

Development of a new CaHPO₄ (Monetite) self-setting cement

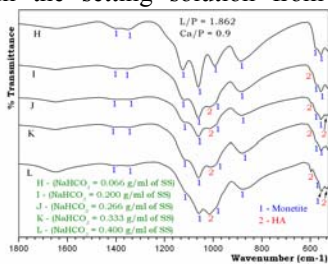
Tarang Desai, Sarit.B. Bhaduri, and A. Cuneyt Tas

School of Materials Science & Engineering, Clemson University, Clemson, SC 29634

Statement of Purpose: Monetite (CaHPO₄) and Brushite (CaHPO₄·2H₂O) are the two most resorbable phases at and around neutral pH values among all the calcium phosphates (CaP) [1], making them ideal for bone/dental repair applications. While brushite cements are already available in the market in the form of ChronOS™ Inject [2], according to our knowledge, there have been no reports of bone/dental cements consisting only of monetite. The aim of this project is to develop and evaluate the properties of an inexpensive monetite based cement for bone/dental repair starting with H₃PO₄ and Ca(OH)₂. Since monetite does not contain H₂O groups in its chemical formula, we hypothesize that these cements would be stronger than brushite based cements, while retaining their solubility.

Methods: (materials and analytical procedures used) H₃PO₄, de-ionized H₂O, NaHCO₃ and an organic acid were used to prepare the setting solution/liquid part of the cement formulation. Pure Ca(OH)₂ constituted the sole powder component of the cement formulation. Mixing the setting solution and the powder in appropriate quantities led to the formation of a paste like material which had self-setting properties. Phase characterization of the material was performed via X-ray diffraction, FT-IR, and ICP-AES analyses. SEM was used for the microstructural evaluation of the cement. Setting time of the cement was determined using Gillmore needle apparatus. Pellets with an aspect ratio of 1.5 were prepared and compressive strength measurements were performed. Dissolution behavior of the cement in PBS and α-MEM was evaluated. Cement was also soaked in SBF to study its apatite-inducing ability. The apatite coating was characterized by SEM, XRD and FTIR. *In-vitro* cell culture was performed on neat cement discs to study the growth and mineralization behavior of rat osteoblast cells.

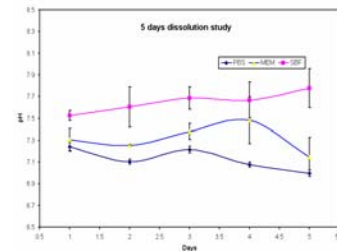
Results / Discussion: The XRD spectrum of dried and subsequently powdered cement shows that Monetite (CaHPO₄) is the main component of the self-setting cement. FT-IR data also supported the findings of the XRD spectra. However, increasing the NaHCO₃ content in the setting solution from 0.066 g/ml to 0.4 g/ml



increased the proportion of apatite in the cement as seen from the chart on the left. The initial setting time (T_i) of the cement was found to be around 18 minutes and the final setting time (T_f) was 33 minutes

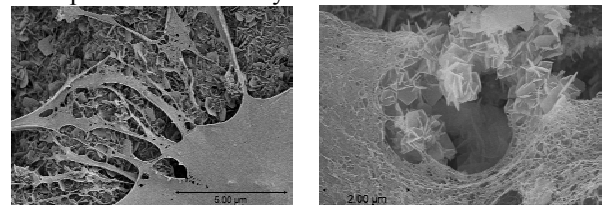
according to the Gillmore Needle test (ADA # 61). Compressive strength tests were carried out on cylindrical samples (l/d=1.5) stored at 25% humidity or 100% humidity. Wet cement samples had an average compressive strength of 2.2 MPa, whereas the strength of dry cement samples was 7.9 MPa. Pre-weighed amounts of cement pieces were used for dissolution studies in PBS,

MEM and SBF for a period of 3 and 5 days. ICP-AES analyses of the cement samples both before and after the PBS- and MEM-soaking showed that the Ca/P molar ratio



increased from 0.98 before the start of soaking to 1.14-1.18 by the end of the dissolution period. SEM analyses of the samples after PBS and MEM soaking showed the growth of apatitic flakes

and a slight change in the microstructure of the cement surface. SBF-soaked samples showed very heavy deposition of “Posner cluster” like apatitic CaP on the surface of the cement showing the bioactivity of this material [3]. Pictures below showed rat osteoblasts on the cement surface and it was evident that the cells proliferated and developed a collagen matrix, which is interspersed with CaP crystals.



Conclusions: This study demonstrated that a self-setting cement comprising monetite as the main phase and apatitic calcium phosphate as its trace phase can be developed with potential applications in the orthopedic/dental fields. The setting time of this cement was clinically acceptable and it maintained a neutral pH (≈ 7) in various media. The formation of a thick and uniform apatitic layer on the cement surface after soaking in SBF suggested that the material was bioactive. Rat osteoblasts seemed to undergo mineralization on the surface of this cement, and thus, this biocompatible material could have potential applications as a bioactive scaffold material. The most significant application of this material could be realized in crano-maxillofacial repair where current cements based on brushite and hydroxyapatite have shown complications of fibrous tissue encapsulation and low bioresorbability, respectively [4]. Although this cement is not currently injectable, ionic modifications to this formulation can improve its injectability, and could also contribute to the attainment of higher compressive strength values.

References:

- ([1] Chow L.C. U.S. Patent # 5525148. 1996) ([2] Bohner M. U.S. Patent # 6733582. 2004; Mathys Medical and Stratec Medical, Switzerland) ([3] Ducheyne P. Biomaterials 1999; 20: 2287-2303) ([4] Rechenberg B.V. J Cranio-maxillofacial surg. 2005; 33: 37-44.)