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Research article

Phosphorus solubility in basaltic glass: Limitations for phosphorus immobilization in glass and glass-ceramics

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ABSTRACT

The composition of sewage sludge from urban wastewater treatment plants is simulated using P-doped basalts. Electron microscopy analyses show that the solubility of P in the basaltic melt is limited by the formation of a liquid-liquid immiscibility in the form of an aluminosilicate phase and a Ca-Mg-Fe-rich phosphate phase. The rheological behavior of these compositions is influenced by both phase separation and nanocrystallization. Upon a thermal treatment, the glasses will crystallize into a mixture of inosilicates and spinel-like phases at low P contents and into Ca-Mg-Fe phosphate at high P contents. Hardness measurements yield values between 5.41 and 7.66 GPa, inside the range of commercial glasses and glass-ceramics. Leaching affects mainly unstable Mg^{2+}-PO_4^{3-} complexes.

1. Introduction

Vitrification is a widespread inertization technique that can be applied to the remediation of both hazardous and non-hazardous wastes to reduce the volume of the disposal material (and thus the necessity of landfills) and to immobilize the toxic elements of the raw waste in the glass structure. Several examples of inertization by this approach can be found in the literature: polluted soils (Careghini et al., 2010; Navarro et al., 2013), radioactive wastes (Ciecińska et al., 2015; Davydov et al., 1996; Hrma et al., 2014; Pioro et al., 2001), incineration ashes (Cheng, 2004; Cheng et al., 2002; Haugsten and Gustavson, 2000; Jung et al., 2005; Kavouras et al., 2003; Romero et al., 2001). The production of glass-ceramics from these glasses enables further inertization due to the emplacement of toxic elements in the structure of minerals (Binhussain et al., 2014; Garcia-Valles et al., 2007; Mymrin et al., 2014; Varitis et al., 2015). The glass-ceramic process also provides recycled materials with superior mechanical properties (Marinoni et al., 2013; Teixeira et al., 2014). These glasses and glass-ceramics – apart from those made using radioactive wastes – may have applications in the building industry such as pavements or wall covers (Romero and Rincón, 1997).

Sewage sludges (SS) from urban wastewater treatment plants (UWWTP) have a good potential as one of the raw materials for an inertization matrix because their compositions are roughly similar to that of basalt (Rincon, 2016) (Table 1). This matrix could be tested to host contaminant and hazardous wastes like galvanic sludge (Garcia-Valles et al., 2007). However, the higher abundance of some elements, such as phosphorus and calcium, in the sludge compared to basalts or any natural igneous system requires experimental studies to understand how the compositional variation affects their properties and their long-term stability.

Phosphorus is an essential nutrient, as it is present in the structure of several biomolecules such as DNA or RNA, in cell membranes, and in the inorganic fraction of bone. Low phosphate levels limit the growth in both terrestrial and aquatic systems, hence the amount of soil phosphate has long been complemented using fertilizers. Sewage sludge may be a substitute for these (European Council, 1986). However, an exceeding amount of phosphorus may cause two environmental issues:

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Table 1
Chemical composition (wt%) of sewage sludge from wastewater treatment plants in Catalonia and the basalt used as a raw material for the production of glass. The WWTPs are identified by the name of the town they serve.

	Centelles	Vic	Taradell	Torelló	Manlleu	Tona	Prats	Roda	St. P. Ribes	Basalt
Al_2O_3	10.40	10.55	11.29	5.35	9.92	11.20	11.35	9.86	13.71	14.37
SiO_2	16.60	17.45	24.19	10.54	19.49	23.59	20.69	18.33	31.6	44.63
CaO	21.25	19.64	14.92	14.34	21.46	22.4	18.85	18.61	30.27	10.26
TiO_2	0.80	0.59	0.75	0.41	0.61	0.96	0.57	0.59	2.00	2.55
Na_2O	1.94	2.19	2.97	1.09	1.27	1.64	1.53	1.85	1.53	3.36
MgO	3.94	3.04	2.35	2.15	2.91	4.85	3.00	3.23	3.36	10.20
MnO	–	0.25	–	–	–	–	–	0.16	0.00	0.17
Fe_2O_3	16.96	21.17	19.97	37.16	18.37	3.03	17.01	20.73	4.32	12.86
K_2O	4.00	1.26	3.00	1.63	2.39	7.22	4.04	2.36	1.80	2.01
P_2O_5	22.29	17.52	19.56	25.64	22.57	23.78	21.15	20.29	7.74	0.56
SO_3	0.92	1.61	0.16	0.37	–	0.38	0.18	0.46	2.86	–
Cr_2O_3	–	3.93	–	0.13	–	–	0.86	2.22	0.00	0.04
NiO	–	–	–	0.13	–	–	0.14	–	0.82	0.02
CuO	0.32	0.28	0.33	0.2	0.15	–	0.27	0.42	0.10	0.01
ZnO	0.18	0.31	0.16	0.63	0.21	0.23	–	0.65	–	0.01
SrO	0.24	0.23	0.16	0.23	0.36	0.58	0.23	0.23	0.12	0.10
BaO	0.17	–	0.18	–	0.29	0.14	0.12	–	0.12	0.07

