J Mater Sci (2006) 41:5227–5230
DOI 10.1007/s10853-006-0440-x

Calcium phosphate silicate ceramics for heavy metal immobilization and antibacterial activity in waste water

Flora Barba · Pío Callejas

Received: 30 September 2005 / Accepted: 27 February 2006 / Published online: 3 August 2006

Abstract In the present work we have prepared a hydroxyapatite (HA)–silica porous ceramic material for the immobilization of heavy metals (Pb, Cd, Zn). This material, shaped as Raschig rings, is obtained by extrusion starting from urban and industrial wastes. Additionally, it has been proved that when Ag or Cu is added over the rings surfaces, these ceramics also have a bactericidal activity.

Introduction

Certain waters from mines or industrial plants are contaminated by heavy metals. The threat of this metal pollution to public health and wildlife has led to an increased interest in developing systems that can neutralize its toxic effects.

Likewise recycling has become a world wide primary necessity due to the increasing production of solid waste. The use of ceramic, glass and glass–ceramic waste forms is a standard mean for treating hazardous radioactive and mixed residues for environmental conscious disposal [1, 2].

On the other hand, the atypical crystalloid-chemical features of apatites produce a structure very tolerant to ionic substitutions of divalent or trivalent cations (heavy metals and others) or metalloids (anions like F^-, CrO_4^{2+}, AsO_4^{3-} , etc.) [3, 4].

In the present work we have prepared a hydroxyapatite (HA)–silica porous ceramic material for the immobilization of heavy metals (Pb, Cd, Zn). This material, shaped as Raschig rings, was obtained by extrusion starting from urban and industrial wastes. Additionally, it has been proved that when Ag or Cu is added over the rings surfaces, these ceramics have also a bactericidal activity.

Experimental procedures

Synthesis

Calcined (800 °C–12 h) animal bones, ICN Biomedicals, USA, (43.4 wt%), diatoms filters refused in beer companies (26.3 wt%) and paper industry sludge (30.1 wt%) were used as raw materials. They provided HA, silica and calcium carbonate, respectively (Fig. 1), to the mixture.

Homogeneous mixture of the raw materials with appropriate granulometry was obtained by sieving (< 0.5 mm) and attrition milling with alumina balls (30 min). Medium particle size after milling was about 6 μm. From this powder, the paste for extrusion was prepared using 2.5 wt% of a plasticizer (carboxymethylcellulose: Optapix C 1000 G, Zschimmer & Schwarz, Germany) with binding properties and 30% humidity. A laboratory manual vertical extrusion machine with a die of 5 mm internal diameter and 9.5 mm external diameter was used to form tubes of 200 mm length.

The green bodies were dried and sintered (heating and cooling rate: 6 °C/min, 1150 °C–1 h and 1100 °C) in an electric furnace (SATER, Spain) in air.

F. Barba (✉) · P. Callejas
Instituto de Cerámica y Vidrio, CSIC, Campus de Cantoblanco, c/Kelsen no 5, 28049 Madrid, Spain
e-mail: flora@icv.csic.es

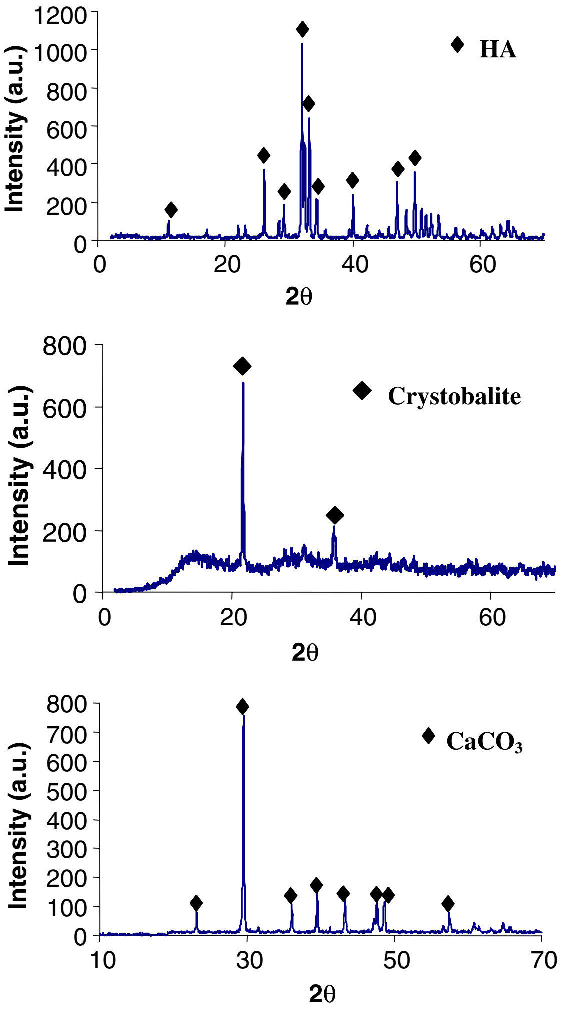


Fig. 1 XRD patterns corresponding to raw materials

Characterization

The chemical composition of the mixture was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), using a Thermo Jarrell Ash Model Iris Advantage spectrometer.

