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Surface dissolution of calcium phosphate glass ceramics in dilute acid conditions

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Abstract

Calcium phosphate glass–ceramic materials in the P_2O_5–CaO–SiO_2–K_2O system were prepared from mineral and industrial waste raw materials. They were characterized by chemical analysis, scanning electron microscopy (SEM) and X-ray diffraction (XRD). Tricalcium phosphate (α and β-$Ca_3(PO_4)_2$), tetracalcium phosphate ($Ca_4P_2O_9$) and glassy phases were identified in various proportions. The materials were treated in water, ammonium citrate, ammonium acetate and citric acid solutions. The mechanism of attack of the different phosphate phases in dilute acid conditions was established mainly following the P, Si, Ca, K concentrations versus time by inductively coupled plasma optical emission spectroscopy (ICP–OES). The results show that these glass–ceramic materials can be used as controlled released fertilisers.

Keywords: Acid attack; Calcium phosphate; Glass ceramic

1. Introduction

Ceramic or glass materials in the P_2O_5–CaO–SiO_2–K_2O system are expected to be useful in many applications as biomaterials,[1,2] controlled released fertilisers[3,4] and filters for waste water.[5] It may also be possible to incorporate Ag, Cu, Au or Mn elements, with demonstrated bactericide power,[6] into these glass or ceramic materials so that they can be used in refrigeration towers or in air-conditioned systems. A material's application is directly related to its limitable property. Therefore, it is essential to know the nature of the constitutional phases (glassy or crystalline), and their dissolution capacity, as well as their chemical composition, in order to evaluate the "attackability" of these materials in different media.

In this work, several different compositions of glass–ceramic fertilizers within the system described above have been prepared from waste raw materials. Three different glass–ceramics were produced with the same phases but in different proportions. We have also determined the attack mechanism operating in these materials

2. Experimental

2.1. Initial materials and processing

Starting materials were (1) bone (ICN Biomedicals, USA) and phosphorite (Logrosán, Cáceres, Spain), to introduce calcium phosphate; and (2) glass cullet (CAM), feldspar (Segovia, Spain) and potassium carbonate (Panreac RA) to provide silicon and alkaline oxides (Table 1). They were milled and sieved to under 63 μm. Three different compositions were prepared from the initial raw materials: A (40% calcined bone + 35% glass cullet + 25% K_2CO_3), B (25% calcined bone + 25% phosphorite + 50% feldspar), and C (80% calcined bone + 10% phosphorite + 10% feldspar). These mixtures were heated in an aluminium silicate crucible at 10 °C/min to 1400 °C for 30 min and afterwards quenched in water. The resulting glass–ceramic frits (Table 1) were grounded in an agate mortar and subsequently sieved to obtain a powder with a particle size ranging $0.3 < d < 0.5$ mm.

2.2. Instrumentation and methods

The phases present in the glass–ceramic materials were identified by XRD using a diffractometer D5000 Kristalloflex 710 Siemens (Karlsrube, Germany) with graphite monocromator and CuK_α radiation.

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Table 1
Chemical analysis (wt.%) of the initial raw materials and prepared glass ceramic materials

Oxide	Raw materials				Materials		
	Bone (calcined)	Feldspar	Glass cullet	Phosphorite	A	B	C
P_2O_5	39.5	–	–	23.1	15.8	13.5	30.9
CaO	37.4	0.43	11.8	45.0	38.8	18.0	41.4
SiO_2	4.39	67.5	72.5	27.2	29.3	49.8	18.4
K_2O	1.62	10.5	0.81	0.07	7.28	5.76	2.09
Na_2O	0.58	2.28	12.8	0.33	4.85	1.28	0.80
Al_2O_3	0.53	17.3	1.30	1.15	1.57	10.6	3.89
MgO	0.89	0.04	0.42	0.19	0.22	0.38	0.61

The morphology of the materials and qualitative chemical compositions of phases was studied by SEM using a C. Zeiss DSM-950 fitted with an energy-dispersive spectrometer (EDS, Tracor Northem).

