IN VITRO BIOACTIVITY OF A TRICALCIUM SILICATE CEMENT

Morejon-Alonso L.[(1)], Bareiro O. [(1)], Dos Santos L.A.[(1)], Garcia Carrodeguas R.[(2)]

[(1)] Escola de Engenharia, Dep. de Materiais, Universidade Federal do Rio Grande do Sul, Porto Alegre (RS), Brasil, loreley.morejon@ufrgs.br
[(2)] Departamento de Cerámica, Instituto de Cerámica y Vidrio - CSIC, Madrid, Spain

ABSTRACT

Tricalcium silicate is the major constituent of Portland cement and the responsible for their mechanical strength at early stages. In order to be used as and additive of conventional calcium phosphate cement (CPC), in vitro bioactivity of a calcium silicate cement (CSC) after soaking in simulated body fluid (SBF) for 14 days was study. The cement was obtained by mixing Ca_3SiO_5, obtained by sol-gel process, and a Na_2HPO_4 solution. The morphological and structural changes of the material before and after soaking were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed the formation of a layer of a Hydroxyapatite (HA) onto the CSC cement after soaking for 1h in SBF that became denser with the increase of soaking time. The study suggests that Ca_3SiO_5 would be an effective additive to improve the bioactivity and long term strength of conventional CPC.

Keywords: Tricalcium silicate, calcium silicate cement, calcium phosphate cement, in vitro.

INTRODUCTION

Ca_3SiO_5, also named C_3S, is considered the most important constituent of ordinary Portland cement (OCP) due to their spontaneous development of strength (spontaneous consolidation) towards water and their influence on the setting time of pastes [(1)].

Although it is quite known that silicon-containing materials have bioactive properties [(2,3)] and recent studies showed that C_3S powders [(4)], cement based [(5)] and ceramics, could induce the formation of hydroxiapatite (HA) after soaking in SBF and had a stimulatory effect on cell growth in a certain concentration range [(6)]; it is unknown the effect of some additives to a liquid component for the use of C_3S as a self-setting material or as an additive for others hydraulic cements.

On the other hand, calcium phosphate cements (CPC) are widely used as bone repairing and substituting materials in many dental and orthopedic applications due to their excellent biocompatibility, osteoconductivity and osteotransductivity [7]. Particularly, α-TCP-based CPC, when mixed with aqueous Na_2HPO_4 solution, set as the result of the dissolution of α-TCP particles and the precipitation of an entanglement of calcium deficient hydroxiapatite (CDHA) crystals [8]. For these materials, the low mechanical strength is their main limitation, and controlled addition of C_3S could be an effective way to increase the strength of them. Thus, the aim of this work was to study the in vitro bioactivity of a Ca_3SiO_5/Na_2HPO_4 cement, in order to use C_3S as and reinforcement additive for conventional α-TCP-based CPC.

MATERIALS AND METHODS

Tricalcium silicate powders were synthesized by sol–gel route [4], using $Ca(NO_3)_2.4H_2O$ and $Si(OC_2H_5)_4$ (TEOS) as precursors and calcined at 1400°C for 48h. Cements were obtained by mixing C_3S powders (mean diameter of particle size 14,56 μm) and 2.5 wt./vol. % Na_2HPO_4 aqueous solution in a liquid/solid ratio of 0.4 mL/g. Pure distilled-deionized water was also used as mixing liquid to prepare control samples.

In vitro bioactivity study was carry out in simulated body fluid (SBF) prepared according to the procedure described by Kokubo [9] at 36.5°C using a ratio volume/area of 0.1 cm^3/mm^2. The 24h-set pastes were soaking in SBF for 14 days, and after preselected soaking time, gently rinsed with deionized water followed by drying at room temperature.

Mineralogical composition of C_3S was determined by X-Ray Diffraction (XRD) in a PHILLIPS® diffractometer (X´Pert MPD) and Cu-target. Diffractograms were recorded employing Ni-filtered radiation (λ = 1.5406 Å), and anodic voltage and current of 40 kV and 40 mA, respectively. The step size was 0.05° and the time/step ratio was 1 second.

Morphological variations before and after soaking in SBF were characterized by Scanning Electron Microscopy (SEM) using a JEOL microscope (JSM-6060). Samples were previously coated with a thin layer of gold.

RESULTS AND DISCUSION

Fig. 1 shows the XRD pattern of the C_3S powder. The results showed that Ca_3SiO_5 was formed as principal phase (JCPDS 13-0209, 09-0352), however the most intense characteristic peaks for CaO (JCPDS 37-1497) were founded; probably owing to the evaporation of TEOS during the synthesis, even though the reaction took place under stoichiometric conditions (Eq. A). This result is in contradiction with previous studies reported, in which C_3S can be obtained without free CaO, at temperatures above 1400℃ with calcinations times of 2h [4].

$$3Ca(NO_3)_2.4H_2O_{\,(s)} + Si(OC_2H_5)_4 = Ca_3SiO_{5\,(s)} + 4C_2H_5OH + 6H_2O + 10NO_{2\,(g)} + 3/2\ O_{2\,(g)} \quad \text{(A)}$$

