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**Editors** Annelies Malfliet, Peter Tom Jones, Koen Binnemans, Özlem Cizer, Jan Fransaer, Pengcheng Yan, Yiannis Pontikes, Muxing Guo, Bart Blanpain



# Fe-Si-GLASSES AS GEOPOLYMER PRECURSORS: DECREASING THE AMOUNT OF ACTIVATING SOLUTION?

Lieven MACHIELS<sup>1</sup>, Lukas ARNOU<sup>1</sup>, Yiannis PONTIKES<sup>1</sup>, Peter Tom JONES<sup>1</sup>, Bart BLANPAIN<sup>1</sup>

<sup>1</sup> Department of Metallurgy and Materials Engineering, KU Leuven, 3001 Heverlee, Belgium

*lieven.machiels@gmail.com, lukas.arnout@student.kuleuven.be,  
yiannis.pontikes@mtm.kuleuven.be, peter.jones@mtm.kuleuven.be,  
bart.blanpain@mtm.kuleuven.be*

## Abstract

*Geopolymers are alkali-aluminosilicate binders which can be used as an alternative for Ordinary Portland cement in construction applications. They are synthesised by the dissolution of a precursor material in an alkaline activating solution, followed by polymerisation of the dissolved constituents, commonly in presence of a soluble silicate. Si-rich glasses, as occurring in volcanic rocks and metallurgical slags, can be high-value precursors for geopolymers. The present article focusses on Fe-Si rich glasses containing low amounts of Al-Mg-Ca-Na-K and reveals a strong dependence of the physical and mechanical properties (e.g. strength, porosity) of the geopolymers to the ratio of precursor to activating solution.*

## Introduction & objective

Geopolymer binders are formed by dissolution of a reactive precursor material (e.g. metakaolin, fly ash, GGBFS) in a highly alkaline solution, which becomes oversaturated in silica, alkalis, and other constituents, which polymerise and condense into a material which is generally X-ray amorphous at room temperature, but crystalline when heated to higher temperatures. A water based activating solution is used containing alkali hydroxides (e.g. NaOH, KOH) on one hand, which determine the high pH (12-14) required for dissolution of the precursors and sources of silica on the other hand (e.g. silica fume, soluble silicates  $\text{Na}_2\text{O} \cdot x\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ), resulting in increased silica saturation in solution. The amount of activating solution used is determined by different factors, such as the reactivity of the precursor, the curing conditions applied, the desired geopolymer chemistry and the required workability of the mixture. Most commonly, a pourable mixture is required, but others techniques can be applied for more viscous mixtures, such as vibro-compaction, extrusion, injection moulding or pressing. The objective of the present article is to determine the relation between geopolymer synthesis conditions, i.e. activating solution/precursor ratio, and thus mixture viscosity, and geopolymer properties, i.e. compressive strength, microstructure and porosity. The geopolymers synthesised derive from glasses rich in Fe and Si with minor Al, Mg, Na, Ca, K.

## Geopolymer synthesis

Glass was synthesised on lab scale from synthetic metal oxide powders. The following glass chemistry was used (in wt%) SiO<sub>2</sub>: 40, Fe<sub>2</sub>O<sub>3</sub>: 30, CaO: 15, Al<sub>2</sub>O<sub>3</sub>: 8, MgO: 2, all other metal oxides: <1. The powders were melted at 1450°C in a Pt crucible under an Ar-air atmosphere and quenched in water to obtain a glass with limited crystalline impurities (<5 wt%). The glass was milled in a ball mill to a grain size of 4 µm (d50). To prepare geopolymer mortars, dry powder mixes were prepared by premixing milled glass overnight with standard norm sand (DIN EN 196-1) in 1:3 weight ratios in a Turbula mixer. As activating solution a 50:50 weight mixture of NaOH (10M) and Na-silicate solution (composition SiO<sub>2</sub>:25.5-28.5 wt%; Na<sub>2</sub>O 7.5-8.5 wt%, density 1.35-1.38 g/ml) was used. Premixed dry powders were mixed with the NaOH and Na-silicate solutions in the ratios shown in Table 1.

