Proceedings of the
Fourth International

Slag Valorisation Symposium

Zero Waste

15-17 April 2015
Leuven, Belgium

Editors Annelies Malfliet and Yiannis Pontikes

KU LEUVEN

SYNTHESIS AND CHARACTERISATION OF POROUS INORGANIC POLYMERS FROM FAYALITE SLAG

Lubica KRISKOVA, Peter Tom JONES, Hans JANSSEN[2], Bart BLANPAIN, Yiannis PONTIKES

[1] KU Leuven, Department of Materials Engineering, 3001 Heverlee, Belgium
[2] KU Leuven, Building Physics Section, 3001 Heverlee, Belgium

Lubica.Kriskova@mtm.kuleuven.be, Peter.Jones@mtm.kuleuven.be, Hans.Janssen@bwk.kuleuven.be, Bart.Blanpain@mtm.kuleuven.be, Yiannis.Pontikes @mtm.kuleuven.be

Introduction

Inorganic polymers (IP) possess excellent mechanical properties as well as superior fire and chemical resistance.[1] They are typically formed at room or slightly elevated temperatures by reaction of silica- and alumina-rich precursors with an alkali solution (usually based on K or Na).[2] However, some recent studies have shown that IP may also be formed from an iron-aluminosilicate precursor. In such a case, the iron becomes a part of the amorphous IP binder.[3, 4] Regarding porous IP, Bell and Kriven[5] used H_2O_2 and Al powder as foaming agents. Al as a foaming agent has also been used in the work of Vaou and Panias[6], where foamed IP from perlite were synthesised.

In this paper, porous IP from FeO-SiO_2 rich slag were synthesised and the effect of various amounts of Al addition on the properties were investigated.

Materials and methods

The as-received slag was crushed using a disc mill (FRITSCH, pulverisette 13) and milled in a ball mill (Retsch PM4) for 2 hours at 200 rpm using 5 mm diameter stainless steel milling balls. The coarse fraction was removed by sieving the slag using an 80 µm sieve. Chemical composition was determined by means of X-ray fluorescence spectroscopy (XRF, Philips PW 2400). The slag mineralogy was determined by X-ray diffraction analysis (XRD, PW 1830 Philips) using CuKα radiation of 45 kV and 30 mA. The X-ray patterns were collected with a step size of 0.02° and step time of 2 s. ZnO powder was used as an internal standard.

Porous inorganic polymers were prepared by mixing the slag with activating solution (SiO_2/Na_2O = 1.14) of solid/liquid ratio equal to 3.7 in a Hobart mixer for 2 min. Subsequently, a suspension of 2 ml distilled water and various amounts of fine Al

powder (0.05, 0.07, 0.1 and 0.15 wt.% of solid fraction) were added and the mixing continued for 20 s. Samples were cast in polystyrene moulds with dimensions of 100 × 100 × 100 mm^3 and cured at room temperature.

Thermal conductivity measurements were performed using the guarded hot plate method. For this purpose, the casted samples were machined and measurements were conducted on samples 100 x 100 x 40 mm^3. Compressive strength was measured on 40 × 40 × 40 mm^3 samples by means of a Schenck-RM100 compression testing machine. Three samples per composition developed were measured and the average values are reported.

Results and discussion

The slag was received in a form of small granules of glassy black appearance. The XRF chemical analysis, Table 1, revealed that the main slag components, FeO, SiO_2, ZnO and Al_2O_3 comprise more than 93 wt.%. Regarding the mineralogy, an amorphous phase (64 wt.%) and fayalite (Fe_2SiO_4, 26 wt.%) were identified as main phases, while wüstite and spinel were also present in small quantities.

Table 1: Chemical composition of as-received secondary copper slag

	FeO	SiO_2	ZnO	Al_2O_3	CaO	PbO	MgO	Na_2O	Cr_2O_3	others
wt.%	57.4	26.4	6.2	3.4	2.3	0.7	0.7	1.0	0.7	1.2

The formation of IP from various FeO-SiO_2 slags after activation with Na-based alkali solution has been demonstrated by several authors already,[3, 7] and will therefore not be discussed further. The foaming of the material was achieved by the production of H_2 gas during the oxidation of aluminium in a basic environment, eq. (1).

$$2\ NaOH + 2\ Al + 6\ H_2O \Rightarrow 2\ NaAl(OH)_4 + 3\ H_2 \quad (1)$$

Macrographs of the synthesised foamed IP are presented in Figure 1. One can see that the amount of added Al powder had a significant effect on the final pore structure. While the pores are fine and homogeneously distributed when 0.05 wt.% of Al was added, they become progressively coarser with increasing amounts of added Al. In the case where 0.15 wt.% of Al was used, the formed pores are coarse and non-homogeneously distributed. This may be caused by insufficient mixing, but more probably the inhomogeneity in the pore structure is caused by the coalescence of formed H_2 bubbles.