The microstructure of the sintered rings was observed by field-emission SEM (FE-SEM; Model S-4700, Hitachi Company, Ltd., Tokyo, Japan).

The powder XRD patterns of the rings were colleted using a Siemens D5000 X-ray diffractometer, Kristalloflex 710 (Germany).

Bulk density of the green and sintered bodies was determined by the Archimedes method using Hg. True densities of the sintered rings were determined in an He pycnometer (Multipycnometer, QuantaChrome, USA). Total porosity in the sintered materials was calculated from bulk and true density values.

Specific surface areas were determined by the BET method (Monosorb Analyzer MS-13, QuantaChrome, USA), using liquid N_2 as adsorbate.

Test of heavy metals immobilization

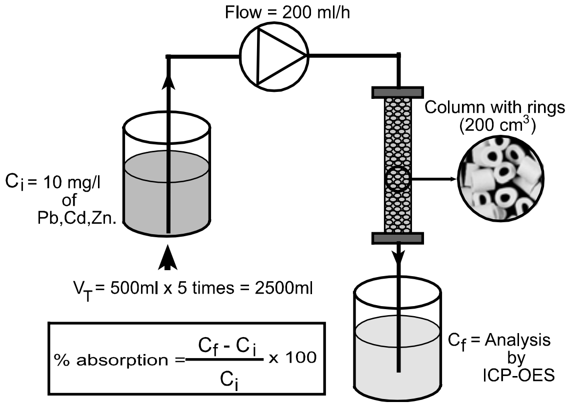
An experimental device was designed to evaluate the ability of the obtained ceramic materials to retain heavy metals in dynamic conditions as detailed in Fig. 2. A 200-ml column-reactor was used. It was completely filled with the Raschig rings so that the water could circulate easily and preferential flows could be avoided. The reactor was placed in a standing position and was connected to a vessel with 500 ml of the heavy metals solution (10 mg/l of Pb, Cd, Zn) and to a disposal-waste vessel to collect the solution once it had passed through the column. A pump was installed so that a constant flow of 200 ml/h of the heavy metals solution was maintained. The tests were conducted to introduce the 500 ml solution for five times successively in the column. Finally the aqueous samples were taken to measure the concentration of heavy metals by ICP-OES and to determine the amount of heavy metals retained by the ring ceramic materials ($\sigma < 0.4$).

Lead, cadmium and zinc were supplied in the form of nitrates. In all cases a 1000 mg/l stock solution was prepared from which the desired heavy metal concentrations were obtained.

Tests with microorganisms

The rings were coated by a monolayer of Ag or Cu using a EMS 550 sputter coater.

The culture medium was made with three types of bacteria: *Bacillus* sp. 19500, *Chromobacterium violaceum* CECT 494T and *Escherichia coli* K12 CECT 433. The total population was found to be 66×108 UCF/ml in the 15:61:24 ratio, respectively.



$$\% \text{ absorption} = \frac{C_f - C_i}{C_i} \times 100$$

Fig. 2 Test of heavy metal immobilization

The tests were conducted both in the absence and in the presence of the microorganisms.

Results and discussion

Hydroxyapatite has been proposed to be responsible for the ionic exchange that leads to the immobilization of heavy metals from waste-waters [5–8]. However, it is not possible to obtain sintered pieces of this phase alone, due to its decomposition at temperatures higher than 1000 °C, and because the mechanical properties of HA are extremely low. Stability of HA can be increased by adding an excess of CaO to the material [9, 10] and the mechanical properties can be improved by the presence of SiO_2 by at least a factor of four [11]. Using as raw materials, urban and industrial wastes such as animal bones, diatom filters refused in beer companies and paper industry sludge, the final material was formulated in the system P_2O_5–CaO–SiO_2–Al_2O_3–$(AlK)_2O$ to obtain HA and silicate phases.

Mechanically stable Raschig rings cylinders of approximately 30 MPa and Weibull modulus $m = 6$ [11], with the chemical analysis reported in Table 1 and with external diameter 7.96 ± 0.08 mm, internal diameter 3.9 ± 0.1 mm and height 7.7 ± 0.2 mm dimensions were obtained. The influence of the firing temperature (1100–1150 °C) on the final dimensions was found to be negligible. The green and bulk densities, the total porosity and the specific surface area (BET) are reported in Table 2.

