

# EFFECTS OF Ca-RICH SLAG ADDITION ON FAYALITE SLAG-BASED INORGANIC POLYMERS

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## Introduction

Inorganic polymers (IP) are typically produced by mixing alkali activators with solid precursors<sup>1</sup>. Next to alumina- and silica-containing precursors, the feasibility of making IP by using water granulated fayalite slag (Fay), a Fe-rich by-product from copper metallurgy, has been already demonstrated<sup>2</sup>. In fact, by scanning a wider envelope of non-ferrous slags for the synthesis of IP, it was also found that higher calcium contents in the slag delivered higher compressive strength<sup>3</sup>. This is related to the higher glass forming ability of the systems with higher CaO/FeO and CaO/(FeO+SiO<sub>2</sub>) ratios, thus, the more amorphous and reactive starting slags, but it might also be linked to the different chemistry of the IP formed<sup>4</sup>. If the second is true, this would imply that as the chemistry of the IP shifts from the (Na-)Fe-Si-O to the (Na-)Fe-Ca-Si-O domain, the compressive strength of the emerging material also increases. Conceptually, this could be explored if it is true by doping the system with Ca<sup>2+</sup>, yet, it is known that the solubility of Ca(OH)<sub>2</sub> at high pH is very low<sup>5</sup>. This is however not a problem for ground granulated blast furnace slag (GGBFS) and ladle metallurgy stainless steel slags (LM), both documented to lead to C-S-H reaction products when alkali activated. By serendipity, both afore mentioned slags are available in Flanders in substantial volumes, which opens a window of industrial symbiosis for the synthesis of slag-only engineered materials. Therefore, in the research herein, binary mixtures of GGBFS and LM with Fay (slag) were developed, in an attempt to deliver IP with higher mechanical strength.

## Materials and Methods

Industrially produced Fay, GGBFS and LM (slags) from Belgian metallurgical companies were used. The chemical composition of these slags was determined by X-ray fluorescence spectroscopy (XRF, Philips PW 2400). X-ray diffraction analysis (XRD, PW 1830 Philips) was used for minerals identification, both for the slags and the synthesised inorganic polymers. The qualitative analysis was performed using the "X'Pert High Score Plus" PANalytical software. For quantitative analysis, 10 wt% of analytical grade crystalline corundum Al<sub>2</sub>O<sub>3</sub> was used as the internal standard and the "Topas® Academic" software was subsequently used for the calculation of the amount of the amorphous phase.

The as-received slags were pretreated to obtain precursor powders with similar particle size distribution (PSD), measured by laser scattering (MasterSizer Micro Plus Malvern). For this purpose, the slags were initially dried at 100°C for 24 h, the Fay and GGBFS were then disk milled, and at the end, all slags were ball milled with stainless steel balls till the desired finesses was achieved. LM is already fine as received, thus there is no need for disk milling.

For sample preparation, three types of samples were synthesised (Table 1). GGBFS and LM were added at identical FeO/CaO molar ratio (2.5) to enable direct comparison of two Ca-rich slag blended IP systems. 100% Fay based IP was named as “100Fay”, while samples with 20 wt% GGBFS and 15.75 wt% LM addition were named as “20GFay” and “15.75LFay” separately. Solutions of NaOH and Na-silicate, mixed in SiO<sub>2</sub>/Na<sub>2</sub>O and H<sub>2</sub>O/Na<sub>2</sub>O molar ratios of 1.2 and 22.2, were used as activator and added at the solid to liquid (S/L) ratio of 5.5. Distilled water was added to keep the workability of the IP pastes in the mixing process (Table 1). The IP paste was cast in rectangular plastic moulds (25 mm × 25 mm × 20 mm), then vibrated for 2 minutes on a vibration table to remove the possible entrapped air. Afterwards, all samples were pre-cured for 24 hours at 90°C in an autoclave under atmospheric pressure, and then de-moulded and cured in a moisture room with 90% relative humidity at 21°C for another 6 and 27 days. The 7-day and 28-day compressive strength was measured using a Schenck-RM100 compression testing machine, at a crosshead speed of 2 mm/min.

**Table 1:** The percentages of water added with respect to the amount of activating solution and resultant S/L ratios

Sample Name	100Fay	20GFay	15.75LFay
Ca additives added (wt%)	-	20	15.75
Water added (wt%)	-	4.7	10.5
S/L ratio	5.5	5.3	5.0

## Results and Discussion

### Raw materials and reaction products

**Table 2:** Chemical composition of slags used in this study

Oxide (wt%)	CaO	FeO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	ZnO	CuO	MnO	Cr <sub>2</sub> O <sub>3</sub>	F	others
Fay	1.9	41.8	31.3	7.9	-	0.3	1.1	9.6	0.6	0.7	1.2	-	3.7
GGBFS	43.2	0.3	34.2	8.7	0.4	0.4	9.0	-	-	0.3	-	-	3.5
LM	57.8	0.3	28.5	1.2	-	-	8.0	-	-	0.3	0.6	2.6	0.8

The XRF results (in Table 2) indicate that while GGBFS and LM are Ca-rich materials, Fay is rich in Fe and Si but poor in Ca consistent with that reported in literature<sup>2,6</sup>. The XRD results show that Fay has 77 wt% amorphous contents with fayalite and hercynite

being the two main crystalline phases. GGBFS is an essentially amorphous material (95 wt% amorphous contents) with merwinite being the only crystalline phase detected. LM was mainly crystalline with 20 wt% amorphous contents. Most of the Ca present is in the dicalcium silicate ( $\gamma$ -C<sub>2</sub>S), cuspidine, bredigite and mayenite. In synthesised IP, the QXRD results show no new crystalline phases for all formulations developed.