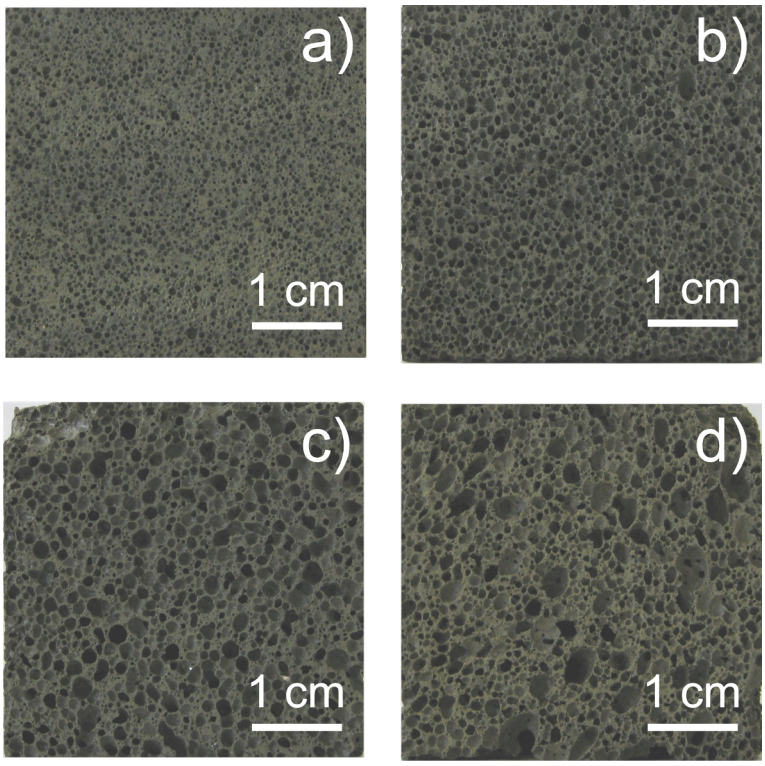

Figure 1: Macrographs of foamed inorganic polymer samples
a) 0.05 wt.% Al, b) 0.07 wt.% Al, c) 0.1 wt.% Al and d) 0.15 wt.% Al

In view of the different pore structure obtained as a function of Al addition, the physical and mechanical properties of the foamed IP were also different, Table 2. The density of the samples decreased from 1.45 g/cm^3 for 0.05 wt.% Al down to 0.76 g/cm^3 for 0.15 wt.% Al, while the highest density was found for samples foamed with 0.05 and 0.07 wt.% of Al. It is worthwhile mentioning that the slag density is approximately 3.6 g/cm^3, thus in all cases the foaming resulted in highly porous microstructures.

In line with the decrease in density, a decrease in thermal conductivity was also observed, from about 0.35 W/m.K to 0.16 W/m.K when the Al addition increased from 0.05 to 0.15 wt.%, Table 2.

Regarding the mechanical strength, this was measured on samples cured for at least 90 days at room temperature. The compressive strength decreased gradually from 15 to 1.5 MPa as the Al powder content increased from 0.05 to 0.15 wt.%.

Table 2: Physical and mechanical properties of foamed inorganic polymers

	Al content (wt.%)			
	0.05	0.07	0.1	0.15
compressive strength [MPa]	15.4 ± 1.9	5.3 ± 1.2	3.1 ± 0.5	1.5 ± 0.5
density [g/cm^3]	1.45 ± 0.04	1.00 ± 0.02	0.82 ± 0.01	0.76 ± 0.02
λ [W/m.K] at RT	0.348	0.215	0.186	0.156

Conclusions

Porous inorganic polymers were synthesised by alkali activation of FeO-SiO_2 based slag and various amounts of fine Al powder. The oxidation of Al in alkali environment caused formation of H_2 gas and resulted in in-situ foaming. The amount of added Al had a significant impact on the physical and the mechanical properties, such as compressive strength, density and thermal conductivity.

References

1. Z. Liu, N.-n. Shao, D.-m. Wang, Qin, Jun-feng, T.-y. Huang, W. Song, M.-x. Lin, J.-s. Yuan and Z. Wang, "Fabrication and properties of foam geopolymer using circulating fluidized bed combustion fly ash", *International Journal of Minerals, Metallurgy and Materials*, **21** (1) 89-94 (2014).
2. J. Davidovits, "Geopolymer Chemistry and Applications", (2011).
3. L. Machiels, L. Arnout, P. Jones, B. Blanpain and Y. Pontikes, "Inorganic polymer cement from Fe-silicate glasses: varying the activating solution to glass ratio", *Waste and Biomass Valorization*, **5** (1) 12-29 (2014).
4. S. Onisei, Y. Pontikes, T. Van Gerven, G. N. Angelopoulos, T. Velea, V. Predica and P. Moldovan, "Synthesis of inorganic polymers using fly ash and primary lead slag", *Journal of Hazardous Materials*, **205-206** (0) 101-110 (2012).
5. J. L. Bell and W. M. Kriven, "Preparation of ceramic foams from metakaolin-based geopolymer gels ", *Ceramic Engineering and Science Proceedings*, **29** (10) 97-112 (2010).
6. V. Vaou and D. Panias, "Thermal insulating foamy geopolymers from perlite", *Minerals Engineering*, **23** (14) 1146-1151 (2010).
7. S. Onisei, Y. Pontikes, P. Lemmens, L. Machiels, P. T. Jones, B. Coletti and B. Blanpain, "Synthesis of inorganic polymers from granulated slag of secondary copper production, Porto, Portugal ", in *Proceedings of 4th international Conference on Engineering for Waste and Biomass Valorisation*, 2012.