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# SYNTHESIS AND HIGH TEMPERATURE TRANSFORMATIONS OF Fe-RICH INORGANIC POLYMERS

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## Introduction

As it is already known, severe spalling occurs when concrete is subjected to temperatures higher than 300 °C, causing serious damage to concrete structures. Being a hydrate, hardened OPC concrete can release water in an explosive manner when subjected to the sudden heat produced by an intense fire. Cracking and spalling are common occurrences when normal concrete is exposed to such conditions. The sudden loss of structural strength can result in catastrophic collapse.

Unlike OPC, inorganic polymer is effectively a glass. The absolute volume of water contained in the pore structure is low, and upon thermal treatment, phase transformations are expected to occur in conjunction with liquid phase sintering. To that extent, an inorganic polymer can also be seen as a water insoluble, unfired, ceramic.

In this work, a fayalite slag-based inorganic polymer is investigated for its potential to be used as a heat resistant material. The effect of various additions of refractory  $\text{Al}_2\text{O}_3$  and the influence of two different types of activating solutions, Na-based and K-based, were also studied.

## Materials and Methods

A water granulated fayalitic slag, FS, was used. The chemical composition was determined by XRF (PW 2400 Philips). Preparation of the samples involved mixing the slag with 5 wt.% and 10 wt.% of analytical grade  $\text{Al}_2\text{O}_3$  and activating solution. Two types of activating solutions were used, Na-based and K-based: in the first solution, the  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio was 1.2 and in the second one the  $\text{SiO}_2/\text{K}_2\text{O}$  ratio was 1.1. The solid/activating solution ratio was kept constant at 5.4 for the samples with

Na-based activating solution and at 5.6 for the samples with K-based. As the viscosity of the pastes varied when  $\text{Al}_2\text{O}_3$  was added, small additions of water were made to adjust it at comparable levels (max 3 wt.% water/paste). The resulting paste was poured into rectangular plastic moulds (25 mm × 25 mm × 20 mm). Samples were cured for 24 hours at 90 °C in a steam autoclave and then in a moisture room (90 % humidity) for 28 days. Afterwards, part of the samples was heated at 3 °C/min, till 500 °C and 800 °C, under static atmosphere and with 3 hours soaking time; cooling took place inside the muffle furnace. Mechanical properties were measured in compression, with a head displacement rate of 2 mm/min (Model 8872, Instron). For the analysis of the microstructure and microchemistry, a FEG-EPMA (JXA-8530F, JEOL) operated at 15 kV and 15 nA, was employed on polished surfaces after carbon-coating. The crystal structure of the slag and samples was determined by quantitative X-ray powder diffraction analysis (D500, Siemens). Diffraction patterns were measured in  $2\theta$  range of 10–70° using  $\text{CuK}\alpha$  radiation of 40 kV and 40 mA, with a 0.02° step size and step time of 2 s.

## Results and discussion

The chemical composition of FS appears in Table 1. The main components of the slag are FeO,  $\text{SiO}_2$  and ZnO. The material also contains small amounts of  $\text{Al}_2\text{O}_3$ .

**Table 1:** Chemical composition of the slag used in the experiments

FS	FeO	$\text{SiO}_2$	ZnO	$\text{Al}_2\text{O}_3$	CaO	$\text{Cr}_2\text{O}_3$	$\text{P}_2\text{O}_5$	MgO	PbO	MnO	CuO	$\text{SO}_3$
wt.%	49.57	27.13	8.35	6.82	1.61	1.05	0.98	0.98	0.61	0.56	0.52	0.49

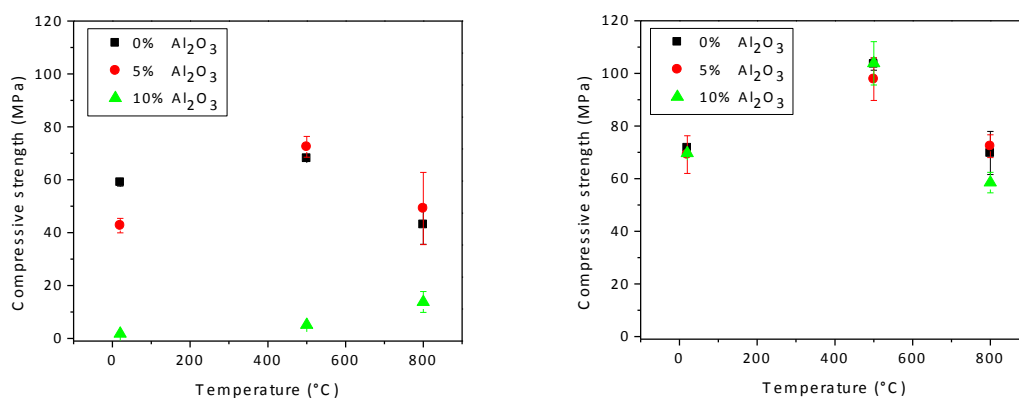
The samples after the heat treatment presented a reddish colour which becomes brighter as the temperature is increasing, indicating changes in the microstructure and most probably the oxidation of iron and/or formation of hematite.

