

Electronic Supplementary Information

## Cement retarding mechanism of phosphonates and their interaction with aluminium

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### Materials

**Cement** Characteristic particle distributions were obtained on a Malvern Mastersizer 2000 and are reported in Table 4.

Table 1: Particle size distribution of alite

|                                  |      |
|----------------------------------|------|
| d (0.1) [ $\mu\text{m}$ ]        | 1.8  |
| d (0.5) [ $\mu\text{m}$ ]        | 12.9 |
| d (0.9) [ $\mu\text{m}$ ]        | 58.3 |
| n                                | 1.1  |
| Blaine [ $\text{m}^2/\text{g}$ ] | 3243 |

### Methods

**Pore solution analysis:** Pore solution was separated using following procedure: 180 g aliquots of the cement paste with a w/c = 0.4 and the appropriate amount of additive which is necessary to receive an induction period of 7h were placed into a stainless steel cylinder ( $V_{\text{max}} = 200 \text{ mL}$ ) connected to a nylon 5  $\mu\text{m}$  membrane filter, both by Sartorius (Sartorius Stedim Biotech GmbH, Göttingen, Germany). Afterwards air pressure of 4 bar was applied to the steel cylinder. Filtrate was collected for 1 min after pressure application. Afterwards, the received filtrate was instantly filtered through a 0.45  $\mu\text{m}$  syringe filter. The total sample preparation time was therefore around 3 min.

**ICP-OES:** Preparation of the solution: 0,5 mL filtered pore solution were acidified with 0,1mL  $\text{HNO}_3$  8mol/L and diluted with 3,4 mL MilliQ-Water.

Pore solution was analyzed with the Spectro Ciros Vision from SPECTRO Analytical Instruments GmbH&Co.KG. The measurement conditions are summarized in table 1.

Table 2: Conditions for ICP-OES measurement

| Operation condition/ Instrument part | Value/Type            |
|--------------------------------------|-----------------------|
| Spectral length                      | 125 nm – 769 nm       |
| Detector                             | CCD , Resolution 9 pm |
| RF generator                         | 27,12 MHz             |
| Plasma viewing                       | radial                |
| Plasma and shear gas                 | Argon                 |
| Nebulizer                            | Pneumatic, Crossflow  |
| Torch Injection Diameter             | Quartz 1,8 mm         |
| RF power                             | 1400 W                |
| Pump rate                            | Pumping rate 2        |
| Cooling gas flow                     | 12 l/min.             |
| Auxillary gas flow                   | 1 l/min.              |
| Nebulizing gas flow                  | 0,85 l/min.           |
| Number of replication per sample     | 3                     |

|                  |            |            |            |            |            |            |            |            |            |            |            |
|------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Integration time |            |            |            |            |            | 12 s       |            |            |            |            |            |
| Flush time       |            |            |            |            |            | 30 s       |            |            |            |            |            |
| Element          | Al         | Ba         | Ca         | Cl         | Fe         | K          | Mg         | Na         | P          | S          | Si         |
| $\lambda$ in nm  | 167,0<br>7 | 455,4<br>0 | 422,6<br>7 | 134,7<br>2 | 259,9<br>4 | 404,7<br>2 | 285,2<br>1 | 330,2<br>3 | 177,4<br>9 | 180,7<br>3 | 251,6<br>1 |

For calibration the following standards were used:

Certipur® MultiXXI ICP Multielement standard solution 10mg/L; Certipur® Multi IV ICP Multielement standard solution 1000 mg/L ; Certipur® Sulfur ICP standard solution 1000 mg/L ; Certipur® Phosphorus ICP standard solution 1000 mg/L ; Certipur® Chlorid ICP standard solution 1000 mg/L

The standards were diluted to the concentrations stated in table 2.

