

THE INFLUENCE OF ACTIVATING SOLUTION ON THE KINETICS AND COMPRESSIVE STRENGTH OF AN IRON-RICH SLAG PASTE

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Introduction

The influence of the activating solution on aluminosilicate inorganic polymers (IPs), also called geopolymers¹, has been investigated extensively in the past. More recently iron-rich materials, as precursors for IPs, have attracted increased interest as well. Some examples of these iron-rich materials are ferronickel slag², fayalitic slag³ and bauxite residue⁴. Despite the increased interest, the influence of the activating solution on such materials has only been scarcely investigated.

Increasing concentrations of both alkalis and silicates lead to increased compressive strengths of the IP up to an optimum. Further concentration increases led to lower compressive strengths.^{2,5} The type of alkali atom also influences the compressive strength. For instance, Komnitsas *et al.*² showed that for an IP from ferronickel slag, the compressive strength at low silicate concentrations is higher for K-based solutions than Na-based solutions and vice versa at high silicate concentrations. The effect of the water content of the activating solution has been investigated by Kriskova *et al.*⁶, showing a decrease in compressive strength with increasing dilution. Additionally, Machiels *et al.*⁷ also report decreased compressive strength at low liquid/solid ratios (L/S = 0.30). Overall, trends seen for geopolymers are also present in iron-silicate IPs, but the influences are not quantified in detail.

Activating solutions with various alkali atoms (M = Na/K), moduli (SiO₂/M₂O) and water ratios (H₂O/M₂O) are prepared and mixed with an iron-rich precursor. Their influence on the kinetics, structure and compressive strength is reported and discussed.

Experimental methods

The precursor slag used in the present work was a synthetic slag from a pilot plant. The chemical composition of this slag, obtained by X-ray fluorescence (XRF), was (in wt%) FeO 45, SiO₂ 33, CaO 11, Al₂O₃ 4 and MgO 2.

Inorganic polymer pastes were obtained by mixing various activating solutions (alkali atom $M = \text{Na}$ or K ; $\text{Si}_2\text{O}/\text{M}_2\text{O} = 1.6$ or 2.0 ; $\text{H}_2\text{O}/\text{M}_2\text{O} = 25$ or 30 ; water/slag $\text{W/S} = 0.28$) with the precursor slag. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed using a Bruker Alpha-P with diamond measuring crystal. Spectra in the range of 4000 cm^{-1} to 380 cm^{-1} , with a resolution of 4 cm^{-1} were obtained using 32 scans per measurement. Vicat measurements were in accordance with EN 196-3, while isothermal calorimetry was performed in a TAM Air. The temperature was kept at 20°C and approximately the first 30 minutes were discarded to avoid errors due to equilibration.

Mortars were prepared by mixing the slag with the activating solutions using liquid/slag ratios in order to obtain a W/S ratio of 0.28 . After 30 seconds, CEN standard sand (mass ratio sand/slag 2.58) was added slowly over another 30 seconds, followed by continued mixing for 2 minutes. The compressive strength of the mortars was assessed according to EN 196-1. Curing was performed in hermetically sealed plastic boxes at 20°C , and compressive strengths were measured at 2, 7 and 28 days. Four samples were used for each measurement.

Results and Discussion

The main bands in the infrared spectra (Figure 1a), around $900 - 1000\text{ cm}^{-1}$, correspond to Si-O-T stretching; Si-O rocking bands ($400 - 500\text{ cm}^{-1}$) can also be seen.⁸ Both of these bands experience a shift as a consequence of the formation of an IP. In the area of the Si-O-T stretching band of the IPs, a smaller band is also present at slightly lower wavenumbers most likely due to residual unreacted material. The small peak due to O-H vibration of the water present is seen around 1650 cm^{-1} (together with a broad peak around $3000\text{-}3500\text{ cm}^{-1}$, not shown in Figure 1). Another small peak around 1400 cm^{-1} may indicate C-O stretching originating from possible carbonation during curing.⁶

Comparison between the calorimetry results and setting time measurements (Figure 1b) shows that the peaks in the heat flow correspond closely to the (exothermic) setting of the polymeric network. The heat flow decreases slowly after the initial reaction peaks, evidencing the typical continued reorganisation and hardening of the IPs. Increasing the $\text{SiO}_2/\text{M}_2\text{O}$ ratio of the activating solution delays the setting of the IP. Higher silica contents usually correspond to lower alkalinity of the solution, decreasing the dissolution rate⁹ which will delay setting.

