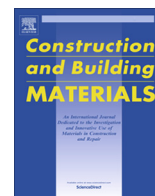




Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Early hydration of Portland cement studied under microgravity conditions

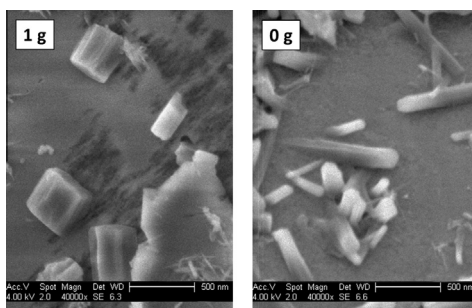
 Markus R. Meier^a, Manasit Sarigaphuti^b, Prinya Sainamthip^b, Johann Plank^{a,*}
^a Technische Universität München, Chair for Construction Chemistry, Lichtenbergstr. 4, 85747 Garching, Germany

^b Siam Research and Innovation Co., Ltd., 51 Moo 8, Tub Kwang, Kaeng Khoi, Saraburi 18260, Thailand

HIGHLIGHTS

- Portland cement CEM I 42.5 N hydrated for 10 s only.
- Nano-sized ettringite crystals are detected on cement surface.
- Ettringite growth was compared under terrestrial and micro gravity.
- Under microgravity, more crystals at higher aspect ratio are formed.
- Similar effect was observed when PCE superplasticizer was admixed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 20 January 2015

Received in revised form 31 March 2015

Accepted 1 May 2015

Available online xxxxx

Keywords:

 Crystal growth
 Nucleation
 Microgravity
 Portland cement
 Hydration
 Ettringite

ABSTRACT

Early ettringite formation from an industrial CEM I 42.5 N hydrated for 10 s at terrestrial and micro gravity conditions was studied in the presence and absence of a polycarboxylate (PCE) superplasticizer. The cement produced very tiny hexagonal ettringite crystals ($l \sim 180$ nm, $d \sim 250$ nm). The microgravity resulted in $\sim 25\%$ more crystals at slightly higher aspect ratio (1.4 versus 0.8 at 1 g). In the presence of PCE, generally larger ettringite crystals ($l \sim 325$ nm, $d \sim 225$ nm) were formed. Microgravity seems to hinder the growth of ettringite on the lateral faces.

© 2015 Published by Elsevier Ltd.

1. Introduction

Ordinary Portland cement (OPC) constitutes a physical blend of cement clinker fabricated in a high temperature solid-state reaction at ~ 1450 °C and a calcium sulfate (gypsum, hemihydrate or anhydrite) [1]. In the cement mill both components are finely interground resulting in the well-known, dry OPC powder [2].

* Corresponding author at: Chair for Construction Chemistry, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany. Tel.: +49 (0) 89 289 13 151; fax: +49 (0) 89 289 13 152.

E-mail address: sekretariat@bauchemie.ch.tum.de (J. Plank).

The addition of calcium sulfate aims at decelerating the early hydration of the clinker phase tricalcium aluminate, C_3A , the most reactive of all clinker phases. When mixed with water, this phase dissolves instantaneously (i.e. within less than one second) whereby significant amounts of $Al(OH)_4^-$ are leached into the aqueous phase to form hydrates whose composition differ, depending on the presence or absence of sulfates. In the latter case, micrometer-sized, large platy crystals of C_2AH_8 and C_4AH_{13} result which immediately overgrow the pore space between the cement particles and produce an unwanted “flash set” [3]. Whereas in the presence of calcium sulfates, such phenomenon is avoided by

the formation of initially only nanometer-sized, needle-shaped crystals of ettringite, a mineral represented by the formula $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12 \text{H}_2\text{O}]_2 \cdot (\text{SO}_4)_3 \cdot 2 \text{H}_2\text{O}$.

Ettringite possesses a columnar structure whereby $\text{Al}(\text{OH})_6$ octahedrons situated in the center are surrounded by CaO_8 polyhedrons. Stacks of sulfate anions and water molecules are present in the outer sphere of this pillar [4]. Ettringite can be synthesized easily by combining aqueous solutions of $\text{Ca}(\text{OH})_2$ and of $\text{Al}_2(\text{SO}_4)_3$. There, within 1 s only, nanosized ($1 < 50 \text{ nm}$) colloidal crystals of ettringite not visible for the eye, but precipitate from the solution as evidenced by occurrence of a light scattering phenomenon (Tyndall effect) [5]. After $\sim 5 \text{ s}$, a white crystalline precipitate starts to occur and the suspension becomes increasingly cloudy. Precipitation is practically complete after $\sim 20 \text{ s}$ only. Under the scanning electron microscope, the characteristic needles of ettringite exhibiting hexagonal shape and aspect ratios of ~ 10 – 20 are observed.

Currently, two different concepts exist which describe the mechanism of nucleation and crystallization of inorganic minerals. The early model (“nucleation theory”) which is based on the works of Gibbs, Frenkel, Zeldovich and others [6–8] presents that crystal growth occurs when an early nucleus reaches a radius where the volume energy is larger than the surface energy. Nuclei which are smaller than the “critical radius” dissolve again whereas those which are larger can grow. More recent work suggests however a more complicated mechanism involving so-called “precritical clusters” [9]. According to this theory, crystal growth starts from metastable aggregates (“pseudo phases”) which may or may not exhibit the structure of the final crystal [10,11]. Further growth of those early seeds occurs through diffusion and convection enhanced transport of ions/molecules.

