ALKALI-ACTIVATION OF Fe-RICH SLAG USING MIXED Na-K SOLUTIONS

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Introduction

Inorganic polymers (IPs) are typically obtained by alkali-activation of inorganic precursor materials, often residues from other industries such as fly ash, ground granulated blast furnace slag or non-ferrous metallurgy (NFM) slag.[1] The majority of inorganic polymers has been created by activation with alkali-silicate solutions, where the alkalis are usually either sodium (Na) or potassium (K). However, research on the combination of both Na- and K-silicate activators is scarce, and mainly focused on aluminosilicate precursors whereas the NFM slags are richer in iron.[2]

The effect of using mixed-alkali solutions is still unclear and seen to vary in literature. Duxson *et al.*[3] reported an increased compressive strength for metakaolin-based geopolymers activated with mixed-alkali solutions with respect to data obtained when single-alkali solutions were used, and attributed this to a further unspecified mixed-alkali effect (MAE). A strength increase of mixed-alkali-activation with respect to sodium-based activation of fly ash was seen by Leong *et al.*[4] at elevated temperatures (60°C). However, at room temperature decreased strength was reported. Phair and van Deventer[5] also observed a negative interaction of both alkalis, leading to decreased strengths for mixed-alkali activated fly ash with respect to pure-alkali activated samples. In another study, Chuah *et al.*[6] reported a strength decrease going from Na- to K-activated fly ash, with mixed-cation alkali-activation yielding intermediate strengths.

The effect of activation with mixed Na/K-solutions is still unclear, and possibly depends on the precursor. Furthermore, alkali-activation of iron-rich precursors, such as NFM slags, has only been scarcely investigated and even more so with respect to mixed-alkali solutions. Therefore, this work aims to investigate the mixed-alkali-effect by activation of a synthetic NFM-like slag with both pure Na- and K-silicate solutions as well as mixed Na/K-silicate solutions.

Materials & methods

A synthetic, iron-rich slag resembling a non-ferrous metallurgy slag was used as precursor in this work. The chemical composition (Table 1) was determined by X-ray fluorescence (XRF, PW2400, Philips). The phase assemblage was obtained by X-ray diffraction (XRD; D2 PHASER, Bruker), with quantification performed by means of Rietveld analysis, using the TOPAS Academic V5 software. The result showed an amorphous content of > 97 wt%, with trace amounts of magnetite (± 1 wt%) and quartz (< 1 wt%). The slag was milled to a specific surface area of 4500 cm^2/g, as determined by the Blaine permeability method, and activated using alkali-silicate solutions. Activating solutions with different types of alkalis (M) were used: either Na, K or a 50-50 mix (Na/(Na+K) molar ratio = 0.5). Additionally, a molar SiO_2/M_2O ratio (Modulus, *Ms*) of both 1.6 and 2.0 was used, while the molar H_2O/M_2O ratio was kept constant at 25. In all experiments, the H_2O/precursor weight ratio is 0.28. The naming convention is M-x, where M is the alkali atom or mixed, and x is Ms. Reaction kinetics were investigated using isothermal calorimetry at 20°C (TAM Air, TA Instruments). Mortars were produced as described in EN196-1[7], though with a precursor/sand weight ratio of 2.58 in order to maintain the same volume ratio and a liquid/precursor weight ratio as needed to obtain a H_2O/precursor ratio of 0.28. Their compressive strength was tested using an Instron 5985 with load cell of 250 kN, at a speed of 2 mm/min. Finally, nitrogen adsorption-desorption porosimetry was conducted at 77 K (Tristar 3000, Micromeritics) after samples were degassed at 60°C for 24 h. The surface area was determined using the Brunauer-Emmett-Teller (BET) method, the micropore volume (V_μ) was determined using the t-plot method and mesopore volume (V_m) and the pore size distribution was obtained by Barrett-Joyner-Halenda (BJH) analysis. The "total" pore volume (V_t) as discussed in this work consists of a summation of V_μ and V_m, *i.e.* macropores are not considered in the discussion.

Table 1: Chemical composition of the slag

Oxides	FeO	SiO_2	CaO	Al_2O_3	MgO	Other
Composition (wt%)	45	33	12	5	3	1

Results & discussion

Calorimetry results (Figure 1) show differences in the kinetics of activation with Na-based, K-based and mixed-alkali solutions. At low Ms the exothermic peak due to formation of the IP occurs slightly faster for K-based IPs than for Na-based IPS, while the opposite is observed at high Ms. Therefore, the reaction rates of K-based IPs are more affected by the Ms than Na-based IPs. Even though the mixed-alkali solutions have a Na/K ratio of 1, the reaction rates appear closer to those seen for K-based IPs. This suggests that the effects of K^+ during activation dominate the reaction rates in the presence of both Na^+ and K^+. At low Ms, the exothermic peak appears slightly

faster in the mixed-alkali solution than both of the Na- or K-activated samples, suggesting a synergetic effect of Na^+ and K^+ in the activating solution.

