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INFLUENCE OF THE CHEMISTRY OF VITRIFIED RESIDUES ON THE PROPERTIES OF BLENDED INORGANIC POLYMERS WITH CALCINED KAOLINITIC CLAY

Elise FRANCOIS^{1,2}, Jan ELSSEN¹, Yiannis PONTIKES², Lieven MACHIELS²

¹ KU Leuven, Department of Earth and Environmental Sciences, 3001 Leuven, Belgium

² KU Leuven, Department of Materials Engineering, 3001 Leuven, Belgium

*francois.elise@gmail.com, jan.elsen@ees.kuleuven.be,
yiannis.pontikes@mtm.kuleuven.be, lieven.machiels@gmail.com*

Introduction

Inorganic polymers (IP), produced through the alkaline activation of aluminosilicate rich materials, have been proposed as a sustainable alternative to Ordinary Portland Cement, which is responsible for 8 % of the anthropogenic CO₂-emission.¹ Commonly used aluminosilicate sources to synthesize IPs are Ground Granulated Blast Furnace Slag (GGBFS)² and calcined kaolinitic clay, i.e. metakaolin (MK).³ The goal of this work was to find alternative glassy precursors to replace GGBFS in a GGBFS-MK-based IP, on the one hand due to the limited availability and high price of GGBFS on the market and on the other hand considering the possibility of designing the glass chemistry in order to have optimal properties in the final glass-metakaolin-based IP.

Materials and methods

Materials

BanahCEM (MK-based IP precursor powder), GGBFS and the activating solution were provided by Banah U.K.⁴, a British company specialised in IPs. Glasses were synthesised on lab-scale to mimic vitrified residues formed in the plasma gasification of highly calorific waste materials, such as RDF from municipal solid waste, for energy production.⁵ The chemical composition, determined with XRF, is given in Table 1.

Table 1: Bulk normalised chemical composition of the raw materials (in wt.%)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Others
GGBFS	36.0	14.5	0.4	39.9	6.9	0.7	0.2	1.6
GGBFS-glass	34.0	10.4	14.2	32.3	1.7	0.8	2.4	4.4
Mg-glass	27.1	13.4	14.1	31.7	8.1	0.6	3.6	1.3
K-glass	28.2	8.9	13.7	30.5	2.3	8.5	4.8	3.2

Three glasses were synthesised by melting pure oxide mixes in a bottom loading furnace for half an hour at a temperature of 1550 °C in an Ar-atmosphere and were quenched in water afterwards. A first glass was synthesised in order to mimic the GGBFS chemistry and is called GGBFS-glass. Two other glasses were synthesized with a higher content of either Mg or K and are called Mg-glass and K-glass, respectively. All glasses have a higher Fe-content compared to the original GGBFS.

Reactivity

The reactivity of the raw materials is an important property, since it is responsible for the rate of dissolution of the precursor and the release of network-forming cations, among others, into the solution and eventually it will determine the kinetics of gelation and thus setting time and hardening of the IP.⁶ The reactivity is influenced by the chemical composition of the material, the glass content, the particle size distribution and the specific surface.² The last three parameters were aimed similar for the GGBFS and the glasses in order to be able to investigate the influence of the chemistry. Considering that none of the existing formulas^{2,6} take into account the amount of K and Na present in the materials, which are nevertheless important cations since they act as network-modifiers, a new formula is proposed: $(\text{CaO}+\text{MgO}+\text{K}_2\text{O}+\text{Na}_2\text{O})/(\text{SiO}_2+\text{Al}_2\text{O}_3)$. This formula needs to be further expanded and needs to include Fe^{2+} as well as Fe^{3+} , and eventually be correlated with properties through statistical analysis. Still, even in its present simple form, it is a useful tool as will be shown by the results below. The obtained values for the three glasses developed are 0.84 for the GGBFS-glass, 1.09 for the Mg-glass and 1.24 for the K-glass.

Methods

Pastes were prepared by the procedure provided by Banah U.K. and with a liquid (activating solution and water) to solid (banahCEM and GGBFS or glass) mass ratio of 0.73 (Table 2). Using Vicat testing, the setting time of the pastes was determined and by means of calorimetry, the heat flow during the formation of IP was measured. Mortars were prepared by making the pastes and adding CEN-sand and water, with dimensions of 40 x 40 x 160 mm³ according to a procedure provided by Banah U.K. Mortars were stored at a temperature of 20 °C in closed plastic boxes. The microstructure was investigated with SEM. Uniaxial compressive strength and three-point bending tests with a span of 100 mm were performed after 33 and 28 days respectively, with an Instron mechanical testing device.

Table 2: Proportions of raw materials for the preparation of the samples (in wt. %)

wt.%	BanahCEM	GGBFS or glass	Water	Activating solution	CEN-sand
Paste	50.4	7.3	4.9	37.4	0
Mortar	19.8	2.8	3.5	14.6	59.3

Results and discussion

Figure 1 gives the heat flow over time (graph) and the initial setting time (table). The heat flow displays a broad peak which represents the formation of reaction products.³ The K-glass IP reaches first its maximum, followed by the GGBFS and the Mg-glass IP. The peak of the GGBFS-glass IP is smeared out. The same is valid for the setting time, first the K-glass IP sets, followed by the GGBFS, Mg-glass IPs and finally the GGBFS-glass IP.

