

# EFFECT OF ACTIVATING SOLUTION ON THE SYNTHESIS AND PROPERTIES OF POROUS Fe-Si-Ca-RICH INORGANIC POLYMERS

Lubica KRISOVA, Yiannis PONTIKES

Department of Materials Engineering, KU Leuven, 3001 Heverlee, Belgium

*lubica.kriskova@kuleuven.be, yiannis.pontikes@kuleuven.be*

## Introduction

Inorganic polymers (IP) are typically formed at room or slightly elevated temperatures by reaction of a precursor with an alkali solution.<sup>1</sup> As precursors, amorphous-based aluminosilicates or iron-aluminosilicates from various sources (natural or synthetic) are used.<sup>2,3</sup> Due to their relatively low environmental footprint they are considered to be a greener alternative for commonly used Ordinary Portland cement (OPC). IP of different densities can be used for various applications, as construction or insulating material. Foamed IP can be synthesised for instance *via* chemical in-situ foaming.<sup>4</sup> In this process, foaming agents, such as Al, Si or Zn are added to the IP paste before it hardens.<sup>5</sup> Metallic powder reacts with water and hydroxide in an alkaline environment, liberating hydrogen gas. This, if entrapped in the IP, leads to the expansion of the IP paste and formation of IP foam. However, to achieve good foaming results, two rivalling processes, setting and expansion, need to be mastered and therefore the kinetics of the foaming have to be optimised. Furthermore, by controlling the foaming kinetics a desirable porosity and pore structure can be achieved, and that has an obvious effect on mechanical and physical properties. It is therefore the aim of this work to understand how parameters, such as activating solution molarity and concentration (water content), affect the foaming kinetics and resulting foam properties.

## Materials and Methods

Finely milled synthetic Fe-Si-Ca based slag with a Blaine fineness of 4200 cm<sup>2</sup>/g was used to synthesised the foamed IP. For this purpose, the slag was mixed with the activating solution for 10 min (2× (3' mixing + 2' holding)) using a hand mixer (Bosch MFQ4070) and the paste was foamed by addition of 0.3 wt% of fine Al powder (99.9%, AEE). The foam stability was increased by addition of 0.02 ml commercial surfactant (SB2, Sika) per 100 g of slag. As activating solution, Na-silicate solutions with SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio of 1.4 to 2.0 and water content of 65 and 75 wt% were used. The slag to solution volume ratio was kept constant at 3.85 g/ml. The temperature of the environment during foaming was kept 20°C. The stability of the temperature was assured by having all the installation inside a water tank with controlled temperature.

