

GLASS FORMING ABILITY OF SLAGS IN THE FeO_x - SiO_2 - CaO SYSTEM AND PROPERTIES OF THE INORGANIC POLYMERS MADE THEREOF

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Introduction

Research and development around greener alternatives for Ordinary Portland cement is intense, and production of geopolymers, derived from aluminosilicate sources, is a possible path forward¹. However, comparatively little work has been done on iron silicate precursors for the synthesis of inorganic polymers (IP), the latter term implying a chemistry wider than the aluminosilicate one. The work herein would like to contribute to this domain. This will allow, in the long run, the valorisation of slags from non-ferrous metallurgy towards higher added value applications, *e.g.* as structural elements.

Work on Fe-rich slags from non-ferrous metallurgy for the synthesis of inorganic polymers started receiving again attention already in 2006², with a number of works contributing and expanding the area of applications (*e.g.* passive fire protection of underground constructions³). Focus on the slag chemistry and impact of cooling on slag reactivity was placed in the work of Pontikes *et al.*⁴, where the importance of the amorphous phase content in combination with its chemistry was demonstrated. Moving towards more Fe-rich compositions and less Al compared to FeNi slags, Onisei *et al.*⁵ investigated inorganic polymers from fayalite slags and their early-age behaviour. In a follow-up work, slags from pure oxides were synthesised and results will soon be communicated⁶.

In the work herein, slags in the FeO_x - CaO - SiO_2 system are investigated. The influence of silica and calcium oxide on the glass forming ability of the slags is assessed. In the next step, inorganic polymers are synthesised and the relation between slag microstructure and strength evolution of the IP is presented.

Experimental

The raw materials used were quartz, metallic iron, iron(III)oxide and calcium oxide. The compositions were designed to represent a parallelogram in the FeO - SiO_2 - CaO ternary

phase diagram, with as boundaries molar ratios $(\text{FeO}+\text{CaO})/\text{SiO}_2$ and FeO/CaO of 2.0-1.0 and 5.0-2.0, respectively. The corners of the parallelogram and a point in the middle were selected. Melting of these mixtures took place in an induction furnace (Indutherm TF4000), in a metallic Fe crucible. The melt was heated 100°C above the liquidus temperature, as calculated by Factsage 7.0 software, Table 1. For the FactSage calculations, the databases FactPS and FToxid were used. The mixture was in equilibrium with metallic Fe, with ferrous iron being the prevalent form, but a mixture of CO and CO₂ gas, in a volumetric ratio $\text{CO}/\text{CO}_2 = 2$, was also bubbled through the melt for 10 min at the end of each heat treatment. Afterwards, the melt was quenched in water. The resulting granules were crushed in a Fritsch pulverisette 13-disc mill and subsequently milled in a Wiener 1S attritor mill, until a Blaine specific surface of $4000 \pm 200 \text{ cm}^2/\text{g}$ was reached. The chemical composition was measured using a Philips PW2400 X-Ray Fluorescence (XRF) spectrometer. The crystalline phases were assessed using a Bruker D2 PHASER X-ray diffractometer. For the quantification, 10 wt% zincite (ZnO) was added to the powder sample as an internal standard and the slag-standard mixture was milled in a McCrone Micronizing mill in ethanol for 5 mins. The qualitative and quantitative analyses were performed using DifffracEVA and Topas Academic software, respectively.

Mortar samples were prepared by mixing the synthesised slags with standard CEN sand and alkali activating solution ($\text{H}_2\text{O}/\text{Na}_2\text{O} = 25$, $\text{SiO}_2/\text{Na}_2\text{O} = 1.6\text{-}2.0$) in a 3L Hobart mixer. The different mortars have the same volumetric ratio of CEN sand over precursor slag (5.6) and the same mass ratio of water over slag (0.28). The compressive strength of the mortar samples was tested after 2, 7 and 28 days with an Instron 5985 testing machine using a 250 kN load cell with a crosshead speed of 2 mm/min.

Results and Discussion

The chemical compositions of the different precursor slags (denoted by S1 to S5) are presented in Table 1. Minor components are alumina (approximately 0.4 mol%), due to the partial dissolution of the alumina tube used around the thermocouple, and magnesium oxide (approximately 0.4 mol%), which is present as impurity in the starting oxide powders. The liquidus temperatures, calculated using FactSage, are in the range of 1103-1169°C (experiments run at 1203-1269°C). The XRD amorphous content, as well as the $(\text{FeO}+\text{CaO})/\text{SiO}_2$ and FeO/CaO molar ratios are also presented in Table 1.