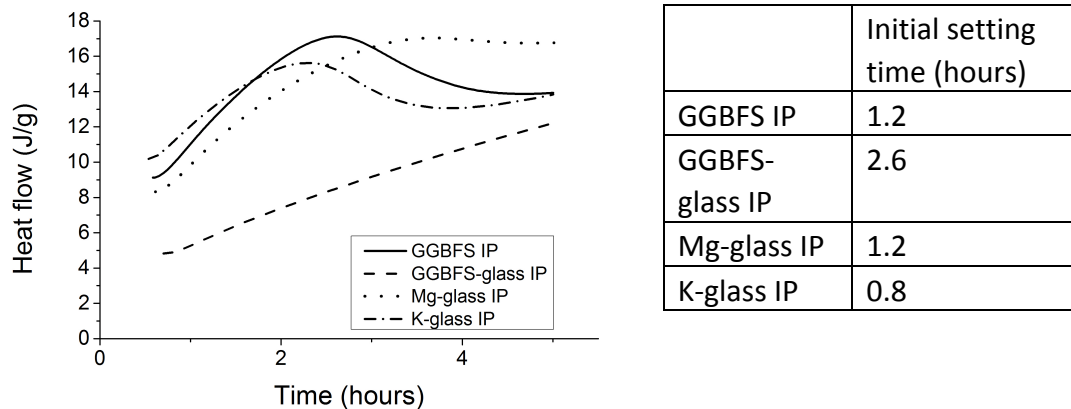


Figure 1: Heat flow over time and the initial setting time given in the table

It appears that the raw material with the highest ratio of network-modifying to network-forming cations reacts the fastest, i.e. the K-glass. It's the first to set and to reach its maximum (Figure 1) during the heat release. The presence of network-modifying cations in the materials resulted in a more rapid release of network-forming cations into the solution, which resulted in the formation of the IP.

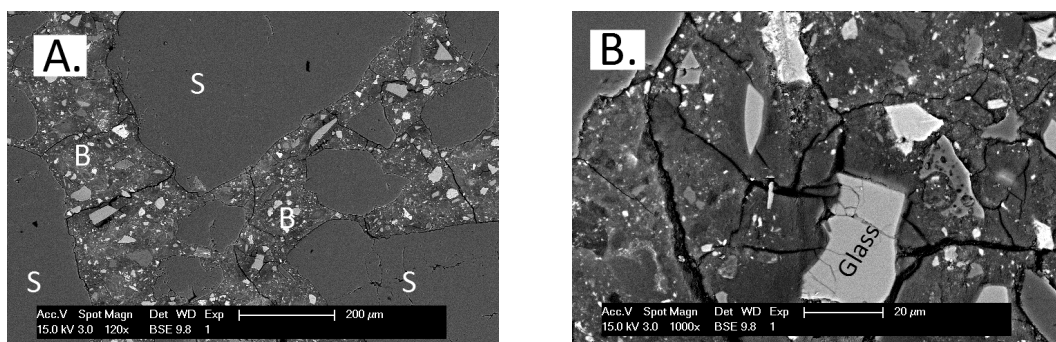


Figure 2: Back-scattered electron images of an IP mortar (S = sand aggregates; B = binder material)

The microstructures of the different IPs are similar. Back-scattered electron images of a representative sample are shown in Figure 2. Minor micro-cracks could be detected throughout the samples. Several non-dissolved glasses and GGBFS particles could still be observed in the matrix.

Although the differing glass chemistry clearly affects the early kinetics of the IP reaction, e.g. the setting, it can be observed that after 28 days of curing similar properties are obtained regarding flexural (6.5 – 9.5 MPa) and compressive strength (62 – 78 MPa) (Figure 3). The fact that there are only small differences in strength is explained by the relative small percentages of glass in the IP mixtures (Table 3), which results only in small differences in IP chemistry and very similar microstructure, particle packing and porosity.

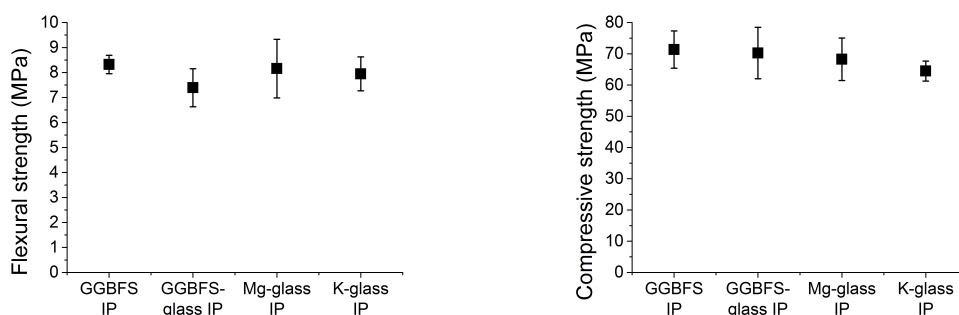


Figure 3: Left: Flexural strength of mortars after 28 days of curing - Right: compressive strength of mortars after 33 days of curing.

Conclusion

The chemical composition of the raw materials to form IP strongly influences the setting time and heat flow during the first hours of reaction. The material with a higher ratio of network-modifying to network-forming cations appears to dissolve and gelate faster which is reflected in a faster setting. However, after prolonged curing time, the mechanical properties and microstructure of the IPs prepared using differing glass chemistries were similar.

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