In Fig. 3 the XRD pattern corresponding to rings obtained at 1150 °C is shown. As observed HA is the main phase present together with calcium silicate and calcium phosphate silicates. A similar XRD pattern was obtained in the case of 1100 °C fired rings. As mentioned before this phase composition is adequate to supply the required ring mechanical stability to support the impacts that take place during the filling as well during the treatment column operation.

Table 1 Chemical analysis of the Raschig ring ceramic materials obtained by extrusion process

Oxide (wt%)	Chemical analysis of the materials
P_2O_5	20.0
CaO	45.0
SiO_2	29.8
Al_2O_3	1.43
MgO	0.70
K_2O	0.88
Na_2O	0.86
Fe_2O_3	0.55

Table 2 Physical properties of the Raschig ring ceramic materials obtained by extrusion process

Physical properties	1100 °C	1150 °C
Green density (g/cm^3)	1.32 ± 0.1	
Bulk density (g/cm^3)	1.41 ± 0.1	1.13 ± 0.1
Porosity (vol%)	54 ± 4	62 ± 4
Specific surface area BET (m^2/g)	0.6 ± 0.1	0.9 ± 0.1

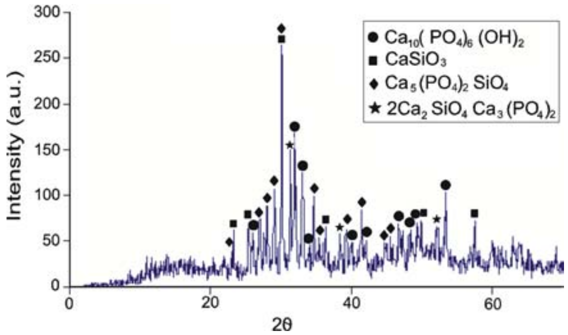


Fig. 3 XRD pattern corresponding to Raschig rings obtained at 1150 °C

In Fig. 4 a SEM micrograph corresponding to Raschig ring −1150 °C is shown. As observed a percolative network of interconnected porous channels with a diameter ranging from 4 to 15 μm were obtained. This percolative open porosity facilitates the immobilization of the heavy metal ions present in the polluted water. In Fig. 5 the Cd, Pb, and Zn absorption fraction for both (1100 °C and 1150 °C) Raschig rings are plotted. As can be seen in both cases a fraction >90% was absorbed. Referring to the operating absorption mechanism, results obtained in our laboratory using sintered pellets with the same ring composition, indicate that the retained heavy metals (Pb, Cd) are not

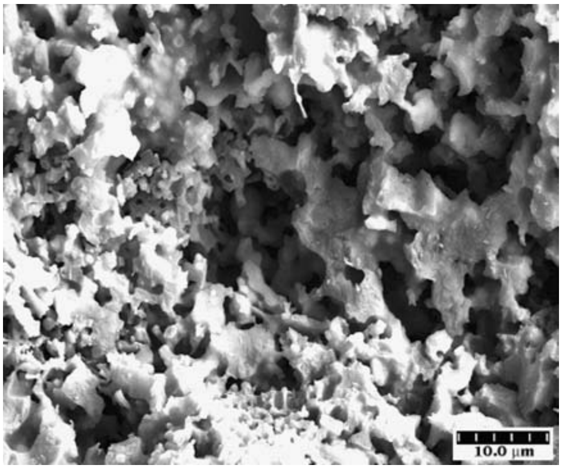


Fig. 4 SEM micrograph corresponding to Raschig ring ceramic material sintered at 1150 °C

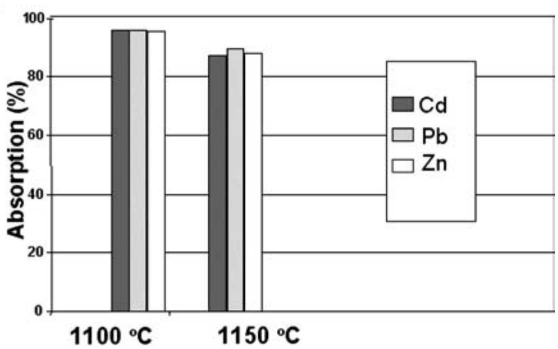


Fig. 5 Cd, Pb, and Zn absorption fraction for both (1100 °C and 1150 °C) Raschig rings

liberated even after a very long water-washing period (24 h) with a continuous stirring of the pellets. By using the LA-ICP-MS (TOF) technique we have observed that the heavy metals are concentrated at the surface with approximately 16 μm depth. After this test, the sample was studied by SEM-EDS. It was clear that the phases richer in P and Ca contained significant amounts of Pb. Those phases with Si and Ca had negligible amounts of Pb. This is an indication for HA immobilization of heavy metals as a part of the HA crystal structure [4, 12].