**Table 1:** Geopolymer synthesis: S/L: solid (glass +sand)/liquid (activator solution) ratio

S/L	Appearance	Mould/shaping
13.33	Apparently “dry” mix	Pressed in steel mould at 30 MPa
8.89	Plastic appearance	Pressed in steel mould at 30 MPa
6.67	Plastic-wet mixture, not pourable	Introduced with a spoon in mould + tapped
4.00	Wet mixture, pourable	Poured in mould + tapped

As the different solid/liquid (S/L) ratios used lead to strongly differing mixture rheology's, different mixing and moulding procedures could be used (Table 1). To be able to produce pourable samples, a solid/liquid ratio lower than 4 was necessary for the given grain size and activating solution. Samples of S/L of 9 and higher could be pressed. Samples of intermediate S/L were introduced in moulds with a spoon and then tapped. Samples were wrapped in plastic foil to prevent water evaporation and cured at room temperature for 2 weeks. The microstructure and porosity was observed on broken and polished surfaces using a SEM-SE (XL30, Philips). Compressive strength was tested after 28 days.

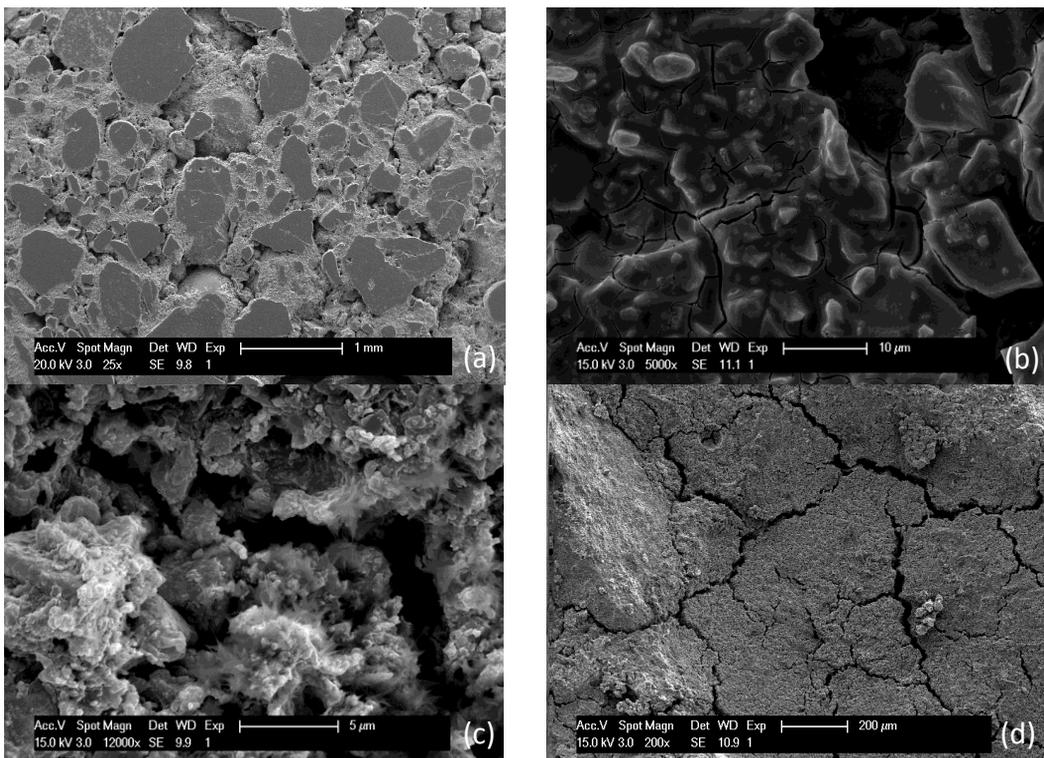
## Geopolymer properties

In samples of all S/L ratios, it could be observed that glass shards are partially dissolved and that they are cemented by the newly formed matrix (*e.g.* Figure 1b). The properties of samples of different S/L have been summarised in Table 2. The major differences between the samples are their porosity and the size of shrinkage cracks. Three pore types are distinguished: large pores (LP > 1 mm), intermediate size pores (IP 100-500 µm) and small pores (SP < 5 µm). LP are mainly present in samples GP6.67 and GP4.00 and represent air entrapped during mixing. In samples GP 8.89 and GP13.33 these pores closed during pressing or did not form as the samples were not completely wetted resulting in easier escape of air. IP are present only in sample GP13.33 and are explained

