

BINARY, TERNARY AND QUATERNARY Fe-RICH SLAGS: INFLUENCE OF Fe AND Si SUBSTITUTION BY Ca AND Al ON THE ATOMIC STRUCTURE AND REACTIVITY

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Introduction

Alkali activated materials (AAMs) and inorganic polymers (IPs) are promising alternatives for ordinary Portland cement (OPC) in terms of CO₂ emissions and advanced engineering properties.¹ Non-ferrous metallurgy slags, in addition to the more commonly used alumino- or calcium-silicates, serve as a potential source material for the synthesis of AAMs and IPs.¹ These slags are chemically rich in iron and silica with small amounts of calcium, aluminium and magnesium oxide. Depending on the treatment process and the place/time of origin, variations in chemical composition and mineralogy are often observed. These variations lead to fundamental differences on the local structure of the precursors, having a great impact on the reaction kinetics and therefore the final properties of the produced IPs.^{2,3} The work in this study reveals details on the effect of altering the amount of network modifying and forming elements on the local structure and reactivity of iron-rich slags. For this purpose, synthetic slags in the FeO_x-SiO₂ binary, FeO_x-CaO-SiO₂ ternary and FeO_x-CaO-Al₂O₃-SiO₂ quaternary system, representing compositions of non-ferrous metallurgy slags, were investigated. ⁵⁷Fe Mössbauer spectroscopy experiments were carried out to study the effect on the state and the environment of Fe ions in the structure after the incorporation of Ca and Al ions. The reactivity of the slags was studied by using isothermal calorimetry and the results are presented herein.

Experimental procedure

Three different synthetic slags were produced, starting from the FeO_x-SiO₂ binary system and subsequently incorporating Ca and Al. The slags were synthesised by melting and quenching pure metal oxides (Fe+Fe₂O₃, SiO₂, CaO, Al₂O₃).³ They were, then, milled in a disc mill (Fritsch Pulverisette 13) and in an attritor mill (Wiener 1S) until a Blaine specific surface area of 4000 ± 200 cm²/g. The chemical composition of

the slags were measured by semi-quantitative wavelength dispersive X-ray fluorescence (XRF) on a Philips PW2400 spectrometer and the crystalline phases were assessed by X-ray diffraction (XRD) measured on D2 Phaser diffractometer (Bruker) (Table 1). Isothermal calorimetric experiments were performed in a TAM Air Isothermal Calorimeter at 20°C. An alkaline solution was prepared for this purpose with molar ratios $\text{SiO}_2/\text{Na}_2\text{O} = 1.6$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 25$. ^{57}Fe Mössbauer spectroscopy measurements were collected in transmission geometry on a constant acceleration spectrometer at 77 K, equipped with a ^{57}Co (Rh) source and calibrated with $\alpha\text{-Fe}$. The IMSG software was used for the fitting of the spectra.⁴

Table 1: Chemical composition in wt% of slags obtained by XRF (estimated relative error 10%), the amount of glass phase in wt% and the crystalline phases observed by XRD

	FeO (wt%)	SiO ₂ (wt%)	CaO (wt%)	Al ₂ O ₃ (wt%)	Others (wt%)	Glass fraction (wt%)	Crystalline phases
Binary	65.6	33.0	0.0	0.0	1.4	87	Fayalite
Ternary	48.3	33.8	16.7	0.0	1.2	93	Fayalite Magnetite
Quaternary	47.8	34.1	12.2	5.1	0.8	97	Fayalite Magnetite

Results and discussion

The spectra for all the samples mainly consist of paramagnetic doublets dominated by contributions corresponding to Fe^{2+} states.⁵ Minor contributions of magnetically split components in the spectra of the ternary and quaternary slag samples suggest the presence of minor amounts of magnetite. The resulting Mössbauer hyperfine parameters (MP) are listed in Table 2.

The MP values of the C1, C2 Fe^{2+} and C3 Fe^{3+} states are quite similar for all samples (see Table 2) and correspond to the glassy phase of the slags.^{3,6} An extra C4 Fe^{2+} state is observed only in the spectrum of the binary slag, it acquires MP values that correspond to those of crystalline fayalite⁵ and its presence is attributed to the higher crystallinity³ of this sample. The local environment of Fe ions in the glassy phase of the slags seems to remain consistent after the incorporation of Ca and Al in the FeO-SiO_2 system. The main differences lie with the presence of crystalline phases.