In a previous work [13] it has been pointed out that HA-ceramics constituted an excellent habitat for microorganisms, e.g., *E. coli*, because of this it has been used as a microbial support in the bioremediation processes. Then in the present investigation one of the objective was to prove that these porous rings with an appropriate bactericide metal [14, 15] coating (Cu, Ag) could also have some bactericidal activity. In Fig. 6 the microbiological normalized population of *Bacillus* sp. 19500 + *C. violaceum* CECT 494T + *E. coli* K12 CECT 433 versus time for Cu and Ag coated Raschig rings is plotted. It can be deduced that in both cases (Cu, Ag) after 72 h the bactericidal effect is almost completed.

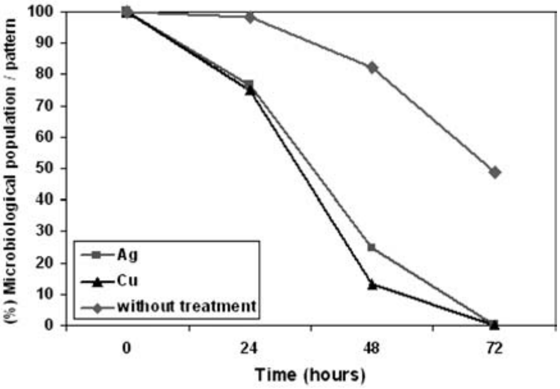


Fig. 6 Microbiological normalized population of *Bacillus* sp. 19500 + *C. violaceum* CECT 494T + *E. coli* K12 CECT 433 versus time for Cu and Ag coated Raschig rings

Conclusions

Ceramic materials (calcium phosphosilicate) Raschig rings shaped from urban and industrial waste by an extrusion method with suitable mechanical and physical properties were obtained. These materials are useful as filters or in separation columns and towers in unitarian operations for water treatments.

These HA containing materials present a percolative porous network (54–62%) which facilitate the high absorption (>90%) of heavy metals as Pb, Cd and Zn.

Additionally the bactericidal effect has been proved (>99% after 72 h treatment) when the rings are coated by Ag or Cu versus Bacillus sp. 19500, *C. violaceum* CECT 494T and *E. coli* K12 CECT 433.

Acknowledgments This work has been supported by the Spanish Ministry of Science and Technology under projects AMB99-1187 and DPI2000-0153-P4-03. We express our gratitude to Prof. Dr. Cesáreo Sainz-Jimenez (Instituto de Recursos naturales, CSIC, Sevilla, Spain) for his assistance in the microbiological tests.

References

1. Rincón JMa, Romero M, Boccaccini AR (1999) J Mater Sci 34:4413
2. Barbieri L, Corradi A, Lancellotti I, Andreola F, Boccaccini AR (2002) Key Eng Mat 206–213:875
3. Nathan Y (1984) The mineralogy and geochemistry of phosphorites. In: Nriagu JO, Moore PB (eds) Phosphate minerals, Springer-Verlag, Berlin, p 275
4. Kim JY, Dong Z, White TJ (2005) J Am Ceram Soc 88(5):1253
5. Ma QY, Logan TJ, Traina SJ (1994) Environ Sci Technol 28(3):408
6. Suzuki S, Itoh K, Ohgaki M, Ohtani M, Ozawa M (1999) Ceram Int 25:287
7. Binner JGP, Reichert J (1996) Br Ceram Proc 55:63
8. Reichert J, Binner JGP (1996) J Mater Sci 31:1231
9. Villora JM, Callejas P, Barba MF (2004) Bol Soc Esp Ceram V 43(1):75
10. Villora JM, Callejas P, Barba MF (2002) Bol Soc Esp Ceram V 41(5):443
11. Villora JM, Baudín C, Callejas P, Barba MF (2004) Key Eng Mat 264–268:2437
12. Reyes J, Castillo M, Martín Rubí JM, Villora JM, Callejas P, Barba MF. Acta XLI Congreso de la Soc. Esp. de Cerámica y Vidrio, Benalmádena, (Málaga), Spain. pg 11, November (2001)
13. García AM, Villora JM, Moreno DA, Ranninger C, Callejas P, Barba MF (2003) J Am Ceram Soc 86(12):2200
14. Nishioka M, Nishimura T, Taya M (2004) Eng J 20:79
15. Machida M, Norimoto K, Kimura T (2005) J Am Ceram Soc 88(1):95