Microgravity presents a particular environment for crystal growth because there, convection is absent. So far, almost all experiments relating to crystal growth under microgravity have been performed with proteins (~ 200 different samples on 39 US Space Shuttle flights). Contrary to normal gravity, highly regular crystals resulting from slower growth were obtained and in many cases it was possible to determine the crystal structure via single crystal X-ray diffraction [12,13]. Interestingly, the growth of only very few inorganic minerals has been studied so far in microgravity environment, among them NaCl [14], thermoelectric $\text{Bi}_2\text{Se}_{0.21}\text{Te}_{2.79}$ [15] and calcium phosphate, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ [16]. For the latter it was found that under microgravity a second new phase, octacalcium dihydrogenphosphate $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5 \text{H}_2\text{O}$ is formed which could explain the demineralization and osteoporosis common among astronauts who experienced extended stays in space [17]. In 1994, a US consortium intended to study cement hydration of a large sample ($\sim 1 \text{ kg}$) on the International Space Station (ISS) [18]. Unfortunately, already during the lift-off of Space Shuttle “Columbia” the equipment was damaged as a result of extreme acceleration, and practically no useful data were obtained as a consequence of premature mixing of cement and water under hypergravity (up to 3 g).

In this work, we report about the short-term (10 s) hydration of a conventional, commercial Portland cement CEM I 42.5 N under microgravity conditions. The experiments were carried out on parabolic flights whereby a zero gravity period of 22 max. is achieved. Owing to this short time period, we focused on the crystal growth of ettringite which precipitates immediately upon contact of cement with water, as presented above. More specific, at the beginning of the 0 g period water was injected into a syringe holding the cement powder, mixed to yield a paste and hydrated for 10 s . Thereafter, the suspension was dehydrated by filtering off the cement and quenching with acetone to stop hydration entirely. The resulting samples were brought back to the ground, analyzed via X-ray diffraction and scanning electron microscope imaging

to retrieve information on the morphology, size, aspect ratio and overall amount of ettringite crystals formed. The data were compared with those obtained from comparative experiments conducted under terrestrial gravity (1 g) conditions in our laboratory. Furthermore, the impact of microgravity on ettringite grown from the same cement sample in the presence of a PCE superplasticizer was studied. From the experiments it was hoped to gain more sight into the crystallization process of ettringite, the prominent mineral occurring in early cement hydration which not only impacts the workability and set behavior of cement, but also provides the anchoring site for most admixtures such as e.g. superplasticizers, and thus is indispensable for their function [19]. Finally, we aimed to contribute to a more thorough understanding of the crystallization of inorganic salts under microgravity, as to this date only so few examples are reported in the literature.

2. Experimental

2.1. Cement sample

A CEM I 42.5 N (OPC Type I) sample produced by Siam Cement Group at the Saraburi plant, Thailand and commercialized under the brand name “Elephant cement” was utilized. Its phase composition as determined via Q-XRD using Rietveld refinement is exhibited in Table 1. Average particle size (d_{50} value) was $12 \pm 1.5 \mu\text{m}$ (Laser granulometer Cilas 1064, Cilas, Marseille, France) and density was 3.19 g/cm^3 (Helium pycnometry). Its specific surface area according to Blaine’s method was $3.443 \text{ cm}^2/\text{g}$.

2.2. Chemicals

As mixing water, deionized water obtained from Millipore Synergy UV was used while reagent grade acetone ($>99.9\%$, Merck KGaA, Darmstadt, Germany) was applied to quench cement hydration.

As superplasticizer, a polycarboxylate (PCE) based on isoprenol poly(ethylene glycol) macromonomer was synthesized via aqueous free radical copolymerization involving 2-mercapto propionic acid as chain transfer agent and sodium peroxodisulfate as initiator. The detailed experimental procedure is described in [5]. In preparation, 30 mL DI water are placed in a three neck-round bottom flask which is heated to $80 \text{ }^\circ\text{C}$ under a stream of N_2 . Then a solution of 85.0 g of IPEG-2400 macromonomer (Liaoning Oxiranchem, Inc., Liaoyang, China), 15 g acrylic acid (Merck KGaA, Darmstadt, Germany), 1.0 g 2-mercapto propionic acid (EGA – Chemie KG, Heidenheim, Germany) and 85 mL DI water are fed continuously into the flask over 3 h using a peristaltic pump. At the same time, a solution of 1.0 g $\text{Na}_2\text{S}_2\text{O}_8$ (Merck KGaA) in 30 mL DI water is added over 4 h . The mixture is stirred for another hour before it is cooled to room temperature and used as is.

The chemical structure and characteristic properties of this PCE sample are exhibited in Fig. 1.

2.3. Experimental procedures

2.3.1. Parabolic flight sequence

The experiments were conducted under the sponsorship of Deutsches Zentrum für Luft- und Raumfahrt (DLR), Cologne during a parabolic flight campaign from October 27–31, 2014 using an Airbus A-300 aircraft. The general flight pattern of

Table 1

Phase composition of the CEM I 42.5 N sample (Siam Cement Group, Saraburi plant, Thailand), as determined via quantitative XRD analysis.

Phases	Content (wt.%)
C_3S , m	64.14
C_2S , m	9.83
C_3A , c	3.15
C_3A , o	1.15
C_4AF , o	13.56
Free lime, Rietveld	0.51
Free lime, Franke	0.43
Periclase	0.25
Anhydrite	0.08
Hemihydrate (TG)	2.98
Dihydrate (TG)	0.00
Calcite	3.38
Quartz	0.18
Arcanite	0.37
Sum	100.00

Download English Version:

<https://daneshyari.com/en/article/6720727>

Download Persian Version:

<https://daneshyari.com/article/6720727>

[Daneshyari.com](https://daneshyari.com)