Research paper

Optimisation and analysis of the synthesis of a cellular glass-ceramic produced from water purification sludge and clay

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ABSTRACT

The sludge generated in the treatment of surface water for human consumption represents an environmental hazard which can be mitigated by the valorisation of this solid waste. This paper presents an analysis of the process parameters and physicochemical mechanisms involved in the elaboration of a glass-ceramic foam using clay and the sludge generated in a drinking water plant. Optimisation of the process conditions was performed by a 3^3 experimental design. For structural purposes, compression strength is the optimising parameter; if used as a catalytic support or filtering medium, porosity and permeability have to be maximised. An open cellular structure can be obtained when the materials are fired in a mould which allows the coexistence of solid, liquid and gas phases. The latter are responsible for foaming and were identified as CO_2, SO_2 and H_2O. Thermogravimetric analysis coupled to mass spectrometry and Mössbauer spectroscopy show that CO_2 was generated mainly from pyrolysis, SO_2 was generated from aluminium sulphate used as a coagulant in the drinking water treatment but H_2O resulting from the decomposition of lepidocrocite at high temperature is likely to be the main agent for the foaming effect.

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1. Introduction

Dense ceramic materials are used in traditional and highly advanced applications, from the building industry to high-temperature superconductors. However, the need for materials with high strength and low weight has led to processes for the production porous ceramic and glass-based materials under the common term of cellular ceramics. Ways to classify these materials can be related to the method of elaboration, structural characteristics (open and closed cells), size of the cells and by the relative importance of crystalline and vitreous components. Generally speaking, they belong to the class of macroporous materials with a pore size larger than 50 nm (Gibson and Ashby, 1999). Fabrication methods involve replication (Pancholi et al., 2007; Manocha et al., 2013; Bhattacharya and Heinrich, 2006; Sooksaen and Karawatthanaworrakul, 2015), direct foaming route (DFR) and in situ generation of gases (Studart et al., 2006; Luyten et al., 2009). The latter process, in presence of a viscous phase which entraps the gas phase, requires the

decomposition of compounds in the solid mixture at medium to high temperature and has been applied to produce cellular ceramics from waste materials (Low, 1980; Bernardo, 2007; Méar et al., 2007; Altinkok, 2007). In many published results, a precursor is added to generate gases (Low, 1980; Méar et al., 2007; Altinkok, 2007) but in some occasions, this precursor (SiC) was present in the recycled waste material (Bernardo, 2007). Clay-based cellular ceramics have been produced by incorporating organic waste materials to provide expansion of the pores by combustion (Eliche-Quesada et al., 2011; Kwame Efavi et al., 2012). Teixeira et al. (2011) report the production of ceramic products using sludge and clay but do not report the enhanced porosity which will be main topic in the present paper.

In previous work (Espejel-Ayala et al., 2013; Ramírez-Zamora et al., 2008), ceramic foams were elaborated by recycling water purification sludge and mixing with pottery clay. The sludge was mainly constituted by quartz, clay minerals, feldspars and organic matter. It was found that by varying the processing conditions and characteristics of the clay-sludge mix, porosity and strength could be varied within wide ranges. Products with high effective porosity may be optimised for use in filters or catalytic support. High total porosity is interesting for thermal insulation. High strength, or more specifically high relative strength (strength divided by density) is interesting if the material is used as an aggregate

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for lightweight concrete or other applications in the construction industry. In the previous paper, neither the formation mechanisms nor the optimal process conditions were fully explored. This work analyses optimum processing conditions for porosity, density, and compressive strength, by using a 3^3 experimental design (Montgomery, 1996) with the following factors: composition (in terms of the proportion of sludge to clay), temperature and particle size. To support the results of the experimental optimisation and provide a more detailed background about the thermochemical processes involved, advanced characterisation of the evolution of the product during heating and the mineral contents of the initial and final products was performed.

2. Experimental procedure

Sludge samples were taken from storage tanks in a drinking water facility situated in the state of Mexico. Red pottery clay was obtained from a nearby alluvial deposit. Sludge and clay were separately dried, ground and sieved to the mesh sizes shown in Table 1. Samples were analysed by means of XRD, XRF, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) coupled to mass spectrometry (MS). XRD analysis was performed in a Bruker D8 Advance Diffractometer in Bragg-Brentano geometry, θ–θ configuration, with Cu-Kα radiation in a 10 to 70° interval. XRF analysis was carried out using a Siemens SRS 3000 X-Ray Fluorescence Spectrometer. TGA/DSC-MS were carried out in a Netzsch STA 449 F1 Jupiter simultaneous thermal analyser equipped with a silicon carbide furnace, operating in nitrogen at atmospheric pressure. The thermal analyser was interfaced to a Netzsch mass spectrometer QMS 403 C Aeolos at 150 °C operating in scan mode at 70 eV. SEM observation was performed in a Philips XL20 scanning electron microscope using a solid state backscattering detector and an Oxford energy dispersive X-ray spectrometer (EDX). Polished sections of the samples were prepared by standard techniques and coated with a 15 nm thick layer of carbon to provide conductivity.