Table 3: ICP calibration

|             |           |          |          |          |          |          |          |
|-------------|-----------|----------|----------|----------|----------|----------|----------|
| Multi XXI   | 0,05 mg/L | 0,1 mg/L |          |          |          |          |          |
| Multi IV    | 2 mg/L    | 5 mg/L   | 10 mg/L  | 50 mg/L  | 150 mg/L | 300 mg/L | 500 mg/L |
| S-Standard  | 200 mg/L  | 300 mg/L | 500 mg/L |          |          |          |          |
| P-Standard  | 0,2 mg/L  | 1 mg/L   | 3 mg/L   |          |          |          |          |
| Si-Standard | 0,5 mg /L | 3,0 mg/L | 10 mg/L  |          |          |          |          |
| Cl-Standard | 0,1mg/L   | 3mg/L    | 5 mg/ L  | 10 mg/ L | 30 mg/L  |          |          |

1,5 mL pore solution were acidified with 0,1mL HNO<sub>3</sub> 8mol/L and diluted with 33,4 mL MilliQ-Water.

**TOC:** TOC values were measured with a High-TOC II from Elementar Analysensysteme GmbH, Germany.

**pH:** pH was measured using a Metrohm Profitrode electrode. The electrode was calibrated by using buffer solutions of pH 7, 10 and 13.

**Scanning electron microscopy (SEM)** was performed using a JSM-IT500 from JEOL. Secondary electron (SE) images were collected of the powders obtained after the hydration of samples was stopped to investigate the morphology of the hydrated samples during the early hydration period (less than 1 d).

**Calorimetry:** The heat flow released during the hydration of cement in presence of the different additives was monitored by isothermal calorimetry (TAM Air) at 20 °C. 3 g of powder was internally mixed in the calorimeter with 1.2 g of water in which the additives were dissolved. All pastes were mixed using the “Bohromir” mixing device with planetary mixers commercially available from Technisch Zeichnen & Grafik Design Grassl. The curves received were further analyzed as described in the experimental section of the manuscript.

**Paste test:** We mixed 60 grams of cement with 24 milliliters of water. The amount of the additive from Table 4 of the main manuscript was added to the mixing water. The paste was mixed for 1 minute. Afterwards, the paste was filled into a ring with a 30 mm inner width and 50 mm height. The ring was lifted, and the diameter of the paste was then measured and summarized in Table 4. For comparison, a conventional PCE was added at a dosage of 0.06%.

Table 4: Flow of cement paste with and without phosphonate retarders

| Additive               | Paste flow [mm] |
|------------------------|-----------------|
| MPA                    | 64.2            |
| EPA                    | 64.9            |
| AMPA                   | 62.2            |
| Foscarnet              | 60.0            |
| PBTC                   | 64.5            |
| EDTMP                  | 63.5            |
| HEMPA                  | 63.2            |
| HEDP                   | 65.1            |
| MDPA                   | 63.5            |
| Reference              | 64.5            |
| Reference + 0.06 % PCE | 92.4            |

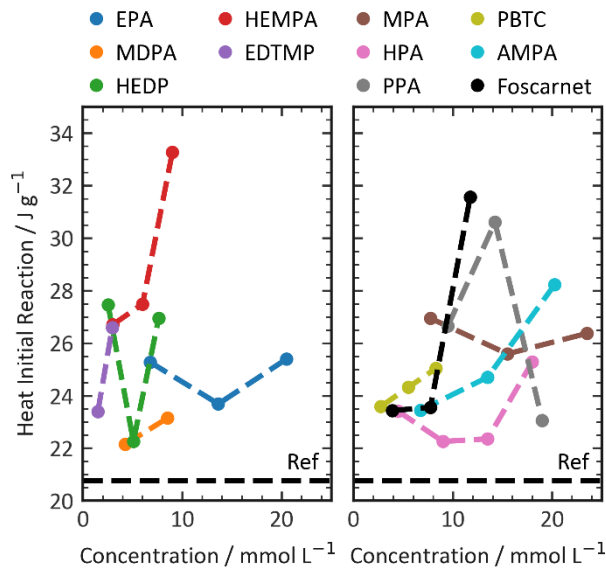


Figure 1: Heat of hydration of the initial reaction in dependence of the additive concentration measure by in-situ calorimetry

