LONG-TERM AGING OF BRUSHITE CEMENTS IN PHYSIOLOGICAL CONDITIONS : AN IN VITRO STUDY.

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INTRODUCTION: An in vitro aging experiment in simulated physiological conditions has been undertaken, with the aim of understanding the physico-chemical aspects of the long term in vivo degradation of brushite cements.

A statistical design of experiment has been established in order to evaluate selected parameters of the initial cement composition on their long term in vitro aging. Four compositional factors were selected : (A) nature of rheological additive (hyaluronic acid–HA vs hydroxyproprylmethyl cellulose–HPMC, appr. 1 %wt), (B) source of sulfate ions ($CaSO_4 \cdot 0.5H_2O$–plaster of Paris vs sulfuric acid, atomic ratio S/Ca = 0.013), (C) magnesium phosphate addition (0 %wt vs appr 8.5 %wt $MgHPO_4 \cdot 3H_2O$) and (D) final cement porosity (35 %vol vs 45 %vol). Thus, 16 different cement compositions were prepared and left for aging in physiological conditions from 1 day up to 16 weeks (37°C, modified Hank's solution free of glucose and Mg ions, renewed every 2–3 days).

Elemental chemical analyses (P, S, Ca, Mg) and pH measurements were used to calculate the state of saturation of the recovered aging solutions with respect to various phases, such as brushite ($CaHPO_4 \cdot 2H_2O$, DCPD), hydroxyapatite ($Ca_5OH(PO_4)_3$, HAp), octocalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$ OCP) and newberryite ($MgHPO_4 \cdot 3H_2O$, DMPT). The phases present in the aged cement specimens were determined by X-ray diffraction.

Already available results show that brushite cement aging is mainly affected by the presence of Mg and by the nature of the rheological additive (HA vs HPMC). Thus, the simultaneous presence of HA and of Mg visibly promotes faster degradation of brushite cements ; with HA and Mg, extensive degradation occurs between 8 and 12 weeks, whereas all the cements containing HPMC keep their full integrity beyond 16 weeks. Solubility calculations confirm the higher solubility of DCPD in brushite cements containing HA and Mg simultaneously. In that case the specific area of brushite is increased. The simultaneous presence of HPMC and Mg increases the supersaturation of the recovered physiological solutions with respect to HAp ; up to 8 weeks, only the aging solutions brought into contact with brushite cements containing HPMC and Mg are supersaturated with respect to OCP.

In conclusion, this study shows that the degradability of brushite cements in physiological conditions is markedly increased by small amounts of additives such as DMPT and HA, which increase the solubility of DCPD in physiological liquids. On the other hand, their stability is strongly increased by the presence of HPMC. Simultaneous addition of HA and Mg to these cements promote OCP and HAp precipitation in surrounding physiological liquids.

A second study is underway to focus on the Magnesium effect. The effects of Magnesium salt nature and granulometry will be investigated.

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