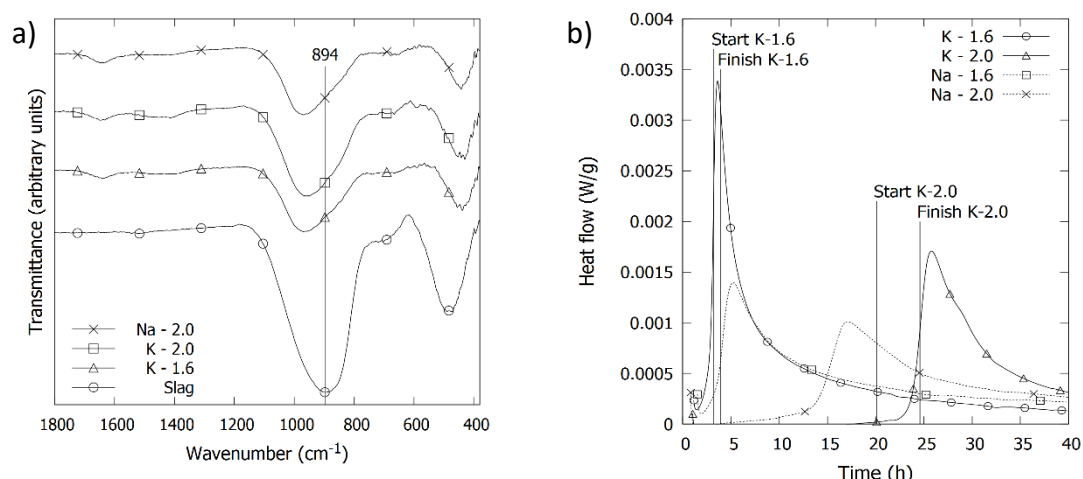


Figure 1: (a) Infrared spectra (1800 cm^{-1} to 380 cm^{-1}) for the slag and prepared iron-rich slag pastes with $\text{H}_2\text{O}/\text{M}_2\text{O} = 25$, various alkali atoms (Na, K) and moduli ($\text{Si}_2\text{O}/\text{M}_2\text{O} = 1.6, 2.0$) as well as (b) calorimetry results and setting times for the same iron-rich pastes

The typical hardening of IPs over time can be seen from the compressive test results (Figure 2). While the early age strength of Na-based IPs can be higher, the final compressive strength of K-based IPs after 28 days is always higher than that of the corresponding Na-based IP. At high $\text{H}_2\text{O}/\text{M}_2\text{O}$ molar ratios the compressive strengths are typically lower due to several factors such as higher porosity¹⁰ and lower reactivity,¹¹ which is also seen here, except for the Na-based IP with a modulus of 1.6, where the compressive strength is retained.

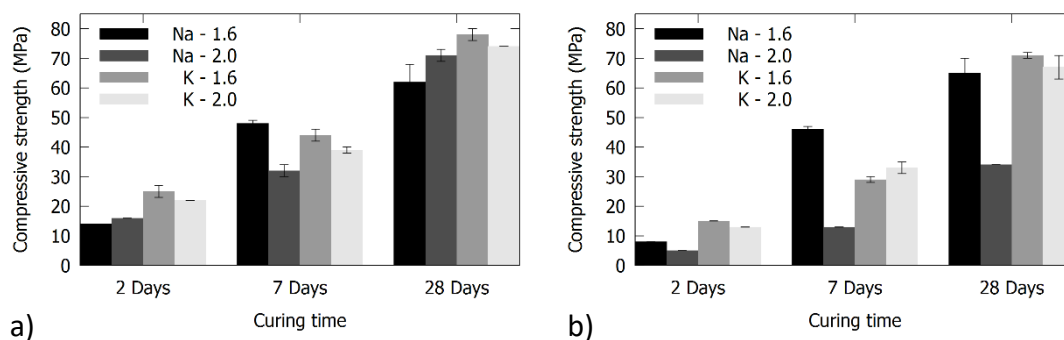


Figure 2: Compressive strength data for iron-rich pastes after 2, 7 and 28 days with various alkali atoms (Na, K) and moduli ($\text{Si}_2\text{O}/\text{M}_2\text{O} = 1.6, 2.0$) and $\text{H}_2\text{O}/\text{M}_2\text{O} = 25$ (a) or $\text{H}_2\text{O}/\text{M}_2\text{O} = 30$ (b). Error bars indicate the 95% confidence interval

Conclusions

The influence of the activating solution on an iron-rich IP was investigated by varying the type of alkali atom and the $\text{SiO}_2/\text{M}_2\text{O}$ and $\text{H}_2\text{O}/\text{M}_2\text{O}$ molar ratios. Both Vicat and calorimetry measurements showed increased setting times for increased $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratios. Compressive strength increases over time, and the final strength is the highest (78 MPa) for K-based IPs with the lowest $\text{SiO}_2/\text{M}_2\text{O}$ and $\text{H}_2\text{O}/\text{M}_2\text{O}$ molar ratios. Increasing the silicate content generally decreased the compressive strength. This decrease was large for Na-based IPs with a high $\text{H}_2\text{O}/\text{M}_2\text{O}$ molar ratio whereas K-based samples are less influenced by the silica content. For Na-based IPs with a low water ratio strength increases from 63 MPa to 71 MPa with increasing $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio.

Acknowledgements

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