JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **9** (1998) 789–792

Synthesis of dahllite through a cement setting reaction

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Dahllite is a synthetic carbonated hydroxyapatite with a carbonate ion content similar to bone mineral. The first objective of this study was to investigate the stoichiometric conditions under which dahllite formation occurs in a powder mixture of α-$Ca_3(PO_4)_2$, $Ca(H_2PO_4)_2$ and $CaCO_3$. The second objective was to identify how these conditions apply to commercially available cement, Skeletal Repair System (SRS^{TM}), and other α-$Ca_3(PO_4)_2$-based cements currently under investigation. The stoichiometric coefficients were found to be a function of both the percentage of carbonate ions incorporated into the hydroxyapatite structure, and the amount of CO_2 released during the reaction. As a consequence, a stability field has been obtained where different initial proportions of the reactants in the powder mixture should give the same reaction product if sufficient CO_2 is released into the solution. However, increasing amounts of $CaCO_3$ in the initial mixture have been shown to affect the solution pH in such a way that only partial reaction of the reactants takes place. SRS^{TM} and other α-$Ca_3(PO_4)_2$-based cements have been located inside the stability field and a comparison between their reported setting and hardening properties has been performed.

1. Introduction

Calcium-deficient hydroxyapatite (CDHA; $Ca_9(HPO_4)(PO_4)_5OH$) is the final product of the setting reaction in several alpha-tricalcium phosphate (α-TCP; α-$Ca_3(PO_4)_2$)-based cement systems [1–3]. These studies have shown that the setting and hardening properties of α-TCP-based cements are explained by the progressive dissolution of the α-TCP phase and the formation of an entangled network of CDHA crystals.

In order to improve the biocompatibility of these cements, several trials have been performed on the modification of the CDHA structure by $CaCO_3$ (CC) to form a calcium carbonate-deficient apatite (CCDA; $Ca_{9-x}(HPO_4)_{1-1.5x}(PO_4)_{5-2.5x}(CO_3)_{3.5x}(OH)_{1+1.5x}$) which is more similar to bone mineral than stoichiometric hydroxyapatite [4–6]. However, the speed of the chemical reaction and its influence on setting and hardening properties was found to be dependent on the acidity of the second active calcium phosphate in the powder mixture [2, 5]. The addition of small amounts of CC into the powder mixture, while modifying CDHA structure into dahllite ($Ca_{8.8}(HPO_4)_{0.7}(PO_4)_{4.5}(CO_3)_{0.7}(OH)_{1.3}$), showed better setting and hardening properties when monocalcium phosphate monohydrate (MCPM) was used [5] instead of dicalcium phosphate (DCP) [4, 7].

The first objective of this study was to investigate the stoichiometric conditions under which dahllite formation occurs in a powder mixture of α-TCP, MCPM and CC, to assess the implications of the assumption that CO_2 is released into the cement to form dahllite or CCDA, and the effects this might have on the final mechanical properties of the cement. The second objective was to identify how these conditions apply to a commercially available cement and other α-TCP-based cements currently under investigation. This is important in order to assess the differences between SRS^{TM} and other α-TCP-based cements when considering setting and hardening properties.

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2. Materials and methods

Equation 1, which occurs in an aqueous medium, was analyzed in order to obtain the stoichiometric conditions under which a mixture of tricalcium phosphate (TCP; $Ca_3(PO_4)_2$), monocalcium phosphate anhydrous (MCPA; $Ca(H_2PO_4)_2$) and CC should give CCDA as the final reaction product. The parameters a, b, c and d are the molar stoichiometric coefficients of the respective chemical species, with a, b and $c > 0$.

$$a\,\mathrm{TCP} + b\,\mathrm{MCPA} + c\,\mathrm{CC} + d\,\mathrm{CO_2} \rightarrow \mathrm{CCDA} \quad (1)$$

Powder mixtures of the reactants were prepared at a calcium to phosphorus (Ca/P) ratio of 1.81 and the pH evolution of the mixtures was measured at a water to powder (W/P) ratio of $20\,\mathrm{ml\,g^{-1}}$ to record any intermediate phase transition. X-ray diffraction (XRD) was performed (40 kV; 30 mA; integration time = 10 s; step scanning = $0.02°(2\theta)$) on the above filtered and dried powders once the solution pH attained equilibrium (72 h) to investigate whether or not reactants were fully transformed into dahllite. The diffraction peaks were indexed in the interval $20 \leqslant (2\theta)° \leqslant 35$ with the appropriate Joint Committee Powder Diffraction Standards (JCPDS) files (9-348 for α-TCP, 9-0390 for MCPA, 5-0586 for CC and 9-432 for CCDA).