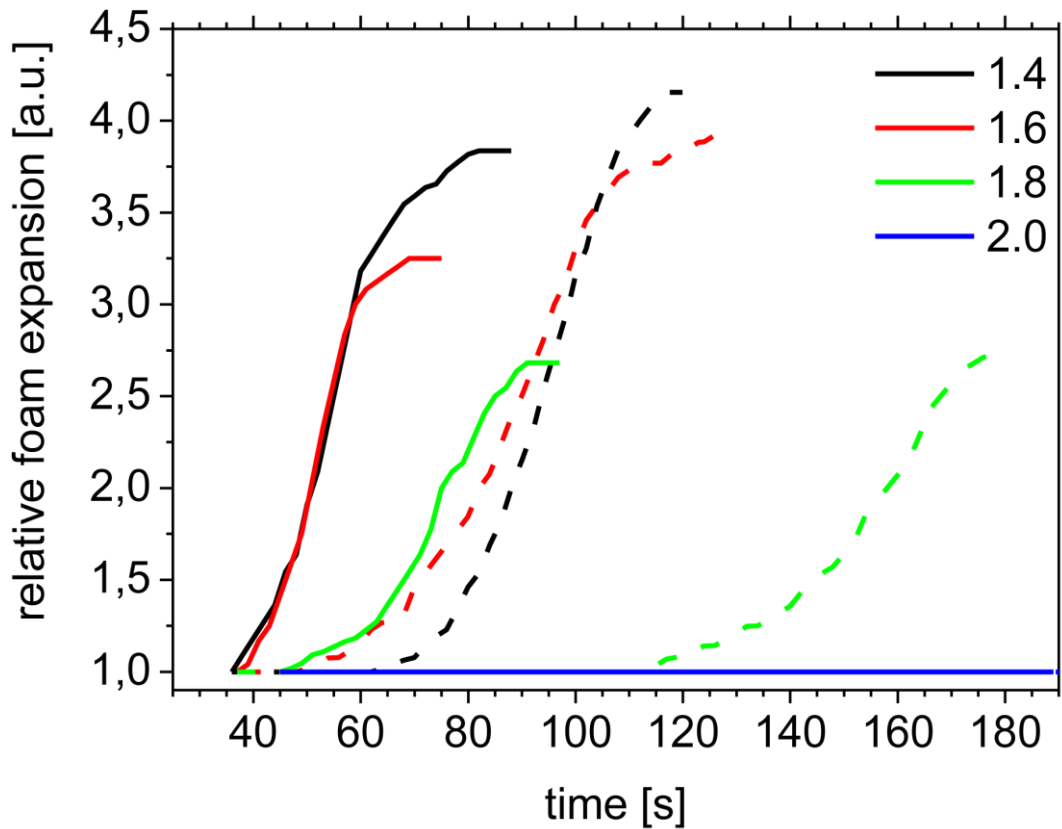
Kinetics of foaming were studied by means of a camera that measured the height of the synthesised foam every 2 sec. Pastes were also cast into EPS moulds prior to their foaming and were then cured at room temperature (RT, +/- 21°C). The structure of the synthesised foams was analysed by means of SEM (Philips, XL 30). The open porosity of the produced foams was measured by a water absorption test (ISO 10545-3:1995). The compressive strength was measured on (4×4×4)cm<sup>3</sup> samples using a 30 kN load cell and a loading rate of 2 mm/min (Instron 4467). Two samples per foam were tested and the average values are reported.

## Results and Discussion

The synthetic slag was designed to resemble the composition of slag from a non-ferrous metal production, Table 1. Due to water granulation, it consisted mainly of amorphous phase (> 93 wt%) while quartz, magnetite, hematite and corundum were present in small quantities.

**Table 1:** Chemical composition of the used synthetic slag (in wt%)

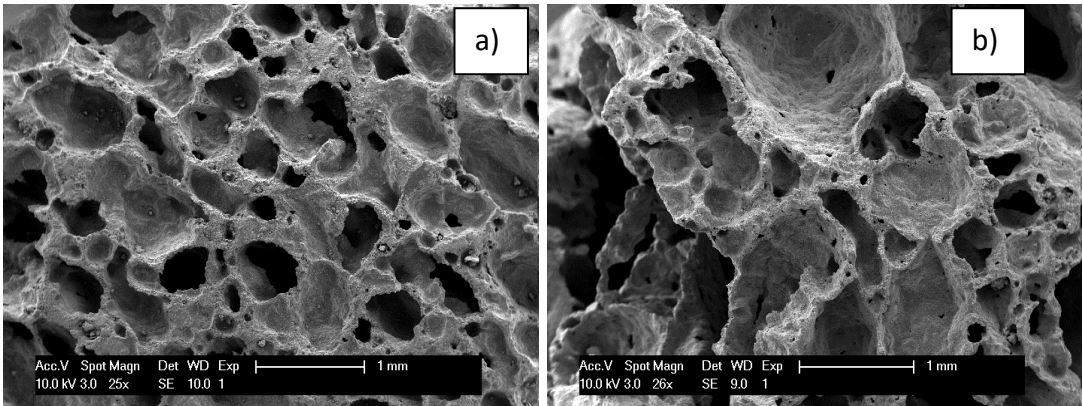
FeO	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	Others
41	36	13	6	2	2