Chemical analysis and the elements released (P, Ca, Mg, Si, Al, K, Na) were determined by ICP–OES, in a Thermo Jarrell Ash model Iris Advantage spectrometer. This equipment uses an echelle optic and a unique charge injection device (CID) solid-state detector to provide complete and continuous wavelength coverage over the typical analytical wavelength range. The elements can be continuously analyzed and simultaneously and rapidly. The detection limits (DLs) range from 0.0001 $\mu g\ ml^{-1}$ for Ca and 0.05 $\mu g\ ml^{-1}$ for P, therefore, it is possible to analyze concentration ranges to the ppb level.

Dissolution was accomplished in different media following procedures appropriate for testing fertilisers according to the different types of soils.[3,7–10] They are described below

2.2.1. *Water solubility (pH = 6.8)*

Place 1.0000 g of sample ($0.3 < d < 0.5$ mm) in a filter of 9 cm diameter. Add distilled water at small quantities to obtain 250 ml of solution. If the solution is turbid, add 1 or 2 ml of nitric acid. P, K, and Ca extracted from the solution, were analyzed.

2.2.2. *Ammonium citrate solubility (pH = 3)*

Place 1.0000 g of sample ($0.3 < d < 0.5$ mm) in a flask with 100 ml of ammonium citrate solution at 65 °C. Seal the flask with a stopper and shack constantly at 65 °C for 1 h. Filter through a buchner and wash with water at 65 °C until the filtrate reaches 250 ml. P, K and Ca were analyzed from this solution.

2.2.3. *Ammonium acetate lixiviation (pH = 7)*

Place 2.0000 g of sample ($0.3 < d < 0.5$ mm) in six plastic vessels (500 ml) with stoppers and 250 ml of ammonium acetate buffered solution at pH 7. Stir moderately for 7 days. Filter. P, Si, Ca, K, Na and Al were determined from this solution.

2.2.4. *Citric acid lixiviation (pH = 5.2)*

Two-hundred and fifty millilitres of 2% citric acid were kept in a 400 ml vessel and P, Si, Ca, Mg, Na, K, Al and Fe are measured by ICP–OES (Blank). The solution was shaken continuously and analyzed by ICP–OES while 0.5000 g of sample ($0.3 < d < 0.5$ mm) were added.

P, Si, Ca, Mg, Na, K, Al, and Fe were determined from this solution.

3. Results and discussion

Chemical analysis and X-ray diffraction patterns of the three materials produced are shown in Table 1 and Fig. 1.

Neither the B nor the C glass–ceramic materials reached a total fusion point at 1400 °C. Material C is richer in glassy phase than material B, although less than material A, which was the only one that fused at 1400 °C. Consequently the sparse crystalline phases present in material A were formed by devitrification on cooling. Microanalysis by EDS was performed previously[3] and showed the presence of Si, K and Al as macroconstituents of glassy phase, while the crystalline phase was made up mainly of P and Ca.

Table 2 shows the solubility results for the glass–ceramic materials in water and ammonium citrate, listed as extraction percentages based on the initial chemical composition.

