Effect of α-tricalcium phosphate milling on the incorporation of calcium sulfate dihydrate during cement setting

M.Bohner, N.Doebelin

Robert Mathys Foundation, Bischmattstrasse 12, CH-2544 Bettlach, Switzerland

INTRODUCTION: Apatite cements harden very slowly. Thus, efforts have been devoted to increase their reactivity, e.g. by means of milling or use of additives. Despite these efforts, there is still little understanding of the kinetics of cement setting. Ideally, a cement should not react for a few minutes, and then harden rapidly. The goal of this study was to assess the effect of a setting retarder (citrate ions) in an α-tricalcium phosphate (α-TCP) based cement containing two setting accelerators, Ca-sulphate dihydrate (CSD) and phosphate ions. Additionally, α-TCP powders milled for various durations were used.

METHODS: α-TCP powder was milled for 15, 75, 150 and 225 min. Particle diameters and specific surface area (SSA) of the resulting powders varied between 7.1–11.9 μm, and 1.93–2.28 m^2/g, respectively. Cements were prepared by mixing 4 g of powder (3.63 g α-TCP, 0.37 g CSD) with 1.72 ml of $C_6H_5Na_3O_7 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 2H_2O$ 0.2 M solution. The citrate concentrations ranged from 0.00 to 0.10 M. The paste was then transferred to a syringe whose tip has been cut off. Fifteen minutes after setting, the samples were placed in 0.15M pH 7.4 phosphate buffer solution at 37ºC. After 6, 24 or 48 hours of incubation, they were taken out and dried at 37 ºC. Finally, the samples were processed to obtain cylinders of 12 mm in diameter.

Characterizations included: setting time, compressive strength, SSA, microstructure (SEM), and composition (XRD and XRF). Additionally, the ability of the blocks to be machined was evaluated.

RESULTS: The setting time of the cement increased almost exponentially with an increase of the citrate concentration. Interestingly, no significant change of the cement setting time was observed between 0.00 and 0.01 M concentrations or between the α-TCP powders milled for 75, 150 and 225 min. The powder milled for 15 min had significantly longer setting times. These results suggest that the presence of an amorphous phase does not modify the initial reactivity (expressed by setting time measurements). The cement SSA increased with an increase of the citrate concentration, but this effect was limited to about 10%. No difference of SSA was detected between 6, 24 and 48 hours of incubation. The ability of the cement blocks to sustain mechanical machining varied significantly according to the milling time: in the 36 samples prepared with powders milled for 15 and 75min, only one sample broke during machining. On the other hand, only 12 out of 36 samples produced with α-TCP milled for 150 and 225 min remained intact. Therefore, not all samples could be tested for compressive strength. Values were close to 30 MPa, i.e. close to previously-reported results. The citrate concentration and α-TCP milling time did not significantly affect the results.

An increase of α-TCP milling time reduced the time until setting completion and decreased the CSD content in the hardened cement. As XRF does not show any difference of sulphur content in the samples and no traces of Ca-sulphate hemihydrate or anhydrite were found in XRD data, the disappearance of CSD may originate from incorporation of sulphate into the apatite structure, or from formation of an amorphous phase.

SEM pictures did not reveal any effect of citrate ions on the cement microstructure, contrary to α-TCP milling time: longer milling time transformed a plate-like structure into a tube-like one with more open and globular microstructures (Fig 1).

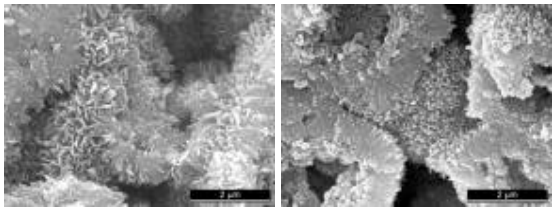

Fig. 1: SEM microstructure; milling time: left: 15min; right: 225min.

DISCUSSION & CONCLUSIONS: Prolonged α-TCP milling (i) does not shorten the cement setting time, (ii) reduces the time until setting completion, (iii) leads to a disappearance of crystalline CSD, and (iv) results in very brittle cement samples.