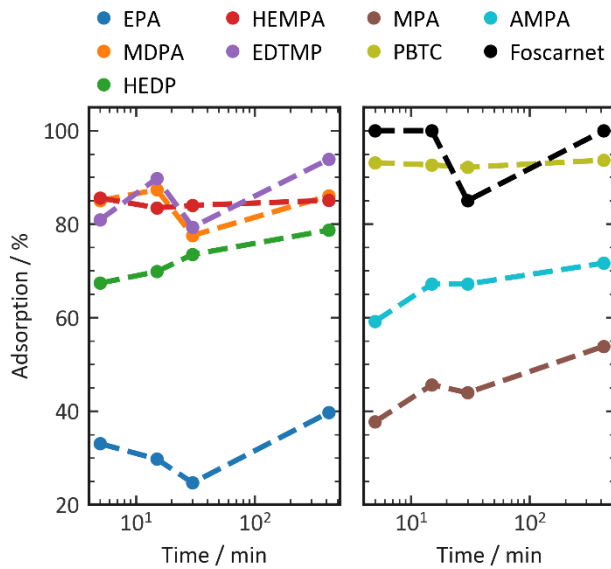


Figure 2: Adsorption profile of the additives over time at dosages needed to achieve a dormant period of 7 h.

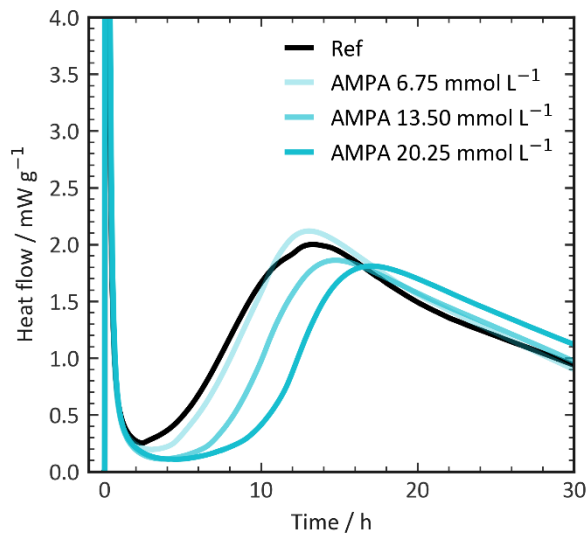


Figure 3: Heat flow curves of cement with and without AMPA at different concentrations.

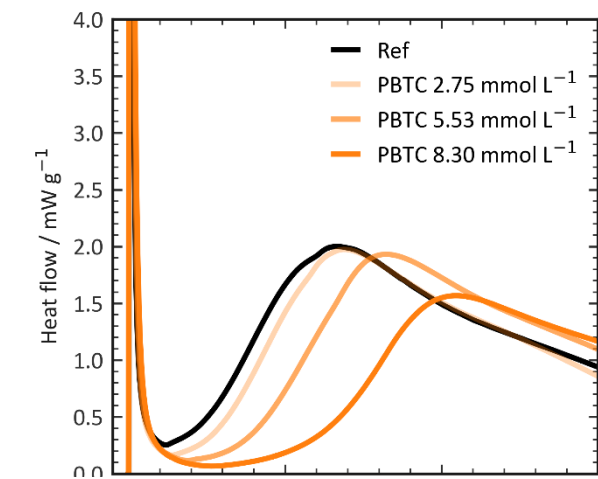
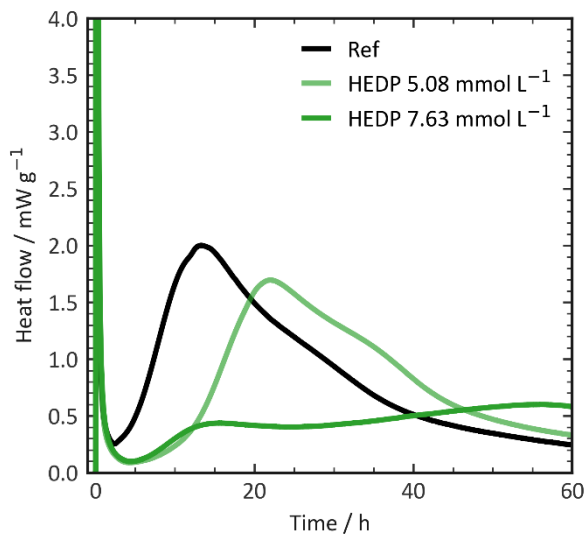


Figure 5: Heat flow curves of cement with and without PBTC at different concentrations.