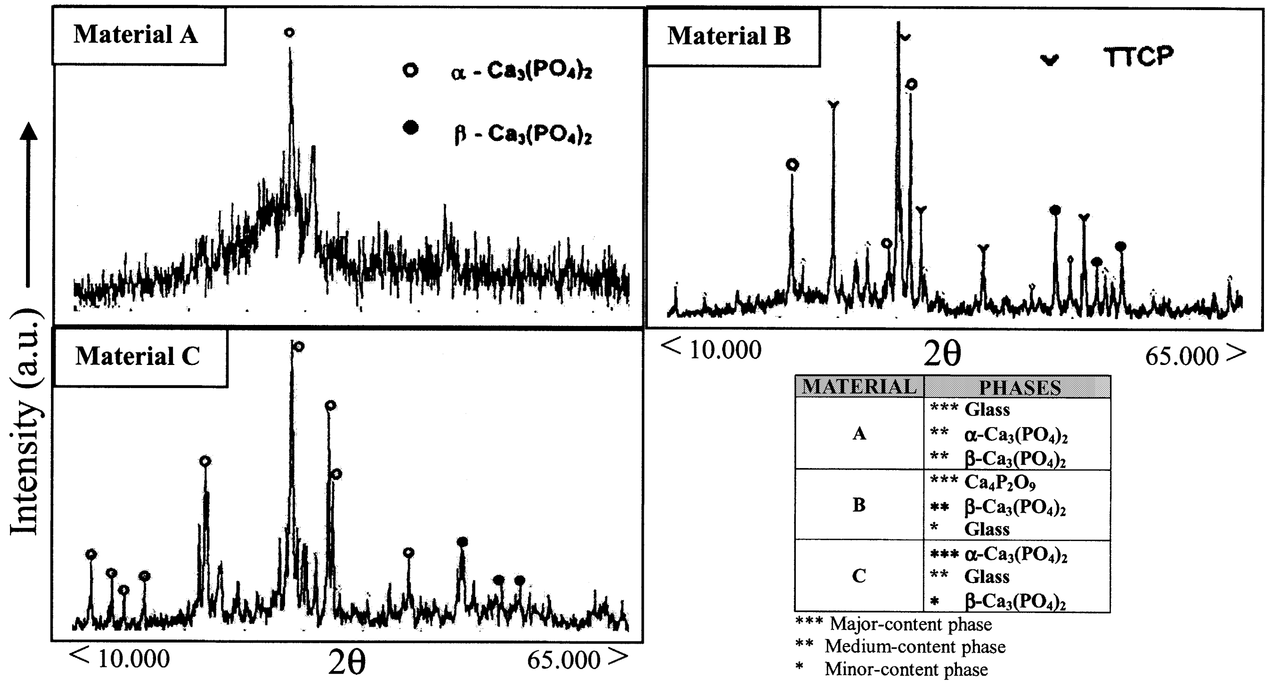
Fig. 2 shows the microstructure of these materials after water and ammonium acetate attacks, as observed by SEM. In these micrographs, the phases separation in material A and a dissolved hexagonal crystal in material B can be clearly seen.

As can be deduced from Table 2, material B is less soluble than A and C in both media.

As shown in Table 3, more elements were analyzed in the ammonium acetate lixiviation solution than in the other solutions. The results also show that material B is the least soluble in this medium.

In all cases, calcium and phosphorous are the elements liberated in the greatest quantity. Taking into account lixiviation percentage with respect to original composition, materials C and A release alkaline elements in a higher level than B. Considering these statements and the phases assigned to each material (Fig. 1), the following interpretation can be suggested:

Material B had two calcium phosphate phases [$Ca_4P_2O_9$ and β-$Ca_3(PO_4)_2$], with an extraction percentage at 7 days close to 47% P_2O_5 and 20% CaO. Conversely its glassy phase is significantly less soluble than the crystalline phases (≈8.5% alkaline oxides and



MATERIAL	PHASES
A	*** Glass ** α-$Ca_3(PO_4)_2$ ** β-$Ca_3(PO_4)_2$
B	*** $Ca_4P_2O_9$ ** β-$Ca_3(PO_4)_2$ * Glass
C	*** α-$Ca_3(PO_4)_2$ ** Glass * β-$Ca_3(PO_4)_2$

*** Major-content phase
** Medium-content phase
* Minor-content phase

Fig. 1. XRD analysis of the obtained glass ceramics.

Table 2
Elements released in each of the three prepared materials (% extraction based on starting oxide content) after attack with water and ammonium citrate

Material	Oxides (elements released)	% Extraction	
		Water[a] (pH ~ 7)	Ammonium citrate[b] (pH ~ 3)
A	P_2O_5	1.04	80.7
	CaO	0.43	63.7
	K_2O	3.00	87.5
B	P_2O_5	0.51	42.2
	CaO	0.30	40.3
	K_2O	0.00	0.42
C	P_2O_5	0.52	70.1
	CaO	0.41	56.1
	K_2O	0.42	16.2

[a] After the powder sample passed through 250 ml of distilled water.
[b] After 1 h shaking with ammonium citrate.

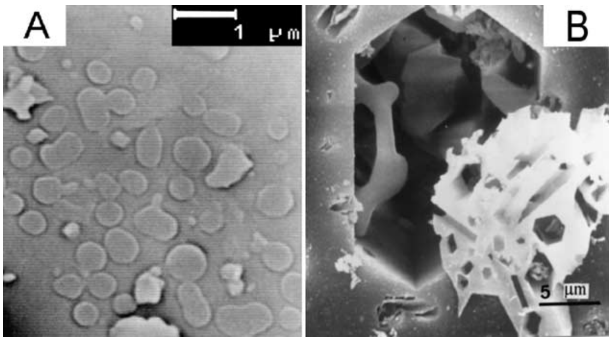


Fig. 2. Micrographs of material A after water attack and material B after 7 days ammonium acetate attack.

