

The Influence of Organic Acids on the Dissolution of Synthetic Hydroxyl-Apatite

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The surface properties of hydroxyl-apatite (HAP) and its reactions with organic acids are important in a number of applications. These include wastewater treatment, where phosphate precipitation can be an effective method to remove phosphorus, heavy metal immobilisation via precipitation of insoluble phosphates, calcium phosphate scale formation in industrial systems and medical applications (bone and tooth disease). Invariably in all these systems, phosphate dissolution/precipitation is extensively influenced by the presence of organic acids. There is however, a lack of published information to allow appropriate evaluation of such effects. The aim of this study was to bring better understanding of the dissolution of calcium phosphate in the presence of small molecular weight organic acids. In this study the hydroxyl-apatite used, was synthesised at 20 °C and at a pH of 7.7 (± 0.1). These conditions of synthesis were chosen because the experimental work intends to simulate wastewater conditions. The produced hydroxyl-apatite was characterised by X-ray diffraction, and was confirmed to be a pure phase. Scanning Electron Microscopy showed that the phase synthesised under such conditions forms small crystals (less than 0.5 μm) in the form of flakes. Chemical analyses showed that this synthetic hydroxyl-apatite had a calcium/phosphate molar ratio of 1.55, which is significantly lower than the stoichiometric molar ratio of 1.67. The hydroxyl-apatite used in experiments, was dried and then crushed and sieved. The fraction between 90–500 μm was washed to remove fines, and used for experiments. The surface area of this dry powder was around 80 m^2/g , as determined using BET.

Experiments were carried out in batch mode at 25 °C and near-neutral pH. Our purpose was to investigate the effects of number of functional groups and of acid concentration on the release of calcium and phosphate from the hydroxyl-apatite. Acetic, oxalic and citric acids, with one, two and three functional groups respectively were selected. To study the influ-

ence of the concentration of organic acids, the experiments were carried out in the concentration range of 10^{-4} to 10^{-2} M, and at an initial pH of 6.7. The results of the organic acid experiments were compared with those from a system containing hydroxyl-apatite and a background electrolyte (control).

Our results indicated that the organic acids had variable effects on the release of phosphate and calcium during hydroxyl-apatite dissolution. The mono-functional acetic acid had no effect on the release of calcium and little effect (increase) on the release of phosphate compared to the control. The increasing concentration of acetic acid increased the final calcium and phosphate concentrations only marginally. For citric acid, the release of phosphate was higher when 10^{-4} M of citric acid was present compared to the control. The final (equilibrium) phosphate concentration further increased with increasing concentration of citric acid. The effects on calcium concentration were variable, and not always consistent with phosphate. In the presence of 10^{-4} M citric acid, the release of calcium was less compared with the control, whereas when higher concentrations of citric acid were present the opposite was true. The influence of the organic acids on hydroxyl-apatite dissolution becomes more pronounced when considering the calcium/phosphate molar ratios in solution. The aqueous Ca/P ratios in the control experiments were lower than in the solid phase, as determined chemically. The presence of organic acids reduces the molar ratio in solution even further, with the strongest effect showed when using the organic acid with the highest number of functional groups.

It is concluded that the presence of organic acids has a major influence on the solubility of hydroxyl apatite. This effect depends on the number of functional groups and the concentration of the acid.