## Mechanical properties

In Figure 1 the results from the compressive strength tests are presented. It is observed that the heat treatment had a different impact per case, with the highest strength in general attained after firing at 500 °C. On the other hand,  $\text{Al}_2\text{O}_3$  addition had an influence depending on the activation solution used. In the binder formed with Na-silicate at room temperature, the addition of  $\text{Al}_2\text{O}_3$  is clearly decreasing mechanical strength. For firing at 500 °C the values are always higher or comparable to those obtained after curing at room temperature, regardless of the  $\text{Al}_2\text{O}_3$  content. For firing at 800 °C, there is a decrease of strength compared to 500 °C for 0 wt.%  $\text{Al}_2\text{O}_3$  and 5 wt.%  $\text{Al}_2\text{O}_3$  addition, but remained at a slightly higher level compared to

room temperature and 500 °C when 10 wt.%  $\text{Al}_2\text{O}_3$  was added. On the contrary, for the samples with K-silicate, the impact of  $\text{Al}_2\text{O}_3$  is minimal; the samples have almost the same strength regardless of the percentage of  $\text{Al}_2\text{O}_3$  added. Also, as an overall observation, all the samples formed with K-based solutions have higher compressive strength than the ones where Na-based was used.

The results described above, i.e. high impact of  $\text{Al}_2\text{O}_3$  on Na-based inorganic polymers and almost no impact on K-based plus the overall better performance of the samples activated with K-silicate, could be attributed to the differences in gel structure and associated viscosity. It is known that the  $\text{K}^+$  ion size is larger than the one of  $\text{Na}^+$ . It is suggested that the smaller silicate monomers and dimers favour ion pairing with the smaller Na cations, whereas K cations favour ion pairing with larger silicate oligomers.<sup>2</sup> Therefore, larger oligomer chains could exist in K-solutions which may result in forming denser gels and possibly lead to higher compressive strength, than in the case of Na-based solutions.<sup>3</sup> At the same time, the K-silicates solutions were observed to have lower viscosities<sup>4</sup> than the analogues of Na-silicates, which may be due to the different extents of hydration of  $\text{Na}^+$  and  $\text{K}^+$ .<sup>5</sup> This property allows higher solid/liquid ratios when K-based solution are used (for a comparable viscosity), which may further lead to a more dense microstructure, phenomena observed by other authors as well.<sup>6</sup>



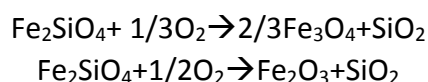
**Figure 1:** Compressive strength results for activation with Na-silicate (left) and K-silicate (right)

### Crystallographic structure

All the samples cured at room temperature, regardless of the activating solution used and the  $\text{Al}_2\text{O}_3$  added, have fayalite and hercynite as the two main phases. These are also the main phases of the initial precursor slag. In fact, in none of the samples

containing Al<sub>2</sub>O<sub>3</sub> (with or without heat treatment), Al<sub>2</sub>O<sub>3</sub> diffraction peaks could be observed. The only plausible explanation is that the quantity added was too low to be detected with this technique, taking into consideration also the fact that the Al<sub>2</sub>O<sub>3</sub> used was of low crystallinity.

After firing, the assemblage of the crystalline phase changes. In all the samples activated with Na-silicates cured at 500 °C, laihunite (Fe<sup>2+</sup>Fe<sup>3+</sup><sub>2</sub>(SiO<sub>4</sub>)<sub>2</sub>) was detected as a new phase, a crystal derived from the oxidation of fayalite. At 800 °C, laihunite disappeared and instead hematite and magnetite were formed. The new peak formed at 21.68 2θ is probably sodium aluminum silicate (Na<sub>96</sub>Al<sub>96</sub>Si<sub>96</sub>O<sub>384</sub> PDF:39-223) or silicon dioxide (SiO<sub>2</sub> PDF:27-605). For the samples with K-silicates after firing, there was a clear difference between the ones with and without Al<sub>2</sub>O<sub>3</sub>. The samples with no Al<sub>2</sub>O<sub>3</sub> additions cured at 500 °C had hematite, magnetite and hercynite as main phases, with a low content of fayalite still remaining. A small peak at 21.61° 2θ was observed which was attributed to silicon oxide (SiO<sub>2</sub> PDF:27-605). The above are attributed to the decomposition (“oxygenolysis”) of fayalite under oxidative atmosphere, towards iron oxides and silica, according to the following reactions:<sup>7</sup>