Table 3
Chemical analysis of elements extracted from the three prepared materials (A, B, and C) by ammonium acetate (pH ~ 7) used to attack the materials for 7 days

Oxides (elements released)	% Extraction		
	A	B	C
P_2O_5	53.8	47.0	64.5
CaO	30.9	20.2	51.6
SiO_2	10.1	0.39	3.44
Al_2O_3	0.95	0.06	0.69
Na_2O	83.5	3.15	73.3
K_2O	62.3	5.41	15.8

0.39% SiO_2). Materials C [α-$Ca_3(PO_4)_2$] and A [α- and β-$Ca_3(PO_4)_2$] have crystalline and glassy phases that are more soluble crystalline and glassy phases than does material B. Additionally, the low ratio of CaO/P_2O_5 extracted in material B (Table 3) can explain why the β-$Ca_3(PO_4)_2$ phase is more soluble than $Ca_4P_2O_9$, that is, because this composition has a higher CaO/P_2O_5 ratio.

Several publications dealing with hydroxyapatite,,[11] glasses,[12] and ceramic materials[13] have tried to explain the solubility of calcium phosphate phases in various media. The authors have not reached a consensus on the possible dissolution mechanism of these series of calcium phosphates. Considering the results obtained in the present investigation, the following solubility order is purposed for the different calcium phosphate phases:

$$Ca_4P_2O_9 < \beta\text{-}Ca_3(PO_4)_2 < \alpha\text{-}Ca_3(PO_4)_2 \qquad (1)$$

Table 4
Liberation sequence of elements in citric acid solution

Material	Liberated elements
A	First seconds: All of them > 3 s: All of them
B	First seconds: Ca, Mg > 3 s: All of them
C	First seconds: K, Na, Si, Al > 3 s: All of them

This assessment is in concordance with some authors.[14,15]

The glassy phases of the glass ceramics were not equally soluble: the high proportions of SiO_2 (49,8%, network former) and Al_2O_3 (10,6%, network stabiliser) in material B formed a more stable glassy network than the ones in A and C. This fact explains the lower concentrations of Si and Al lixiviated in material B, in spite of ts starting composition being higher in both elements than in the other materials, as well as the clear print edge observed in the glassy matrix (Fig. 2B) when the phosphate crystal was dissolved.

During the citric acid attack, we followed the elements lixiviated for the first three seconds. This led us to attempt to describe the initial attack mechanism. Table 4 shows the proposed element liberation sequence. Material B is attacked first on its crystalline phase, which is more soluble than its glassy phase. By contrast, in material C the glassy phase (Si, Al, K, Na liberated) is attacked first. In material A, neither phase seems to be attacked first. All elements were present after the first 3 s of attack.

Thus, the attack mechanism at acid pH could be described by the following equation:

$$Ca_3(PO_4)_2 + 2H^+ \rightarrow Ca^{2+} + 2CaHPO_4 \qquad (2)$$

This mechanism has been also suggested by other authors.[16]

Dissolution of crystalline phases in citric acid starts with Ca^{2+} extraction, due to the propensity of this acid to form complexes with divalent metals.[17] For this reason, material B has an initial Ca extraction rate higher than that of material C, because material C's glassy phase requires an initial proton dissolution and diffusion.

4. Conclusions

- Three glass–ceramic fertilisers with different phases contents produced from waste raw materials were obtained and characterized by XRD and chemical analysis.
- Dissolution kinetics in different media were studied by chemical analysis (ICP–OES) of the filtrates, and it was possible to determine the dissolution sequence for the three calcium phosphates as follows: $\alpha\text{-}Ca_3(PO_4)_2 > \beta\text{-}Ca_3(PO_4)_2 > Ca_4P_2O_9$.
- It was possible to determine the initial attack mechanism on the materials by using an original procedure and the ICP–OES technique.
- The results obtained in the present work open a route for designing new controlled-released glass–ceramic fertilisers (P, Ca, K) starting from waste raw materials such as bones. Use of these waste products may have a positive effect on the environment.

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