Table 2: ^{57}Fe Mössbauer hyperfine parameters of the components used to fit the spectra of the slags

Sample	IS (mm/s)	QS (mm/s)	B_{hf} (kOe)	ΔQS or ΔB_{hf} (mm/s or kOe)	AA (%)	Component
Binary	1.25	2.42	0	0.4	33	C1
	1.14	1.95	0	0.67	48	C2
	0.65	1.19	0	0.22	4	C3
	1.28	3.05	0	0.1	15	C4
Ternary	1.24	2.49	0	0.40	33	C1
	1.12	1.98	0	0.60	57	C2
	0.58	1.17	0	0.33	10	C3
Quaternary	1.22	2.44	0	0.42	33	C1
	1.12	1.93	0	0.60	53	C2
	0.59	1.15	0	0.38	11	C3
	0.44	0.01	502	15.23	3	MC1

IS: Isomer shift (relative to $\alpha\text{-Fe}$ at 300 K), QS: quadrupole splitting, ΔQS : spreading of QS, B_{hf} : magnetic field, ΔB_{hf} : spreading of B_{hf} , AA: relative absorption area; Errors: ± 0.02 mm/s for IS and QS, ± 0.3 T for B_{hf} and $\pm 5\%$ for AA

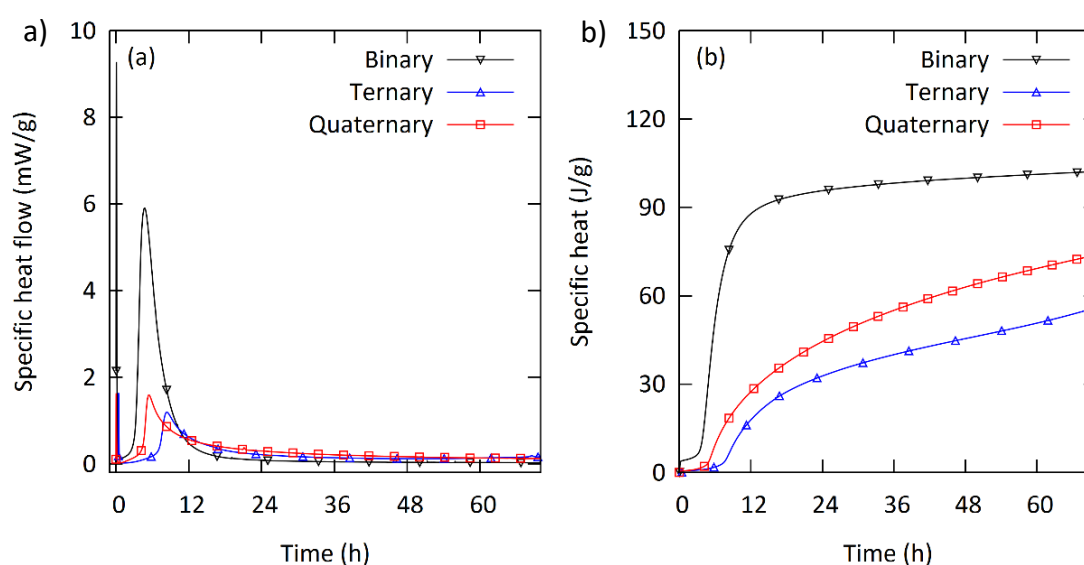


Figure 1: a) Specific heat flow and b) specific heat in isothermal calorimetry at 20°C during the first 70 h after mixing, normalised by the weight of the slag

Isothermal calorimetry measurements were performed to assess the reactivity of the slags in terms of heat release. The maximum heat flow (Figure 1) of the binary and quaternary samples is observed at around 4 hours while the specific heat is higher for the binary sample. For the ternary sample, the maximum heat flow occurs at around 7 hours with lower specific heat with respect to the other two samples. It should be noted that faster reaction kinetics (in terms of heat release) do not

necessarily lead to better properties of the produced inorganic polymer (*e.g.* higher compressive strength). The origin of the high cumulative heat of the binary system is not clear at this point, although, also looking into earlier work² it seems to be connected with the content of Fe in the slag.

Conclusion

Altering the amount of network modifying and forming elements, by incorporating Ca and Al in the FeO-SiO₂ system does not affect the state and the environment of Fe ions in the structure extensively when the amount of Si is not adapted. The reactivity, however, is significantly affected by the binary slag producing more heat in isothermal calorimetry.

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