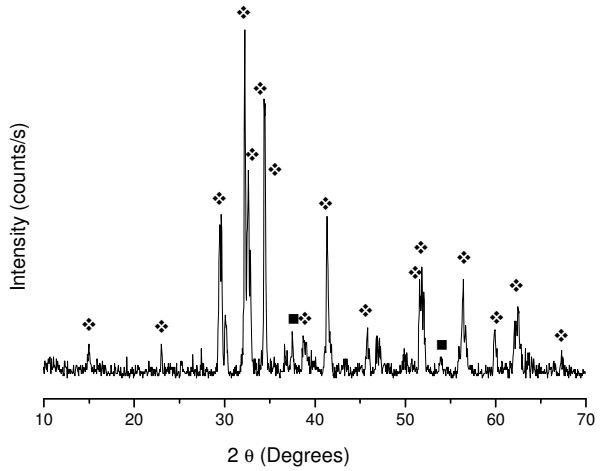

Figure 1. X Ra X-Ray diffraction patterns of Ca_3SiO_5 powder. ❖ Ca_3SiO_5, ■ CaO.

Figure 2 shows the SEM micrographs of the surface and cross-section of the pastes after 1 day-set. In the surface of cement it was found the characteristics aggregated of needle-like crystals of calcium silicate hydrate gel (C-S-H) type I (Fig. 2A) and platy-type II C-S-H (Fig. 2B) [10]. Higher magnifications of surface showed typical hexagonal habits of $Ca(OH)_2$ who growth into a void, where space restrictions are minimal, allowing development of euhedral forms. In cross-section, the pore size

was larger than those on the surface, and tiny particles aggregated, probably of C-S-H gel were observed (Fig. 2D).

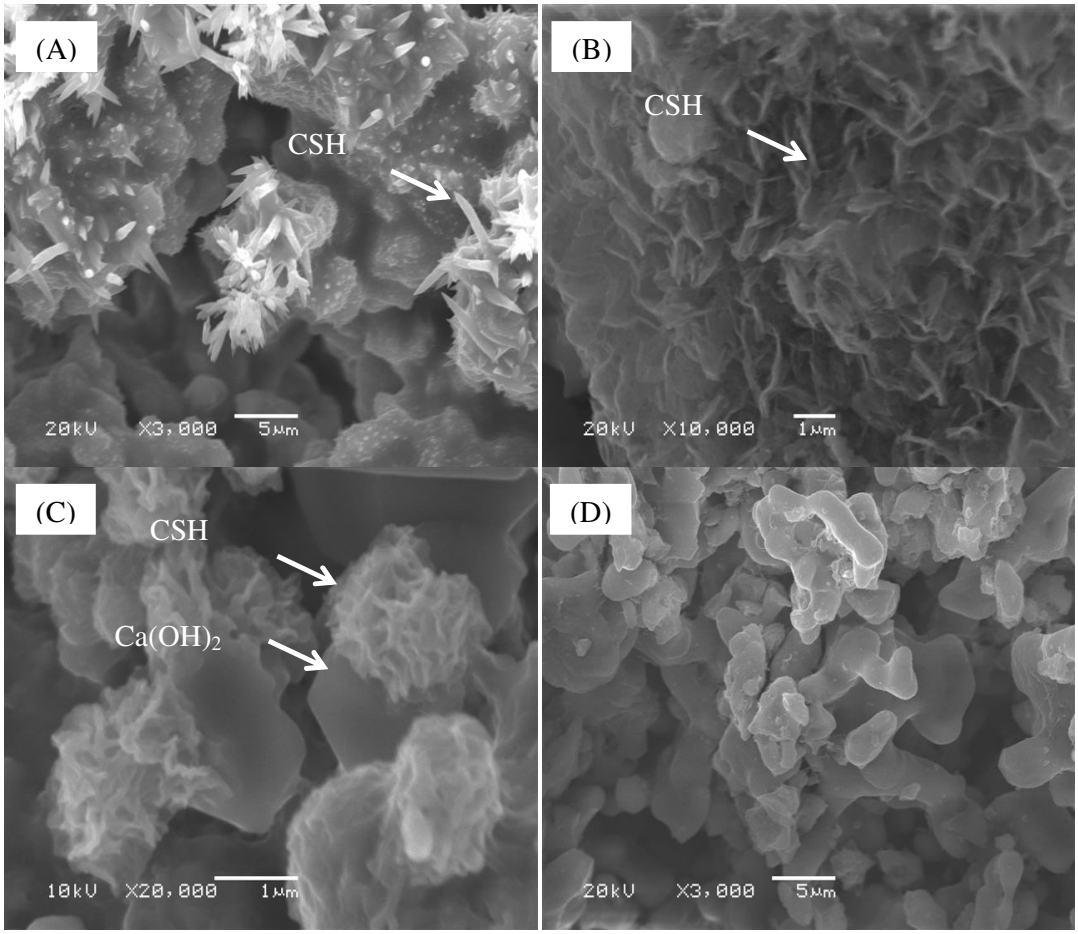

Figure 2. SEM micrographs of the surface and fracture surface. (A), (B) and (C) surface; (D) cross section.

