

Preparation and Characterization of New Self-setting Calcium Phosphate Cements Based on Alkali Containing Orthophosphates

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Introduction

Many different combinations of calcium phosphate cements (CPC) have been investigated since Brown and Chow have reported about these materials. By mixing a powder and a liquid, well applicable paste can be prepared which becomes hardens in a short time by formation of Hydroxyapatite (HAp) or Brushite. New material compositions were introduced, forming no Hydroxyapatite by hardening and showing a higher resorbability.

Materials and Methods

For preparing the cement powders a mixture of Dicalcium- potassium-sodium orthophosphate (CPSP), Tricalciumphosphate (TCP) and Dicalciumdiphosphate (DCDP) was melted at nearly 1600 °C. The melting products were grinded to achieve fine particle sizes. Cylindrical cement samples (d = 6 mm, h = 10 mm) were prepared by mixing the powders (see Tab.1) with an aqueous solution. The setting times (I₁ and F₁) were measured according to the method of Gilmore. XRD were recorded from the powders, the hardened samples and from the cements after storage in SBF solution for 4 weeks. Solid-state ³¹P-MAS-NMR spectra were re-recorded at a field of 14.1T. The in-vitro solubility was tested according to ISO-1993-14.

Table 1
Cement compositions and properties

Sample code	Ratios of CPSP-TCP-DCDP [%]	D ₅₀ -value of particle size range [µm]	Solid content [%]	Initial setting time, I ₁ [min]	Compressive strength after stored in SBF for 1 day* [MPa]	Compressive strength after stored in SBF for 4 weeks [MPa]
DC-1	100-00-00	8.79	83.33	9	0.91±0.2	3.30±1.3
DC-12	40-30-30	9.08	83.33	15	3.6±0.5	6.4±1.1
DC-8	50-25-25	8.78	83.33	10	1.8±0.2	4.2±1.0
DC-5	60-20-20	8.3	83.33	20	1.1±0.2	1.5±0.4
DC-15	30-50-20	4.24	76.92	7	2.2±0.4	2.2±0.4

*samples measured under wet conditions

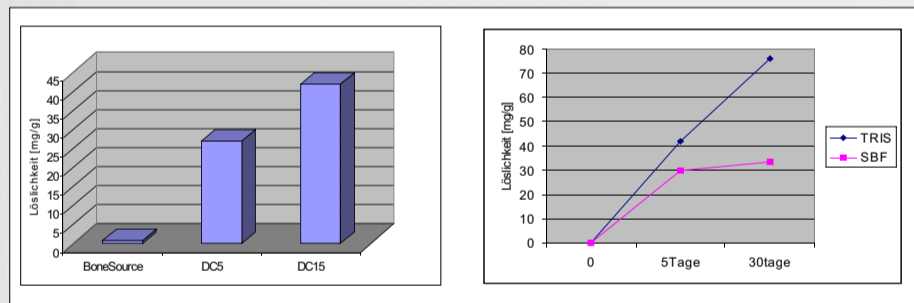


Fig. 1a
Solubility of different CPC's tested according to ISO-1993-14

Fig. 1b
Solubility of DC-15 in TRIS-HCL buffer and SBF solution

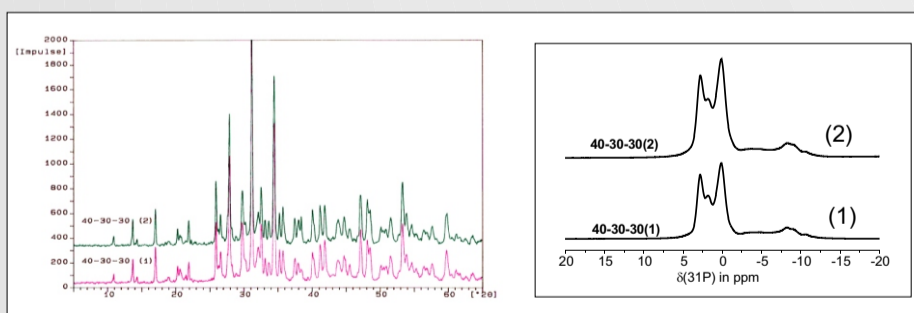


Fig. 2a
X-ray diffraction patterns of DC-12 cement (1) and after being stored in SBF for 4 weeks (2)

Fig. 2b
³¹P-MAS-NMR spectra of DC-12 cement (1) and after being stored in SBF for 4 weeks (2)

