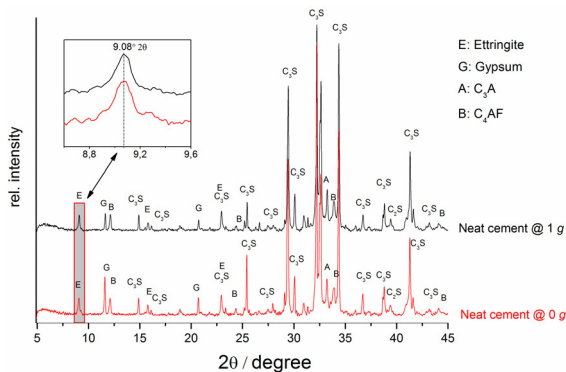


Fig. 6 X-ray diffractograms of CEM I 42.5 R sample, hydrated for 10 s at 1 g and 0 g (w/c = 1.0).

formed (Fig. 7).

To characterize the crystal morphology, also the aspect ratio (the ratio between crystal length and width) were looked at (Fig. 8). At 0 g, both the length as well as the diameter of the crystals decreased significantly (Fig. 8, left). However, the aspect ratios did not change much (Fig. 8, right).

#### 3.2 Cement hydrated in the presence of PCEs

Recently it has been described that polycarboxylate-based superplasticizers can act as strong morphological catalyst for ettringite, and that they can impact the size as well as the aspect ratio of the crystals (Large and Plank 2015a; Large and Plank 2015b; Dalas *et al.* 2015). In the first work, the authors present that this effect greatly depends on the PCE type and structural specifics. To account for such differences, in this study one  $\omega$ -methoxypoly(ethylene glycol) methacrylate (MPEG) ester based PCE (sample S1) and one  $\alpha$ -methallyl- $\omega$ -methoxypoly (ethylene glycol) (HPEG) ether based PCE (sample S2) were selected.

SEM imaging revealed that under normal gravity, the ettringite crystals obtained from the cement paste admixed with polymer S1 exhibit an average length of ~ 600 nm which is smaller than that from the neat cement hydrated in the absence of PCE (~ 800 nm) (Figs. 9, 11). The diameters of the crystals lie at ~ 130 nm which

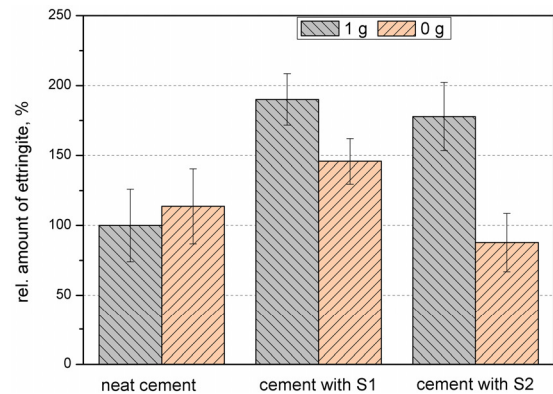


Fig. 7 Relative amounts of ettringite formed from CEM I 42.5 R sample in the absence and presence of the PCE samples S1 and S2, respectively at 1 g and 0 g condition; 100 % corresponds to the amount of ettringite formed by the neat cement at 1 g.

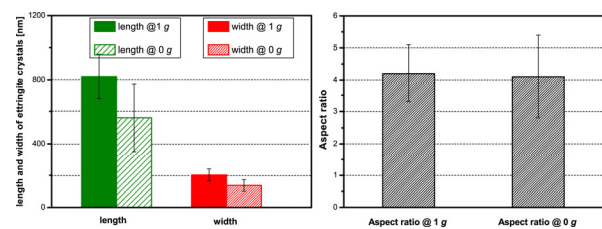


Fig. 8 Average length, width (left) and aspect ratio (right) of ettringite crystals obtained from CEM I 42.5 R under 1 g and zero g, respectively.

compares with ~ 200 nm for those from the neat cement paste. It is obvious that in the presence of PCE polymers, much smaller ettringite crystals are generated. Similar results were obtained for polymer S2 (Figs. 10, 11). There, both the length and width decreased compared to that grown in the neat cement paste. The experiments suggest that both PCE polymers act as morphological catalyst and reduce the size (length, diameter) of the ettringite crystals by 25 - 30 %.

Similar results were found under zero gravity. The size of ettringite crystals obtained from the cement paste admixed with polymer S1/ S2 decreases compared to the ones grown on the surface of the neat cement paste.

Another observation from SEM imaging was that at zero gravity and in the presence of the PCE polymers, the ettringite crystals became more stocky than those under terrestrial gravity, thus suggesting that the aspect ratio had decreased.

Furthermore, compared to 1 g, the amount of ettringite produced at 0 g decreased when the PCE polymers were present, as is illustrated in Fig. 7. This observation was

confirmed by quantitative XRD analysis (spectra not shown here).

The experiments allow to conclude that under zero gravity, the presence of PCE polymers generally leads to smaller ettringite crystals as compared to terrestrial gravity.

Also, under microgravity the aspect ratio of the crystals grown in the presence of the PCE polymers (S1/S2) had decreased compared to terrestrial condition. In other words, the ettringite crystals became more stocky (Fig. 12).