### Compressive strength

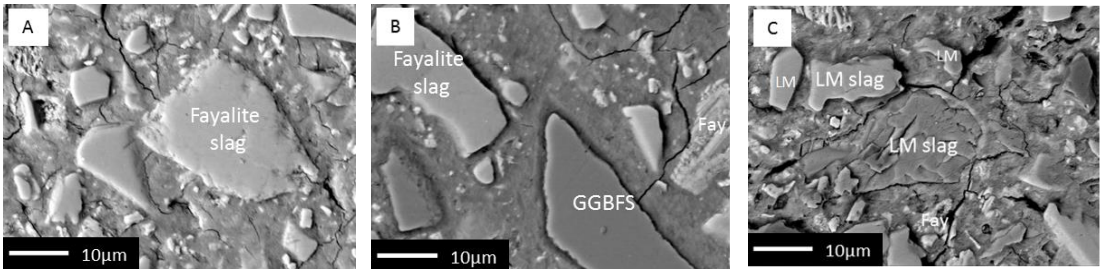
Table 3 shows that the compressive strength of 100Fay and 15.75LFay does not change over time after 7 days curing. Only in 20GFay the strength continues to increase after 7 days. When compared with 100Fay, the addition of GGBFS contributes to increased mechanical strength, but the inclusion of LM shows a negative impact on the strength development.

**Table 3:** Compressive strength of synthesised inorganic polymers

Samples		100Fay	20GFay	15.75LFay
Compressive Strength (MPa)	7-day	66.6±1.1	93.8±1.6	42.2±1.9
	28-day	64.7±1.7	122.0±6.4	43.7±1.8

### Microstructure

Backscattered electron (BSE) imaging of 28-day 100Fay sample is shown in Figure 1a. The light grey particles corresponding to unreacted Fay are well distributed and embedded in the dark grey binder matrix. Two different morphologies were observed for unreacted Fay: undissolved glass phase with flat-polished surface and selectively dissolved Fay with characteristic grooved surface of fayalite dendrites. It is evident that micro-cracks are present in the binder phase. The formation of these cracks is due to shrinkage stress introduced during drying. It seems that the propagation of these cracks is always hindered by slag particles.



**Figure 1:** BSE images of 28-day IP samples (×2000) (a) 100Fay, (b) 20GFay (c) 15.75LFay. Fay: undissolved Fay

In the BSE image of 28-day 20GFay (in Figure 1b), three different greyscale intensities are observed. The unreacted blast furnace slag enriched in Ca corresponds to the dark grey particles while the light grey particle is remnants of the Fe-rich Fay. The phase surrounding the unreacted particles is the binder phase with slightly lighter colour than the GGBFS particles. Compared with the binder phase of 100Fay, the addition of GGBFS leads to a denser binder phase formed with much smaller and fewer

microcracks, especially in the region surrounding undissolved GGBFS. This might be due to the Ca diffused outward from the outer rim of the large GGBFS slag particles, which participated in the binder formation, resulting in a stronger interfacial bonding with the matrix.

In the micrograph of 28-day cured 15.75LFay sample (Figure 1c), big cracks and pores were observed. This can be attributed to the low workability of the IP paste in sample preparation due to high water absorption of LM precursor powders. The small whitish particles with grooved surface are unreacted Fay. Combined with EDS analysis, particles with featured extensive network of cracks can be identified as  $\gamma$ -C<sub>2</sub>S from LM<sup>7</sup>. Compared with GGBFS, the amount of structural elements (Si and Al) dissolved from LM is relatively low. In sample preparation, extra water was added to modify the workability of the paste (in Table 1), which also contributes to the formation of shrinkage cracks.

## Conclusions

In the samples with 20 wt% GGBFS, the compressive strength reached 120 MPa, which is almost two times of that of 100Fay. In contrast, in the sample with 15.75 wt% LM slag, the compressive strength decreased around 30% with respect to 100Fay. It is highly possible that the strength increase in 20GFay was due to the high reactivity of GGBFS in the presence of alkaline activating solution resulting in the formation of a compact microstructure. The strength reduction in 15.75LFay can be attributed to the low reactivity of LM slag, the low workability of blended IP paste and the extra water added during sample preparation. The exact role of Ca, and whether it participates in C-S-H formation or not, remains an open research question.

## References

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