1. Eutrophication: excessive growth of algae and aquatic plants due to a great supply of nutrients resulting in oxygen overconsumption and depletion. Hypoxic conditions cause animal death and stop biological purification of water (Correll, 1998; Werner, 2012). It is considered the greatest threat for surface waters worldwide.
2. Heavy metal input in the soil due to high Cd contents in fertilizers (Werner, 2012).

The application of sewage sludge in agriculture is then limited and requires additional recycling methods (Mininni et al., 2015).

In rock-forming silicate melts, the effect of phosphorus on both melt structure and properties is considered of great importance despite its scarcity (natural igneous melts usually have less than 1 wt% P_2O_5) because it has a strong influence on phase relationships, physical and chemical properties (Dupree et al., 1989; Gan and Hess, 1992; Mysen et al., 1981; Ryerson and Hess, 1980; Toplis et al., 1994; Wyllie and Tuttle, 1964). Even small amounts of P_2O_5 may cause structural variations in the liquid that alter the values of the trace-element partition coefficient by tenths percent (Ryerson and Hess, 1978). The addition of phosphorus to silicate melts is known to influence a number of properties and processes, including the redox state of iron, viscosity and density (Toplis et al., 1994), the formation of an immiscibility gap (Wyllie and Tuttle, 1964), the shift of the liquidus boundary of the silicate minerals, an increase in the silica activity coefficient and the expansion of the liquid immiscibility volume (Ryerson and Hess, 1980).

This paper focuses on the addition of phosphorus to basalt to simulate the inertization of sewage sludge, an appropriate glass-making composition due to its low viscosity at high temperature (<1300 °C). The amount of P that may be bound in basalt is established by determining its solubility in the melt together with an analysis of the structure, thermal evolution, rheological behavior, and macroscopic properties in order to constrain the production process. The obtained materials underwent hardness and chemical resistance tests to establish potential uses.

2. Experimental methods

2.1. Choice of compositional range

The chemical compositions of a series of sewage sludge (SS) from wastewater treatment plants (WWTP) and a basalt from Sant Joan les Fonts (Girona, Catalonia) (Table 1) have been analyzed by X-ray fluorescence (XRF), using a sequential X-ray spectrophotometer Phillips PW2400. The range of phosphorus concentration in sewage sludge has been complemented with data from the literature (Borowski et al., 2014; Folgueras et al., 2003; Forsberg and Ledin, 2006; Hossain et al., 2009; Kikuchi, 1998; Montero et al., 2009; Roig et al., 2012; Wang et al., 2008). Its maximum is 32.98 wt% P_2O_5 (Wang et al., 2008).

2.2. Glass production

A basaltic rock of La Garrotxa (Girona, Catalonia) is doped with $NH_4H_2PO_4$ (ADHP, Reag-Ph.Eur, PA-ACS 131126.1211) to simulate a SS-like matrix. The mixtures are homogenized in a ball mill for 30 min and melted in a Pt-Rh crucible placed inside a globular alumina furnace equipped with SuperKanthal™ heating elements and a Eurotherm® 902 programmer. Each sample is heated at 200 °C for 2 h to decompose the ADHP and then above the melting point at 1450 °C, for 4 h. Part of the quenched glass has been annealed for 12 h at 500 °C.

Some mg of each glass have been remelted at 1450 °C and 1600 °C using a Pt-Rh alloy wire heating system originally designed to obtain spectroscopic data of silicate melts at high temperatures (Mysen and Frantz, 1992; Neuville and Mysen, 1996; Neuville et al., 2014b). The wires have previously been calibrated using salts with known melting points in order to achieve reliable determination of temperature.

2.3. Electron microscopy

Textural information and qualitative punctual chemical analysis of the glasses and the crystalline phases formed during production have been obtained using a JEOL J-7100 field emission scanning electron microscope with EDS detector and backscattered electron detector (FE-SEM-EDS). A thin section of the sample most enriched in P (labeled B32P) has been analyzed using a Hitachi H-800-MT transmission electron microscope (TEM) with energy dispersed analysis of X-rays (EDX), operating at 200 kV in STEM mode using the dark field detector. The beam size used in this mode is around 15 nm. The spectrometer is an Oxford Instruments INCA x-sight, with Si (Li) detector. The map acquisition is accomplished using the INCA Microanalysis Suite, software version 4.09. X-ray maps are obtained selecting the characteristic X-ray peaks for Si, Al, Ca, Fe, Mg and P.