Results

Cements with a surface area about 20 m²/g and a porosity of 40-50% were prepared. Changes in setting time, porosity and strength can be influenced by the ratio of powder to liquid as well as by the particle size and chemical composition of the powders (Tab.1). The solubility was determined in TRIS-HCl buffer solution and also in SBF (Fig.1). There was a good agreement between ion loss in TRIS-HCl buffer solution determined by ICP measurement and the gravimetric method. The solubility of these CPCs was clearly higher than that of a comparable commercial product which was forming HAp. Hydroxyapatite could not be found during forming cements as well as by storage in SBF as it can be seen in XRD (Fig. 2a) and ³¹P-NMR spectra (SP) (Fig. 2b). Looking for the hardening process, (¹H-³¹P)- spectra (CP) and ¹H-NMR were also taken up. Unusually the CP and SP spectra differ, but the CP- can be fitted in the SP-spectra as it can be seen in Fig. 3. Thus a broad signal between -2 and -11ppm was found, which could be assigned to HPO₄ groups. After storage the cements in SBF-solution, these signal level increase slowly with time (Fig. 4) but in the ¹H-spectra the peak for H₂O disappears (Fig. 5)

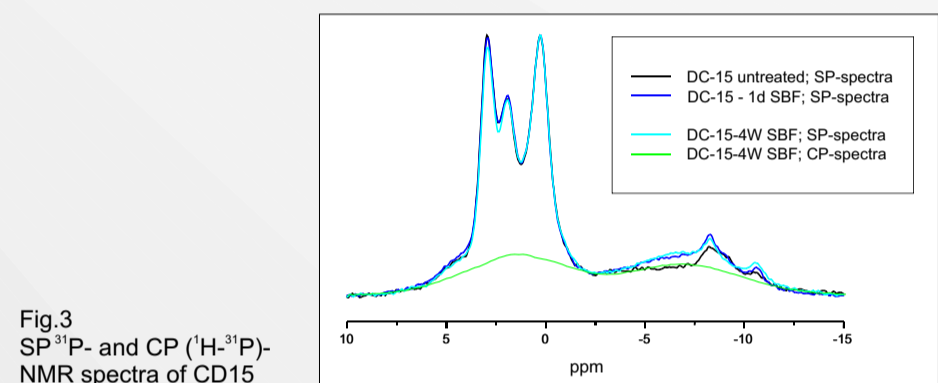


Fig.3
SP ³¹P- and CP (¹H-³¹P)-NMR spectra of CD15

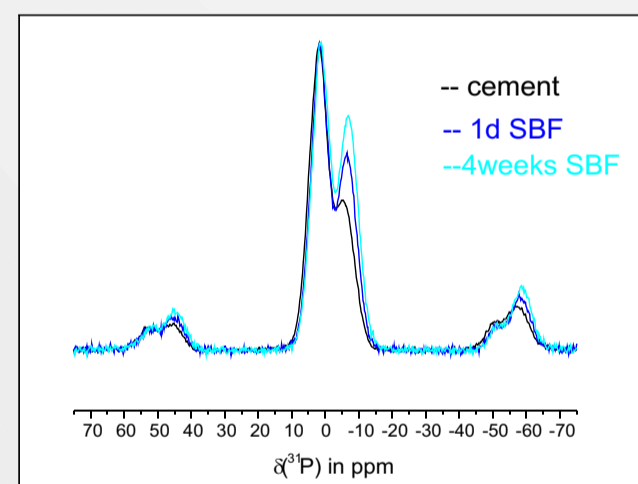


Fig.4
CP (¹H-³¹P)-NMR spectra of CD15 after storage in SBF solution

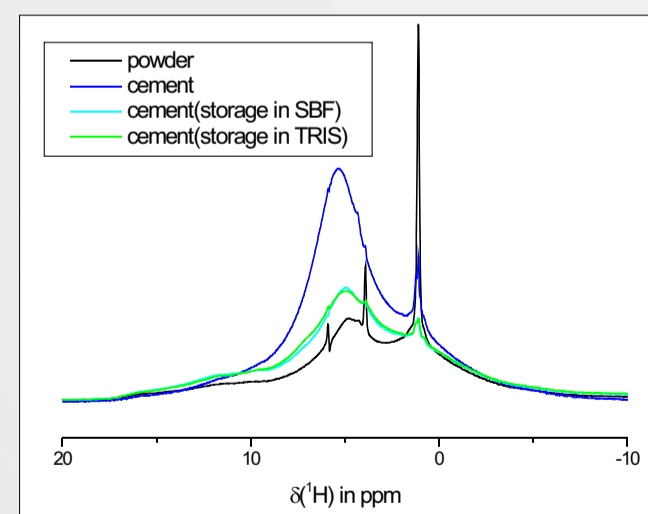


Fig. 5
¹H- spectra of DC15

Discussions

The cements obtained in this work are characterized by the absence of Hydroxyapatite formation. No differences were found between the powders and the cements in XRD. In ³¹P-NMR pattern a broad signal for HPO₄ was seen, that increases by cement formation as well as by storage in SBF. To find more references for structural changes will be the object of our further work.