Fig. 3 shows the SEM micrographs of cement after soaking in SBF at different times. Before soaking, the paste showed compact structure with some micropores. After soaking for 1h, tiny ball-like particles were observed on the surface of the samples (Fig. 3A and B). After soaking for 1day, the layer of HA became denser (Fig. 3C) and higher magnification SEM micrograph showed that the particles of HA were worm-like and many of these particles formed agglomerates (Fig. 4D and F). Seven days after, micropores disappeared, and a compact HA layer of just about 250μm is formed on the surface (Fig. 3E).

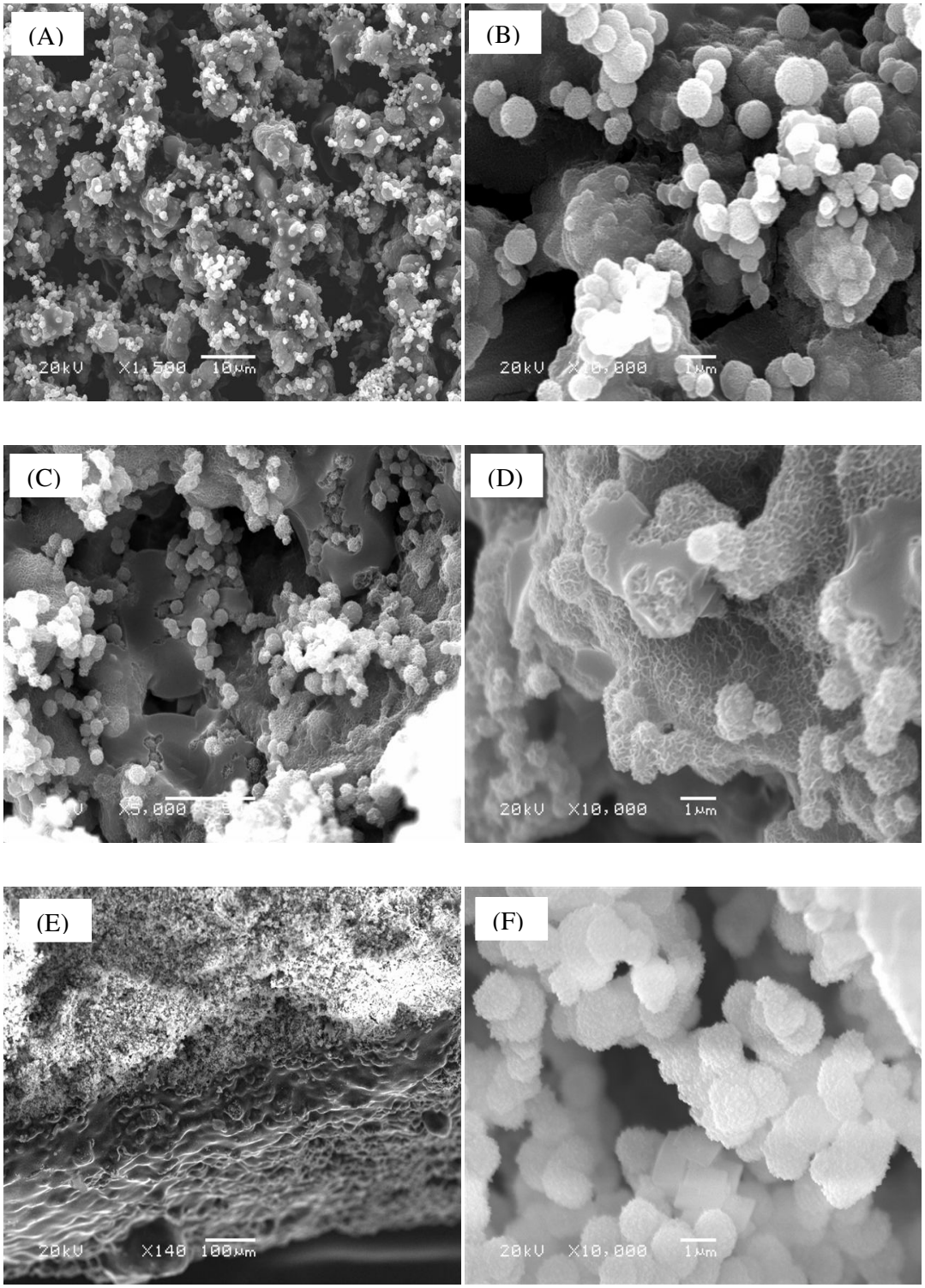

Figure 3. SEM micrographs of the surfaces of Ca_3SiO_5 paste after soaking in SBF solution for 1h (A, B), 1 day (C, D) and 7 days (E, F).

CONCLUSIONS

C_3S can be syntethized by sol-gel method, although considerable free lime is present in final product, which can causes an increase in local pH. The formulation Ca_3SiO_5/ Na_2HPO_4 could induce the formation of HA after 1h soaking in SBF and the layer after one week has 250µm of thickness. For that reason C_3S would be an effective additive to improve the bioactivity and long term strength of conventional CPC.

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