

Corrosion of alkali calcium phosphate bioglasses

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INTRODUCTION: Corrosion is a common process for all glass systems even though in many cases it is scarcely perceivable due to the extremely low corrosion rate values. Calcium phosphate glasses are of interest as bioglasses, while powder samples of different compositions can be used as fertilisers. The leaching process is usually appreciated by mass loss while the release of cations is a process more specific and can be selectively controlled by the structure of glass. An additional possibility is to apply proper heat treatments for the partial crystallisation of glasses in order to develop convenient crystalline phases in which the cations are encompassed in bonds of controllable strength.

METHODS: The investigated samples belong to CaO-P₂O₅-K₂O and CaO-P₂O₅-Na₂O glass systems. They were obtained from homogenized mixtures of CaCO₃, (NH₄)₂HPO₄ and K₂CO₃ or Na₂CO₃·10H₂O analytical grade reagents by melting at 1100°C, respectively 1000°C, and quickly undercooling at room temperature.

The corrosion behaviour was followed at 37°C in static regime by immersion of samples in different solvents simulating biological media (desalinized water, physiological serum and chlorine acid solution with pH 1.5) by measuring the mass of samples maintained in the mentioned solutions at room temperature for different times. The samples mass was determined with an accuracy of 0.1 mg. The glass surface area to solution volume ratio was around 15 m⁻¹ for all samples.

RESULTS: The data obtained in the dissolution static test are expressed by the relative mass loss of samples. For the calcium-phosphate system with 10 mol % K₂O one remarks that up to 50 % substitution of P₂O₅ by CaO, the dissolution rate corresponds to the expected behaviour in the three solutions, i.e. the corrosion resistance decreases in physiological serum and chlorine acid solution, but for a higher replacement of P₂O₅ by CaO the behaviour is changed. This change is not observed for the samples containing 30 mol % Na₂O.

DISCUSSION & CONCLUSIONS: In order to explain the different corrosion behaviour of calcium phosphate glasses in the investigated dissolution media, beside the composition of glasses and solvents is necessary to take into account the short range order characterizing the samples. The structural stability of cations in glass matrices is correlated with their local symmetry.

Pure phosphate glass consists in a continuous random network (polymeric structure) of quasi-tetrahedral PO₄ units wherein phosphorous is four coordinated and only three of the oxygen atoms of each unit bridge to neighboring units, while the fourth is doubly bonded to

the central phosphorous atom. The presence of the modifier like alkali and alkaline earth species decreases the number of bridging oxygens (P-O-P bridge) in PO₄ units, while its negative charge increases. The decrease of corrosion resistance is also due to the presence of the alkali ions that diminish the network consistency [1]. The initial stages of the aqueous reactions always results in the leaching of alkali and alkaline earth species from the surface of the glass to create a P₂O₅-rich surface layer. It is generally believed that in the initial stages of the leaching reaction, the contact of liquid water or vapour water with the glass surface leads to an exchange of alkali and alkaline earth ions in the glass with hydrogenated ions in the aqueous environment. (i.e. ion exchange or interdiffusion mechanism). Another mechanism proposed [2] is based on the diffusion of molecular water into the glass and its chemisorption at the non-bridging oxygen sites where alkali and alkaline earth species reside in the glass. These differences can be discussed also in relation with the cationic radii of the glass network modifiers, because calcium and sodium radii are very close each to other (1.14 Å) and well different from that of potassium (1.51 Å) and, at the same time, in relation with the cationic field strengths.

In the potassium containing samples one observes two leaching stages relative to the incipient dissolution. In the investigated sodium containing samples the highest corrosion stability was observed in physiological serum, while in decationised water and physiological serum one observes after 50 hours the occurrence of a shoulder in the release curve denoting that the glass corrosion is suppressed.

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