

NEW HYDRAULIC CEMENTS BASED ON α -TRICALCIUM PHOSPHATE - CALCIUM SULFATE DIHYDRATE MIXTURES

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INTRODUCTION: Calcium phosphate cements based on α -tricalcium phosphate (α -TCP) - water mixtures have been studied extensively for the last 20 years. Despite these efforts, there is still a need for new alternatives to increase their injectability and create macropores. Here, we propose to study the effect of calcium sulfate dihydrate (CSD) on α -TCP - water mixtures. Several series of experiments were performed where the following factors were varied: (i) the CSD fraction; (ii) the di-sodium hydrogen phosphate dihydrate (DSHPD) concentration in the mixing liquid; and (iii) the amount of mixing liquid.

MATERIALS AND METHODS: The cement samples contained 4.0g powder (α -TCP + CSD) and 1.72mL solution. The CSD amount was varied from 0 to 1.11g, whereas the DSHPD concentration in the mixing solution was in the range of 0.05 to 0.40M. The cement ingredients were mixed for 45s with a spatula in a small beaker. The paste was then placed into two syringes whose end had been previously cut off. The setting time was measured using a so-called penetrometer. Fifteen minutes after setting, the samples were placed into 10mL of 0.15M phosphate buffer solution at 37°C. After one or two days of incubation, the samples were taken out and dried in air at 37°C and later at 110°C until a constant weight was reached. The sides of the cylindrical samples were then flattened, and characterized by measuring the apparent density, the diametral tensile strength, the crystalline composition via x-ray diffraction (XRD), and the specific surface area (BET). Solubility calculations were performed using known solubility data.

RESULTS: A twofold decrease of the cement setting time was observed when 0.1-0.2g of CSD were added into the cement. This sharp decrease was followed by a slow increase of the setting time. Interestingly, the position of the setting time minimum increased towards larger CSD amounts when the phosphate concentration of the mixing solution was increased. Furthermore, the minimum became lower, much broader and flatter. These results suggest an interaction between the CSD

amount and the phosphate concentration. An increase of the phosphate concentration in the mixing liquid led to a decrease of the setting time. A decrease of setting time was also observed when the amount of mixing liquid was decreased. The apparent density of the cement decreased with an increase of the CSD amount, whereas the diametral tensile strength of the cement was rather independent of the CSD amount, the incubation time, or the DSHPD concentration. The specific surface area of the cement samples was increased by the addition of 0.1-0.2g of CSD. However, hardly any changes were observed beyond 0.2g CSD. An increase of the phosphate concentration from 0.1 to 0.2M provoked a small but significant decrease of the specific surface area, but only after one day of incubation. Interestingly, an increase of the incubation time led to a small decrease of the specific surface area. The XRD spectra show that the cement samples contained a mixture of apatite, CSH (resulting from heating up CSD at 110°C) and α -TCP. The peak intensities indicated that the relative intensity of the CSH peak was null below 0.2g CSD and then steadily increased. Simultaneously, the α -TCP peak rapidly increased with a small increase of the CSD amount and then remained stable or even slightly decreased. Interestingly, the phosphate concentration had no effect on the CSH relative peak intensity, but had a large effect on that of α -TCP: a larger phosphate concentration led to larger α -TCP peaks. The results were similar at two days apart from a decrease of the size of the α -TCP peaks.

DISCUSSION: Based on solubility calculations, the present setting time results can be explained according to 4 different effects: (i) CSD increases the supersaturation towards HA/CDHA in the mixing liquid, hence resulting in a decrease of setting time (for small CSD amount); (ii) The dissolution of CSD decreases the solubility of α -TCP in the mixing liquid, hence leading to a slower setting reaction (for large CSD amount); (iii) The presence of phosphate ions in the mixing solution increases the supersaturation towards HA/CDHA in the mixing liquid, hence leading to a shortening of the setting time (for large phosphate concentrations); (iv) The phosphate ions of the mixing liquid react with calcium ions stemming from CSD dissolution, hence increasing the saturation

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of the mixing solution toward CSD, and decreasing
the dissolution rate of CSD (valid at large CSD
amount).

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CONCLUSION: CSD can be used in combination
with phosphate ions to control the setting time of
a-TCP - water mixtures, without affecting their
mechanical properties.