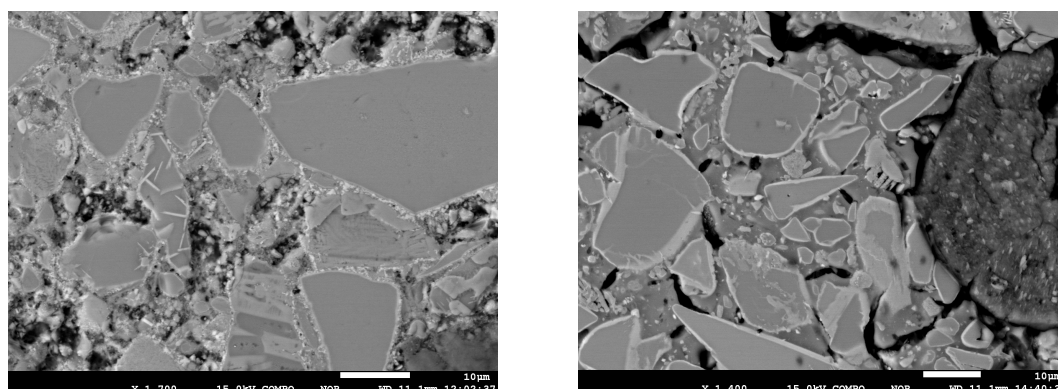
The other two types of samples cured at 500 °C with 5 wt.% and 10 wt.% Al<sub>2</sub>O<sub>3</sub> are similar with the samples prepared with Na-based activating solution at 500 °C and present only three main phases, i.e. hercynite, fayalite and laihunite; no hematite, silica or magnetite was found, suggesting that the addition of Al<sub>2</sub>O<sub>3</sub> is affecting the decomposition and further oxidation of fayalite.

In all the K-silicates based samples heat-treated at 800 °C similar mineral phases were found: hercynite, fayalite, hematite and magnetite. For the sample with no Al<sub>2</sub>O<sub>3</sub> addition though, the peak at 44.44° 2θ (which in the other samples with 5 wt.% and 10 wt.% Al<sub>2</sub>O<sub>3</sub> was attributed to hercynite) is becoming more intense. An explanation is that another phase is formed, possibly potassium aluminum silicate (KAlSi<sub>3</sub>O<sub>8</sub> PDF:20-848 or K<sub>1.25</sub>Al<sub>1.25</sub>Si<sub>0.75</sub>O<sub>4</sub> PDF:32-731) or potassium aluminum oxide (K<sub>1.5</sub>Al<sub>11</sub>O<sub>17.25</sub> PDF:39-50).

## Microstructure

Microstructural analysis indicates that the binder formed with K-silicate is better developed and denser than the one formed through activation with Na-silicate. This difference can be observed at room temperature, but is slightly more obvious for the samples fired at 500 °C. For the samples treated at 800 °C, the difference is becoming obvious and there are clear transformations detected, as illustrated in Figure 2 for

the samples with 5 wt.%  $\text{Al}_2\text{O}_3$ . For both samples, activated either with Na- or K-silicate, the amount of crystals has increased at the expense of the binder compared to the ones without heat treatment. In addition, the remaining binder in the two samples looked quite different: for the Na-activated it is rather inhomogeneous with micro-porosity whereas for the K-activated sample there are highly dense regions with micro-cracks occurring between the different dense pools (probably because of the difference in the thermal coefficients of the phases). Besides the formation of new crystalline grains from the binder, the heat treatment at 800 °C has caused the formation of rims at the boundaries of the slag grains. This layer appears to be slightly different between the Na-silicate and K-silicate samples. For the sample with Na-silicate, a thin layer of a new phase has formed at the edges together with very small Fe-rich crystals, however, in the samples with K-silicate this layer is thicker and less Fe-rich crystals are present. Further analysis is required to relate the changes in microstructure observed with EPMA to the XRD analysis.



**Figure 2:** Sample with 5 wt.%  $\text{Al}_2\text{O}_3$ , treated at 800 °C, after activation with Na-silicate (left) and K-silicate (right)

## Conclusion

The inorganic polymer samples based on fayalite slag and cured at room temperature, reached compressive strength approximately 60 MPa when activated with Na-silicate and approximately 70 MPa when activated with K-silicate. The addition of  $\text{Al}_2\text{O}_3$  in the Na-silicate compositions lead to a decrease in compressive strength, however, in the case of K-silicate formulations and the same curing/firing temperature, the impact was rather small. The highest compressive strength obtained exceeded 100 MPa and was obtained for activation with K-silicate and firing at 500 °C.

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