by the dry mixture rheology and thus the lack of liquid phase. Dry premixing reduces the porosity, but even when premixed glass particles are bound in a concentric layer around sand aggregates, rather than filling the pores between the sand particles (Figure 1a). SP occur in sample GP4.00 and less commonly in sample GP6.67, while in the other samples they are absent (compare Figure 1b with 1c). A possible explanation for these pores is the presence of excess unreacted solution in these samples. In these micro-pores, the micro-structure of the newly formed phases can be observed. Two shapes can be observed: one is platy with triangular surfaces and the other globular.

**Table 2:** Geopolymer properties, S/L: solid liquid; SP: small pores (<5 μm); IP: intermediate pores (100-500 μm); LP: large pores (> 1 mm)

S/L	Pores			Cracks thickness, connectivity	Compressive strength at 28 days
	SP	IP	LP		
13.33		+		<5 μm, not connected	16.8 MPa
8.89				<5 μm, not connected	52.7 MPa
6.67	+		+	<5 μm, more common, not connected	19.4 MPa
4.00	++		+	20-30 μm, common, connected	2.3 MPa



**Figure 1:** SEM-SE pictures of some geopolymers samples. (a) Cut section of GP13.33 showing intermediate size pores (b) GP13.33 showing micro-shrinkage cracks. Note the absence of micro-pores (c) GP4.00 showing triangular platy and globular morphologies, micro-cracks and micro-pores (d) GP4.00 with large penetrative cracks

Shrinkage cracks with a thickness of  $< 1$  to maximum  $5 \mu\text{m}$  can be observed in all samples. Individual cracks can be separate or connected to nearby cracks. Only in sample GP4, cracks are much more pervasive, interconnected and much larger in size (width  $20\text{--}30 \mu\text{m}$ ). The difference in strength of the samples (Table 2) can probably be related to the difference in crack formation and porosity of the samples. The low strength of sample GP4 is due to the large penetrative shrinkage cracks. The presence of these cracks is probably due to excess alkali in solution, which causes shrinkage on dehydration. In sample GP6.67, cracks are much smaller and less connected, resulting in higher strength. The highest strength is achieved in GP8.89 and is probably due to the absence of excess alkali and due to the pressing of the sample in moulds, which leads to a better aggregate particle packing and a better division of the binding phase over the pores. The strength of sample GP13.33 is lower due to its highly porous structure resulting from the dry rheology of the sample, as explained above.

## Conclusions

A binding phase was synthesised from Fe-Si glass and an alkaline activating solution. Mortars where prepared with different glass/activating solution ratios and very different properties were observed. Samples of S/L 8.89 delivered a rheology which could be pressed in moulds and a compressive strength of  $52 \text{ MPa}$  was achieved after curing. On the contrary, pourable samples of S/L 4 had rather low strengths ( $2.3 \text{ MPa}$ ) because of excessive formation of shrinkage cracks. Additionally, pore size distributions varied strongly. While in samples of S/L 8.89 porosity was low, in samples with high S/L ratio's (13.33) mainly intermediate size pores were present ( $100\text{--}500 \mu\text{m}$ ) and in samples of low S/L mainly small size pores ( $<5 \mu\text{m}$ ) and large pores ( $>1 \text{ mm}$ ) were present.

## References

1. J. Davidovits, *Geopolymer Chemistry and Applications*, 3th Edition, Geopolymer Institute, St. Quentin, 2011.