Experimental factors were chosen based on a preliminary study (Ramírez-Zamora et al., 2008). Clay-sludge mixtures, as obtained from the sieving process mentioned before, were produced according to the proportions shown in Table 1, using the minimal amount of water required to obtain a mouldable paste. Samples were produced as small cylinders in a steel mould with a diameter of 40 mm and 50 mm height. For each combination of particle size, composition and temperature, two samples were produced. Firing was performed at temperatures of 1150, 1200 and 1250 °C. The samples were placed in the furnace at room temperature without previous drying. The maximum temperature (1250 °C) was reached in six hours and held for four hours, the heating rate was the same for all samples. Cooling was performed by turning of the furnace and letting the system cool down to room temperature. Variations of this firing cycle were not investigated in the present work.

Compression samples were produced by cutting 30 mm long cylinders with a diamond saw to avoid damage and guarantee parallelism of the faces and tested in an Instron Universal testing machine with a load cell of 5kN at 5 mm/min. The apparent porosity, true porosity, apparent density and true density of the samples were determined by the boiling water method as per ASTM C-20-00 (ASTM, 2010) and water pycnometer as per ASTM C135-96 (ASTM, 2015) respectively. The

Table 1
Factors and levels in the 3^3 experimental design.

Factors	Levels		
	−1	0	1
A. Particle size, μm (sieve no.)	500 (35)	410 (40)	355 (50)
B. Sludge composition, wt.% sludge	30	45	60
C. Firing temperature, °C	1150	1200	1250

open and closed porosities were determined from a combination of Archimedes measurements on the compacts and density measurements on the constituent particles using a pycnometer. Calculations were performed as specified by the norm:

$$\text{Volume of open pores} = W - D$$

$$\text{Volume of impervious portion} = D - S$$

where: D is the dry weight, W is the saturated weight and S is the suspended weight.

The apparent porosity P expresses relationship between the volume of the open pores in the specimen to its exterior volume, V:

$$P\% = [(W - D)/V] \times 100$$

$$V = W - S.$$

The water absorption, A, expresses the relationship of the weight of water absorbed to the weight of the dry specimen.

$$A\% = [(W - D)/D] \times 100$$

The apparent specific gravity, T, of the portion of the test specimen which is impervious to boiling water as follows from:

$$T = D/(D - S).$$

Room temperature transmission Mössbauer spectra of selected samples were recorded with a constant acceleration spectrometer in transmission geometry using a ^{57}Co source in rhodium matrix. Thin absorbers were made by grinding a small piece of each sample. A bronze ring 12.0 mm internal diameter and 2 mm height was placed over a strip of masking tape, filled with 20 mg of the powder, compressed and covered with another piece of masking tape. The absorber is placed in a sample holder in front of the source, kept at room temperature. The experimental spectra were fitted using the Recoil 1.05 programme. The algorithm used is described in Lagarec and Rancourt's (1997) work; the isomer shifts are quoted with respect to α-iron.

3. Results and discussion

3.1. Constituents and phases

The composition of the sludge and clay are given in Table 2. The main constituents of the sludge are quartz, kaolinite and albite (Fig. 1). The high content of Al_2O_3 detected by XRF in the sludge can be associated to the addition of aluminium sulphate ($Al_2(SO_4)_3$) as a flocculent during drinking water treatment. The clay equally consists of kaolinite, albite and quartz, but the diffraction peaks are weak, indicating that large portion of the material is of too poor crystallinity to produce coherent diffraction.

If one considers the relative Si to Al content, it is seen that the mixture would favour the formation of mullite, which is supposed to occur through reactions 1–3 (Castelein et al., 2001; Aksay et al., 1991):

$$\underset{\text{kaolinite}}{2Al_2Si_2O_5(OH)_4} \overset{400-600\ °C}{\rightarrow} \underset{\text{metakaolinite}}{2Al_2Si_2O_7} + H_2O \qquad (1)$$

$$2Al_2Si_2O_7 \overset{600\ °C}{\rightarrow} \underset{\text{spinel}}{Si_3Al_4O_{12}} + SiO_2 \qquad (2)$$

$$3Si_3Al_4O_{12} \overset{1000-1100\ °C}{\rightarrow} \underset{\text{mullite}}{2Si_2Al_6O_{13}} + \underset{\text{cristobalite}}{5SiO_2}. \qquad (3)$$

Some authors report formation of mullite starting at 1100 °C; this compound is considered to be stable up to 1500 °C (Castelein et al., 2001; Aksay et al., 1991). Metal oxides may considerably lower the