3. Results

Equation 1 was solved mathematically after defining the system of equations resulting from the equilibration of the different ionic species. The stoichiometric coefficients were found to be a function of the percentage of carbonate ions theoretically incorporated into the hydroxyapatite structure as well as a function of the amount of CO_2 released during the completion of the reaction (see Equation 2a–d).

$$a = 3 - 1.25x + 0.5\lambda \quad (2a)$$

$$b = -0.75x - 0.5\lambda \quad (2b)$$

$$c = 3.5x - \lambda \quad (2c)$$

$$d \equiv \lambda \quad (2d)$$

As a consequence, a stability field has been obtained where different initial proportions in the powder mixture (a, b and c) should give the same reaction product (x fixed) if sufficient $CO_2(\lambda)$ is released into the solution. This stability field is defined by the area contained within the limits $\lambda = -1.5x$, $\lambda = -6 + 2.5x$ and the plane $x = 0$ in an (x, λ) orthogonal system (see Fig. 1).

SRS™ is composed of 84.73% α-TCP, 3.29% MCPM and 12.34% CC by weight [5, 8]. This composition gives $Ca_{8.82}(HPO_4)_{0.73}(CO_3)_{0.63}(OH)_{1.27}$ as the final setting product which is in agreement with the CCDA obtained for a value of $x = 0.18$. SRS™ is then located inside the stability field for a value of $(x, \lambda) = (0.18, -0.512)$.

Sample mixtures prepared at $x = 0.3$ and $-\lambda$ values of 1, 2, 3, 4 and 5 showed that the amount of CO_2 release increased (immediately after mixing the powder with the liquid and according to visual observations) as $-\lambda$ increased.

Fig. 2 shows the results of XRD performed on dried powder samples once the solution pH had attained equilibrium (after 72 h reaction). CC was detected in all samples and the intensity of the principal reflection to CC increased as $-\lambda$ increased (in direct correspondence to the increasing amounts of CC in the original powder mixtures).

4. Discussion

Equation 2 showed that 1 mol of dahllite ($x = 0.18$) in SRS™ ($a = 2.52$, $b = 0.12$, $c = 1.14$) should be produced through the release of $\lambda = 0.512$ mol CO_2 during cement reaction. However, according to

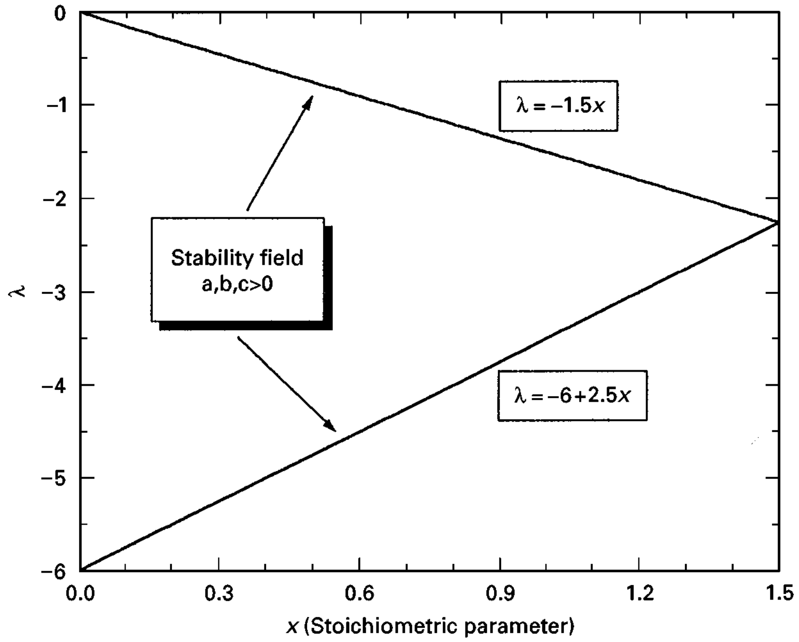

Figure 1 Stability field inside which CCDA with different carbonate content could be formed by a mixture of α-TCP, MCPM or MCPA and CC.