**Figure 1:** Kinetics of foaming, solid line – 65 wt% of water, dashed line– 75 wt% of water in activating solution

The influence of both, water content and molar ratio of the activating solutions, on the foaming kinetics is shown in Figure 1. Starting with the  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio, this does not have a notable influence on the kinetics when increased from 1.4 to 1.6. Further increase of the  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio resulted in delayed initiation of foaming as well as slower foaming (change of the slope). Regarding the foam height (volumetric expansion), it decreases with the increase in the  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio. Both effects were observed regardless of the water content. Furthermore, higher water content resulted in a significant postponement of the foaming initiation as well as higher foam expansion; the latter was increasing for each respective  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio. Regardless of the water content, samples activated with a 2.0 molar solution did not foam. This could be due to the low amount of  $\text{OH}^-$  present in the sample, that was insufficient to break the passivation layer on the Al particle, resulting in no further Al oxidation and therefore also no  $\text{H}_2$  formation.<sup>6</sup>

Considering the foam structure, this was mostly influenced by the water content in the solution. The foams synthesised from the solutions with 65 wt%  $\text{H}_2\text{O}$  showed significantly finer pore structure, Figure 2, as well as lower open porosity. The study on the kinetics aspects had already suggested variations in total porosities attained, yet, the final values, Table 2, are the result of the two concurrent phenomena taking place, *i.e.* foaming on one hand and collapse on the other if the structure cannot sustain the microstructural changes.



**Figure 2:** Foam structure a) 1.4NS65 and b) 1.4NS75

Moreover, the collapsing was more pronounced when the solution with 65 wt%  $\text{H}_2\text{O}$  was used, but regardless of the water content in the solution, it was intensified with the decreasing of the  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio. The above lead to the two observed phenomena: a) the foams synthesised from solution with 75 wt% water were eventually lighter than the foams from solution with 65 wt% water; and b) the final foam porosity also increased with the increased  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio, Table 2.

Furthermore, lower porosities of the foams synthesised with 65 wt% water resulted in substantially higher densities of 0.81 to 0.58  $\text{g}/\text{cm}^3$ , compared to those synthesised with 75 wt% water (0.47 – 0.59  $\text{g}/\text{cm}^3$ ). As expected, the denser foams, originating

from the solutions with 65 wt% H<sub>2</sub>O, gave higher compressive strength, *i.e.* 2.0 to 0.9 MPa compared to 0.2 to 0.3 MPa when 75 wt% H<sub>2</sub>O was used.

**Table 2:** Mechanical and physical properties of the synthesised foams

	Compressive strength [MPa]	Density [g/cm <sup>3</sup> ]	Porosity [%]
1.4NS65	1.98 ± 0.4	0.81 ± 0.01	65
1.6NS65	1.29 ± 0.2	0.65 ± 0.02	75
1.8NS65	0.91 ± 0.5	0.58 ± 0.04	77
1.4NS75	0.33 ± 0.14	0.59 ± 0.01	82
1.6NS75	0.29 ± 0.05	0.50 ± 0.01	84
1.8NS75	0.15 ± 0.04	0.47 ± 0.01	83

### Conclusions

The obtained results indicated that the higher water content in the solutions resulted in delayed foam initiation, but higher volumetric expansion. The increased SiO<sub>2</sub>/Na<sub>2</sub>O ratio for the same H<sub>2</sub>O level, showed a negative effect on the foam expansion. However, due to the improved foam stability, the lightest foam was synthesised from activating solution with high SiO<sub>2</sub>/Na<sub>2</sub>O ratio (1.8) and high water content (75 wt%).

### References

1. J. Davidovits, *Geopolymer Chemistry and Applications*, Saint-Quentin, France, 2011.
2. 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 Biomass Valorization*, **5** 411-428 (2014).
3. 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", *J Hazard Mater*, **205-206** (0) 101-110 (2012).
4. E. Prud'homme, P. Michaud, E. Joussein, J. M. Clacens and S. Rossignol, "Role of alkaline cations and water content on geomaterial foams: Monitoring during formation", *J Non-Cryst Solids*, **357** (4) 1270-1278 (2011).
5. Z. Liu, N.-n. Shao, D.-m. Wang, Q. 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", *Int J Miner Metall Mater*, **21** (1) 89-94 (2014).
6. M. E. Simonsen, C. S nderby, Z. Li and E. G. S gaard, "XPS and FT-IR investigation of silicate polymers", *J Mater Sci*, **44** 2079-2088 (2009).