Table 1: Chemical composition of the different slags in mol% (estimated relative error is 10%), the calculated liquidus temperature T_L , the amorphous phase content assessed by XRD (estimated relative error is 5%) and calculated mole ratios of the bulk composition of iron oxide plus calcium oxide over silica, and iron oxide over calcium oxide

	FeO	SiO ₂	CaO	Other	T_L (°C)	Amorphous	(FeO+CaO)/SiO ₂	FeO/CaO
S1	43.6	34.0	20.9	1.4	1169	67.9	1.90	2.08
S2	54.1	34.7	10.0	1.2	1153	74.1	1.85	5.44
S3	34.1	47.4	17.2	1.3	1103	94.4	1.08	1.99
S4	44.0	46.1	8.4	1.5	1150	90.9	1.14	5.22
S5	45.0	39.5	14.1	1.4	1139	89.2	1.50	3.18

It is observed that for similar FeO/CaO ratios (approx. 2 and 5.2-5.4), lower (FeO+CaO)/SiO₂ ratios result in a higher amount of amorphous. On the other hand, for comparable (FeO+CaO)/SiO₂ ratios, the effect of the FeO/CaO molar ratio is unclear as it shows the inverse effect at high (approx. 1.9) and low (approx. 1.1) (FeO+CaO)/SiO₂ molar ratios. In fact, the glass forming ability of each melt is difficult to predict and shows more complex behaviour than direct relations to the molar ratios presented in Table 1 (depends on viscosity, configurational entropy, distance to eutectic, etc.)^{7,8}; future work will shed more light on this.

The compressive strength of the IP made from the different slags is shown in Figure 1. The early strength (2 days, Figure 1a) seems to be influenced by the availability of silica. A higher SiO₂/Na₂O molar ratio in the solution and lower (FeO+CaO)/SiO₂ molar ratio in the slag result in higher compressive strengths. The slags with lower (FeO+CaO)/SiO₂, *i.e.* <1.50, also have higher amorphous contents. This increases the reactive fraction of the material, which provides an additional explanation for the increased early strength. Increasing the FeO/CaO molar ratio shows to be beneficial for the early strength for slags with low (FeO+CaO)/SiO₂ molar ratios.

Interestingly, the late age strength does not follow a similar trend, which implies that IP synthesis is an ongoing process for at least 28 days (Figure 1b). The maximal 28 days compressive strength was reached for slag S5, which exhibited 53 and 50 MPa for the activating solutions with SiO₂/Na₂O molar ratios of 1.6 and 2.0, respectively. The highest strength increase relative to the 2-day strength is observed for samples with a lower FeO/CaO ratio (S1, S3 and S5), showing that Ca plays an important role in the strength build up in later stages of the reaction.

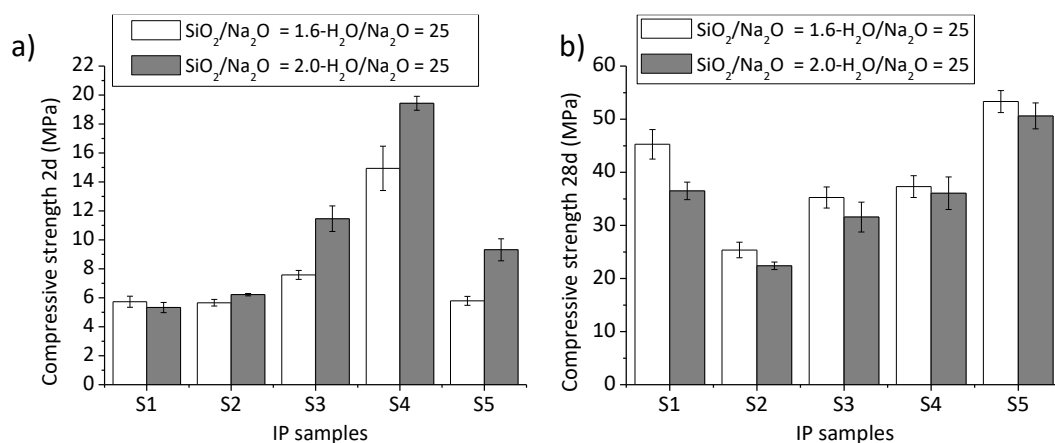


Figure 1: Compressive strength of the different inorganic polymers for 2 days (a) and 28 days (b). The error bars represent the standard deviation on the data

Conclusions

In the studied range of $\text{FeO}_x\text{-CaO-SiO}_2$ slags, a lower $(\text{FeO}+\text{CaO})/\text{SiO}_2$ molar ratio seems to reach higher glass contents. The early strength of the resulting inorganic polymers is mainly influenced by the availability of silica; a higher $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio in the activating solution, a lower $(\text{FeO}+\text{CaO})/\text{SiO}_2$ molar ratio and a higher glass content in the slag lead to higher compressive strength after 2 days of curing. After 28 days, a maximal compressive strength of 53 MPa was observed for slag S5.

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