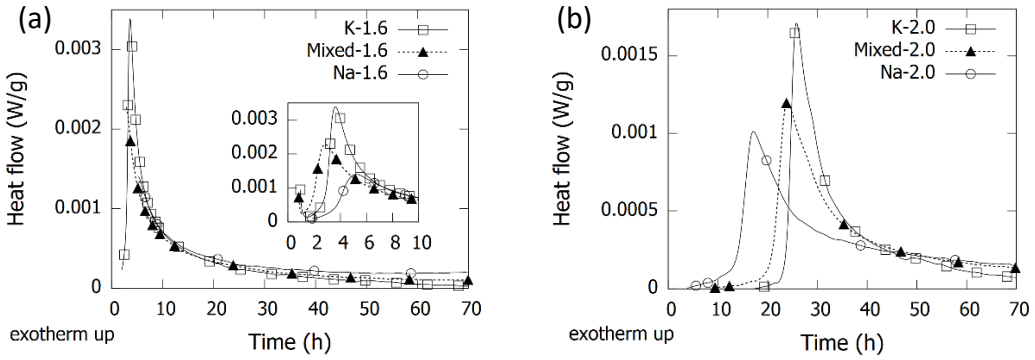

Figure 1: Reaction heat flows in calorimetry for SiO_2/M_2O = 1.6 (a) and SiO_2/M_2O = 2.0 (b)

Compressive strength results (Figure 2a) reveal that while after only 2 days there is no synergetic effect, from 7 days on a significant strength increase is documented when using a mixed-alkali activation; strengths of over 80 MPa were obtained after 28 days for both a high and low Ms. As the effect is more pronounced for a Ms of 2.0 after 28 days, the porosity of these samples was closer investigated. N_2 adsorption (Figure 2b) reveals pseudo-type II isotherms with a H3-like hysteresis curve, as specified by IUPAC[9], often related to slit-shaped pores. For this type of isotherm, the V_m quantification is not very accurate and should be considered in a qualitative way. From the porosity analysis (Table 2), it can be seen that the mixed-alkali activation yields reduced V_μ. On the other hand, both V_μ and average pore size increase with increasing Na/(Na+K) ratio. Therefore, the MAE might be related to a densification of the IP network itself, as indicated by the reduced V_μ and limited or no synergetic effect on V_m. However, it should be noted that compressive strength has been closely linked to open porosity and more specifically to the amount of large pores[9], which are not investigated in this work. Therefore, the link between mixed-alkali activation, porosity and compressive strength is not fully clear. Additionally, other factors, such as the nature of the activated binder product, likely affect the strength as well.

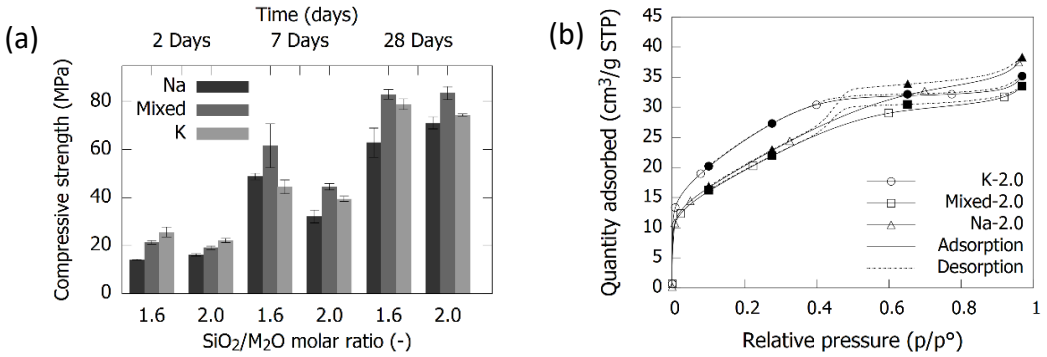

Figure 2: Compressive strength results over time for mortars (a) and N_2 adsorption-desorption curves for pastes with SiO_2/M_2O = 2.0 (b)

Table 2: Micropore volume (V_μ), mesopore volume (V_m), total (Vμ+Vm) pore volume (V_t), average pore size (d_{avg}) and the specific surface area (A_S) for pastes with SiO_2/M_2O = 2.0

	V_μ (cm^3/g)	V_m (cm^3/g)	V_t (cm^3/g)	d_{avg} (nm)	A_s (m^2/g)
K-2.0	$4.71 \cdot 10^{-2}$	$1.67 \cdot 10^{-2}$	$6.38 \cdot 10^{-2}$	3.00	89.09
Mixed-2.0	$4.08 \cdot 10^{-2}$	$2.44 \cdot 10^{-2}$	$6.52 \cdot 10^{-2}$	3.22	72.53
Na-2.0	$4.31 \cdot 10^{-2}$	$3.13 \cdot 10^{-2}$	$7.43 \cdot 10^{-2}$	3.64	74.55

Conclusion

The use of mixed-alkali activating solutions for the formation of inorganic polymers from an iron-rich synthetic slag was investigated. Calorimetry results showed that the reaction rates for mixed-alkali activated samples were more similar to those of K-based IPs. From 7 days on, a mixed-alkali synergetic effect yields increased compressive strengths and after 28 days, compressive strengths of over 80 MPa could be reached. An investigation of the micro- and mesoporosity showed that while there was no significant effect on the mesoporosity, the amount of micropores was decreased for mixed-alkali activated IPs with respect to single-alkali IPs. However, both macroporosity and total open porosity of mixed-alkali activated IPs should be further explored in order to have a better understanding of the mixed-alkali effect.

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