Whereas for the neat cement, under different gravity conditions, the aspect ratio had remained nearly constant (Fig. 12). Furthermore, in the presence of PCE polymers the amount of ettringite formed at zero gravity is always less than of terrestrial gravity, as is illustrated in Fig. 7. All this points to the fact that PCE polymers can impact the crystal growth of early ettringite which presents the main anchoring site for most concrete admixtures. Apparently, because at zero gravity condition convection and sedimentation are absent, the transport of PCE

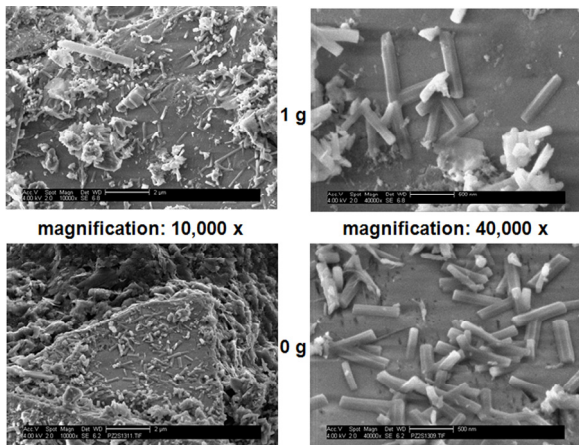


Fig. 9 SEM images of CEM I 42.5 R sample admixed with PCE polymer S1, hydrated for 10 s under terrestrial (top) and zero gravity (bottom) conditions.

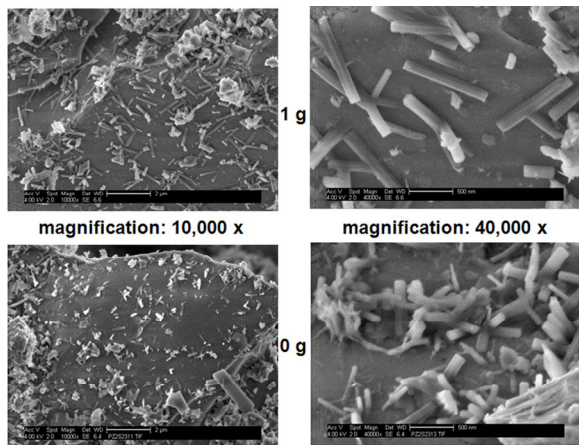


Fig. 10 SEM images of CEM I 42.5 R sample admixed with PCE polymer S2, hydrated for 10 s under terrestrial (top) and zero gravity (bottom) conditions.

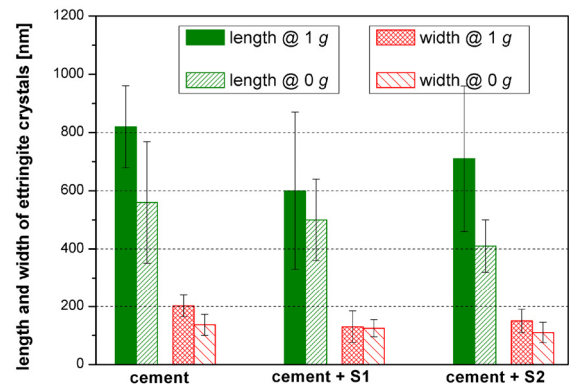


Fig. 11 Average length, width of ettringite crystals obtained from CEM I 42.5 R admixed with PCE polymers S1 or S2 grown under 1 g and zero g conditions, respectively.

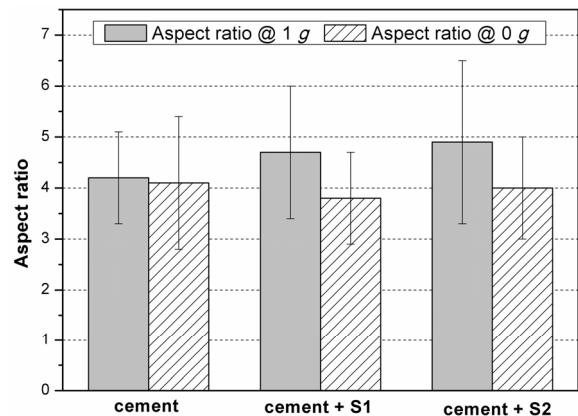


Fig. 12 Average aspect ratios of ettringite crystals obtained from CEM I 42.5 R admixed with PCE polymers S1 or S2, grown under 1 g and zero g conditions, respectively.

polymers to the surface of the ettringite nuclei is strictly diffusion controlled and therefore crystal growth is decelerated.

It should be noted that the results reported here are linked to the specific cement sample tested. Other cement samples may produce different ion concentrations and pH values in the pore solution which influences the growth of ettringite (Goetz-Neunhoeffler *et al.* 2006). However, the principle findings relative to the difference between the terrestrial and micro gravity conditions have been confirmed in a recent flight campaign for other cement samples as well.

#### 4. Conclusions

The impact of polycarboxylate superplasticizers possessing different chemical compositions on ettringite crystallization during early hydration of a CEM I 42.5 R sample was investigated under terrestrial and microgravity conditions.

For the neat cement it was found that under microgravity conditions, the ettringite crystals generally become smaller. This is caused by the absence of convection which decelerates crystal growth. The growth rate of the crystals is then limited by ion diffusion. However, for neat cement the aspect ratio of crystals formed at 0 g is quite comparable to that under terrestrial gravity.

PCE polymers cause a particularly strong effect on the morphology of ettringite crystals, which can be summarized as follows:

1. PCE polymers always (independent of gravity condition) act as morphological catalyst and reduce the size (length, diameter) of ettringite crystals.
2. The aspect ratio of ettringite crystals obtained from the cement paste admixed with PCE polymers under microgravity conditions decreases compared to that from 1 g. The ettringite crystals became more stocky.

The results signify that if mankind ever considers to construct on moon or mars by using a crystallizing binder, then experiments investigating the effect of reduced gravity conditions on the microstructure and the mechanical properties of the hardened material need to be checked.

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