

TAILORING THE PROPERTIES OF POROUS INORGANIC POLYMERS: EFFECT OF THE PRECURSOR

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Introduction

Slag valorisation is a topic of increasing importance for circular economy and increased sustainability within the metallurgical industry. The copper industry, for example, produces annually about 24 million tonnes of Fe-rich slag worldwide.¹ One of the potential valorisation options for this slag is the production of inorganic polymers (IPs).² IPs have a primary binding phase of a disordered silicate network.³ They can be produced by mixing a silica-rich precursor, a slag for example, with an alkaline solution, often at room temperature.⁴ Porous IPs are lightweight materials that can be synthesised by mechanical or chemical foaming.⁵ The latter is done by means of a gas releasing agent (*i.e.* Al, H₂O₂, Si), that is added to the IP paste.⁶ Various process parameters are known to affect the foaming reaction as well as the final foam properties.⁷ This study investigates the effect of the precursor quality, in particular, the amount of CaO in the used Fe-rich copper slag.

Materials and Methods

An industrial slag from secondary copper production was modified with respect to its CaO content by addition of a chemical grade CaCO₃ (99%, Acros organics) in different amounts in order to achieve final CaO concentrations of 10, 15 and 20 wt%. The as-received slag with 5 wt% CaO was also subjected to investigation. The mixtures of slag and CaCO₃ were heated to 1200°C using an induction furnace (Indutherm TF 4000), held for 15 minutes and water quenched. All slags were milled using an attritor mill (Wiener 1S) until a specific surface area of $\pm 4000 \text{ cm}^2/\text{g}$ (according to Blaine method) was reached. The chemical and mineralogical composition of the slags were assessed using X-ray fluorescence (XRF, Bruker S8 Tiger 4 kW Rh) and X-ray diffraction (XRD, Bruker 2D PHASER), respectively. The density was determined by a gas pycnometer (Multipycnometer, Quantumchrome Instruments) and the particle size distribution by means of laser scattering (Mastersizer Micro Plus, Malvern).

The porous IPs were synthesised by mixing the slags with a sodium silicate solution ($\text{SiO}_2/\text{Na}_2\text{O} = 1.6$, $\text{H}_2\text{O} = 75$ wt%) and surfactant (Sodium oleate, 82%, Sigma Aldrich) keeping a solution to slag mass ratio of 0.4. A gas releasing agent (Al powder, 99.9%, AEE) of 0.2 wt% was added to the paste mixture, homogenised for 20 s and cast into a cubic mould ($10 \times 10 \times 10 \text{ cm}^3$). The reaction heat of paste-samples (no surfactant, no Al powder) was determined by isothermal conduction calorimetry (TAM Air, TA Instruments) at 20°C , using an admix ampoule. The expansion of the porous IPs was followed by means of a laser (IL-300, Keyence). Thermal conductivity and compressive strength were measured using a heat flow meter and a 250 kN load cell (Instron 5985), respectively. Computed tomography (Skyscan 1172) and scanning electron microscopy (SEM, Philips, XL30) were performed to investigate the pore structure.

Results and discussion

XRF results confirmed that the CaO composition was correctly altered to the desired target levels. The XRD data revealed that all slags were highly amorphous, and the amorphous fraction exceeded 90 wt% in all samples. All slags contained about 3% magnetite, and the sample with 20 wt% CaO contained an additional 3% wüstite, as the crystalline phases.

All the milled powders showed similar particle size distributions with the D_{10} and D_{90} values about $1 \mu\text{m}$ and $31 \mu\text{m}$, respectively. The density measurements revealed a gradual decline in values, from 3.5 g/cm^3 for the lowest CaO concentration (5 wt%) to 3.2 g/cm^3 for the highest CaO concentration (20 wt%).

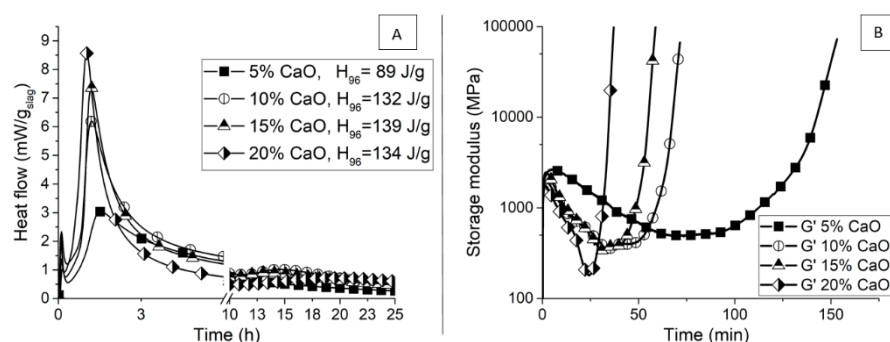


Figure 1: A) Calorimetry measurements, B) rheology measurements of the pastes

All slags, except for the one with 5 wt% of CaO, showed three peaks in the calorimetry measurement, Figure 1A. The original slag, with the lowest CaO content, showed only the first 2 peaks. The initial peak at around 5 min is a result of the wetting and the initial slag reaction. The second peak can be attributed to the main reaction where the polymerisation, as well as further dissolution happens.⁸ The effect of CaO content on slag reactivity can clearly be seen, as the peak becomes more pronounced with

