

Thermo-chemical Study of the Hydrolysis of Amorphous Calcium Phosphate

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Introduction

Amorphous calcium phosphates (ACPs) appear as a transient or constitutive phase in many commercialised calcium phosphate biomaterials such as coatings of metal, orthopaedic prostheses and orthopaedic calcium phosphate cements. They have also been shown to form at the very beginning of surface reactions occurring on implanted bioglasses. In addition, ACPs have been observed in many biological systems, although they do not seem to exist in detectable amounts in hard tissues of vertebrates [1]. It is known that ACPs convert easily into poorly crystalline apatite in aqueous media. This reaction has been suggested to be responsible for the biological performance of plasma sprayed coatings. It is also involved in the setting reaction of a-BSM[®], an injectable Ca-P cement recently commercialised. Despite this wide occurrence the hydrolysis reaction of ACPs has not been the object of extended studies and the aim of this work was to determine the thermal and chemical events involved in the hydrolysis of ACP.

Materials and methods

Amorphous tricalcium phosphate (ACP with Ca/P atomic ratio of 1.5) was prepared by double decomposition between a calcium and a phosphate solution in alkaline media. The samples were lyophilised and heated at different temperatures (200 and 400°C) well under the crystallisation temperature of ACP (630°C). The ACPs obtained were hydrolysed in water at 25°C at neutral pH and 1% weight solid/solution ratio. The thermal events were followed by microcalorimetry and the hydrolysis products were characterised by X-ray diffraction, FTIR and chemical analysis. The progression of the hydrolysis reaction was followed by the determination of the residual amorphous phase using the crystallisation peak observed by DTA. The dissolution enthalpies of the ACP samples and the hydrolysis products were used to determine the enthalpy variations.

Results and Discussion

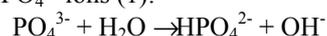
The rate of hydrolysis was strongly dependent on the preliminary thermal treatment of ACP and decreased considerably in heated samples despite similar specific surface areas. The final products were found to be identical. Hydrolysis led to a nanocrystalline apatite rich in OH⁻ and HPO₄²⁻ ions with a Ca/P ratio close to that of the original ACP phase. The thermal events associated with ACP hydrolysis appeared however rather complex. The microcalorimetric curves showed three major events: a sharp exothermic peak on the immersion of the powder (maximum at 2mn), a very broad asymmetric exothermic peak (see Table) followed by a very weak endothermic peak barely detected in heated samples. The first peak is due to the immersion of the powder and the concomitant dissolution of ACP in the hydrolysis solutions. The dissolution heat however represented only a negligible fraction of this peak (less than 0.03%). The heat release, essentially due to the wetting of the powder, appeared slightly weaker for the heated ACP.

Enthalpies of hydrolysis of ACP samples

ACP Samples	1 st Peak (J.g ⁻¹)	2 nd Peak (J.g ⁻¹)	Max 2 nd Peak (h)
freeze-dried	-18.0 ± 0.2	-69.5 ± 0.7	5
200 °C	-11.6 ± 0.2	-180 ± 2	13
400 °C	-11.6 ± 0.2	-192 ± 2	21.5

The major exothermic event (2nd peak) was related to the hydrolysis reaction. Unlike the first peak, it increased strongly in heated samples and represented more than twice the value observed in freeze-dried samples. The excess of heat release in heated samples was assigned to an alteration of the water content of the powder, as revealed by the dissolution enthalpies of heated ACP samples. The data obtained indicated a considerable re-hydration heat of ACP (-12.3 kJ per mole of H₂O). The hydrolysis reaction appeared globally exothermic (-25.9 ± 0.3 kJ per formula unit of ACP: Ca₃(PO₄)₂). These data allowed a determination of the amount of water molecules associated with ACP in wet media. The calculation led to 3 molecules per formula unit. The last endothermic peak was very weak. It overlapped with the strong exothermic peak of the re-hydration and hydrolysis reaction and its enthalpy could not be measured. This peak could correspond to the loss of water molecules from the poorly crystalline apatite formed.

The ACP structure has been described as clusters of 3 formula units: Ca₉(PO₄)₆ (Posner's clusters) and recently theoretical calculations have confirmed the particular stability of these clusters which are found in most crystalline calcium phosphates (2). It seems however that, in precipitated ACP, these clusters is associated with tightly bound water molecules. The loss of these molecules on heating appears reversible and the re-hydration of ACP is the main cause of heat release in heated samples. This process seems rather slow and it determines the progression of the hydrolysis reaction. Several mechanisms have been proposed for the conversion of ACP into apatite. Dissolution-reprecipitation, involving, at neutral pH, the transient formation of octacalcium phosphate (OCP) and internal hydrolysis of PO₄³⁻ ions (1):



leading directly to the formation of an apatitic lattice. The data obtained in our experimental conditions did not reveal transient formation of OCP. The hydrolysis however occurred and seems correlated to the crystallisation into nanocrystals apatite.

Conclusion

The re-hydration of ACP appears to be a major thermal event in determining the hydrolysis of ACP-containing biomaterials.

References

- 1- J.C. Elliott. "Structure and Chemistry of the apatites and other calcium orthophosphates". Elsevier, 1994.
- 2- G. Kanzaki et al. Biomaterials 2001, 22, 2921-2929