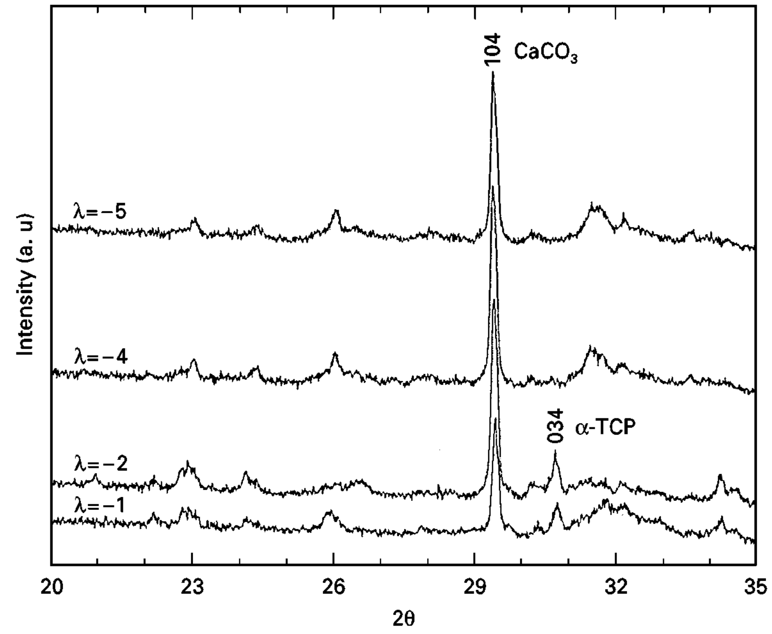

Figure 2 XRD results show partial reaction of CC at equilibrium.

Equation 2, as reflected also in Fig. 1, dahllite should be obtained not just at a specific value of $-\lambda = 0.512$ but for $0.27 < -\lambda < 5.55$. This means that dahllite should be obtained for all those initial (a, b, c) powder mixtures matching the condition of $-\lambda$ in the above range. However, it is known that the average pH of the solution depends on the relative proportions of the reactants (different basicity) in it. As a consequence, the solubility of the reactants and the supersaturation of the solution controlling the precipitation of the reaction product may be affected in such a way that, kinetically, the reaction only partially takes place. This situation was observed (see Fig. 2) for the mixtures (a, b, c) prepared in this study where $x = 0.3$ and $-\lambda$ varied between 1 and 5. In these samples, XRD showed that the reaction was incomplete, which means that the targeted CCDA (7 wt % carbonate content) was not attained despite visual observation of an increasing amount of CO_2 released into the solution as $-\lambda$ increased.

It is important to highlight that, under certain preparation conditions, 85% of the final compressive strength (40 MPa) of a 100 wt % α-TCP cement ($a = 1$, $b = 0$, $c = 0$) was reported to be transformed into CDHA in 13 h [1]. Modification of this cement with additions of CC ($a = 2.6$, $b = 0$, $c = 1$) showed that CC was acting as a retarder of the initial setting and decreased the compressive strength during hardening [4, 7]. However, this was not the case for SRS™ ($a = 2.52$, $b = 0.12$, $c = 1.14$) [5, 8] despite the small difference between the molar stoichiometric coefficients, when 85% of the final compressive strength (55 MPa) was reported to be attained in no more than 4 h after the initial powder and liquid cement mixture. However, full comparison of the above results is not possible due to the differences in reactants used in the cements such as the particle size distributions of α-TCP and the milling method used in the process, both of which drastically affect the setting and hardening of the cement [8].

In order to produce the desired final reaction product in Equation 1, the reaction pH needs to be strictly controlled [9]. In fact, the buffer capacity of CC and its effect on the solubility isotherms of the reactants [10] seems to be responsible for the partial conversion of the reactants into CCDA, as confirmed by XRD at equilibrium (see Fig. 2). These results have highlighted the importance of the capacity of the buffer to control the dissolution–precipitation chemical reactions.

5. Conclusion

It has been shown that dahllite formation through a setting reaction in a commercially available cement (SRS™) occurs by a process involving CO_2 release. However, the same hypothesis should be true for different compositions, not only for dahllite but for other CCDAs, if the appropriate amount of CO_2 is released during the initial mixture of the powder and the liquid phases or during cement setting. In order to prove this, further research is required, involving liquid buffers as pH controllers.

Acknowledgments

This work was supported by a European Grant TMR no. ERBFMBICT972733. The authors thank the CICYT (Dirección Científica y Técnica of Spain) for funding this work through project MAT96-0981. The EPSRC is also gratefully acknowledged for the core grant for the IRC in Biomedical Materials.

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Received 7 May
and accepted 27 May 1998