increased amount of CaO. Also, a slight shift towards faster reaction times is visible. The final peak with its maximum at around 15 h, is only present in adapted slags with CaO content of 10 to 20 wt%, and could probably be assigned to a continuation of dissolution and polymerisation reactions.

Rheological measurements, Figure 1B, demonstrated a clear difference between the samples with various CaO content with respect to their setting time, with higher CaO concentrations resulting in a faster setting. This is in agreement with the calorimetry results showing the reactivity increasing with the CaO content.

The expansion curves, Figure 2C, indicated that the CaO content affected the foaming kinetics, with samples having lower CaO content expanding faster compared to those of higher concentrations. This could be connected to the slower setting times of pastes with lower CaO content resulting in a more easily expandable matrix.

Results of the compressive strength testing (Table 1) indicated that there might be a threshold in the CaO addition and this seems to be at about 10% for the current system; higher or lower CaO content resulted in lower strength values (results for other Al addition levels resulted to the same finding).

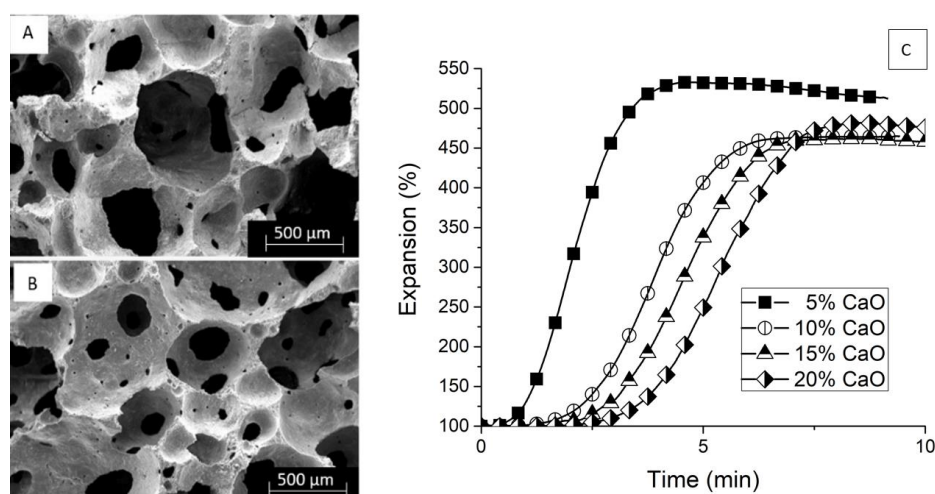


Figure 2: A) SEM image of a 5% and B) a 20% CaO IP, C) Expansion of the IPs after mixing

SEM, Figure 2AB, and μ -CT results (not presented herein) showed that at lower CaO concentrations the interconnectivity between the pores was higher, and the sphericity of the pores was lower. These results could be related to the slower setting time of the low CaO pastes making them more prone to deformations during and after the expansion process. The μ -CT results further revealed that all porous IP samples had similar porosity of 80%. There was no correlation between the CaO content and the porosity. However, the pore size distribution did show some CaO concentration dependence, with more smaller pores present in samples with higher

CaO content. Thermal conductivity (Table 1) of porous IPs seemed not to be affected by the CaO concentration.

Table 1: Compressive strength and thermal conductivity of the porous IPs

Porous IP	Compressive strength (MPa)	Thermal conductivity (W/mK)
5% CaO	0.5 ± 0.1	0.058
10% CaO	0.8 ± 0.1	0.059
15% CaO	0.5 ± 0.1	0.064
20% CaO	0.5 ± 0.1	0.057

Conclusion

This work clearly demonstrated that certain properties and morphological characteristics of porous IPs can be tailored by altering the CaO content of the precursor. Altering the CaO content in order to tailor the composition of the resulting slag could be a cost-effective method to modify Cu slags during the production step, without compromising the quality of the Cu. Optimisation can be done for the setting time and reactivity of the paste, as well as for the expansion time of the IP. The pore size distribution and pore characteristics can be altered without changing the porosity of the polymer. In conclusion, the chemical composition of the precursor should be taken into account during the design and production of porous IPs.

References

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