

The use of ATR-FTIR spectroscopy in the analysis of iron-silicate inorganic polymers

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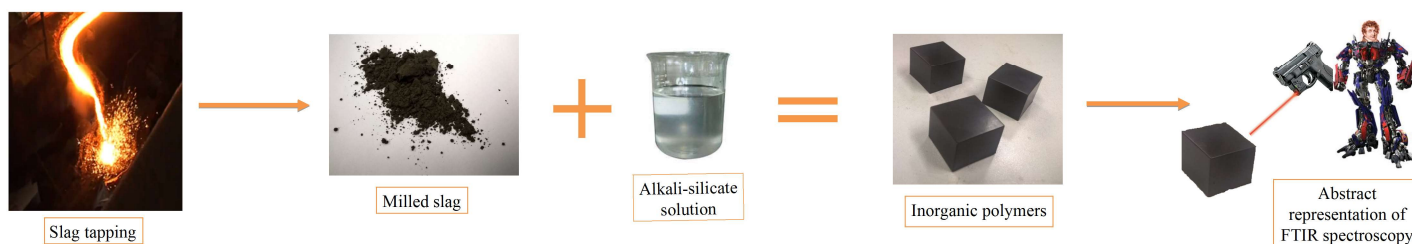
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Introduction

FTIR spectroscopy has been crucial for the analysis of silicate glasses¹, cementitious binders² and inorganic polymers (IP)^{3,4}. The spectra can be coupled to the connectivity of the silicate network^{1,2} and the formation or transformation of phases can be observed for cements and IP^{2,4}. The present paper provides an overview of the ATR-FTIR spectra of iron-silicate slags and IP made therefrom. The considered slags are not applied in cementitious applications today: copper slag^{5,6,7}, plasmastone^{8,9}, treated bauxite residue¹⁰. The overview aims to expose similarities and differences between particular slags, which can increase the understanding of the complex spectra.

Methodology

Attenuated total reflectance Fourier-transformed infrared (ATR-FTIR) spectra from powdered samples were acquired on a Bruker Alpha-P with a diamond crystal, from 4000 cm⁻¹ to 380 cm⁻¹, at a resolution of 4 cm⁻¹ and with at least 32 scans per measurement; the measurements were supported by Opus software. For the calculations of the non-bridging oxygens (NBO), Fe²⁺ is considered to add 2 NBO and Fe³⁺ is assumed to take 1 NBO away by using an alkali atom as charge balancer. This is an approximation, as the role of Fe^{2+/3+} in silicate glasses can possibly vary as a function of the chemical composition and is in several cases still under discussion¹¹.



Results

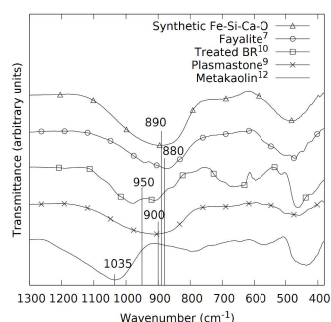


Figure 1: FTIR spectra of precursors

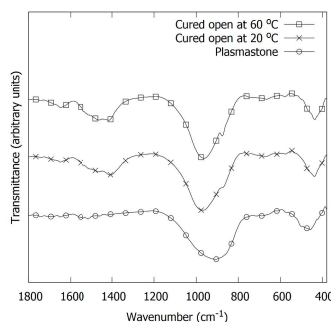


Figure 2: FTIR spectra of plasmastone and its IPs

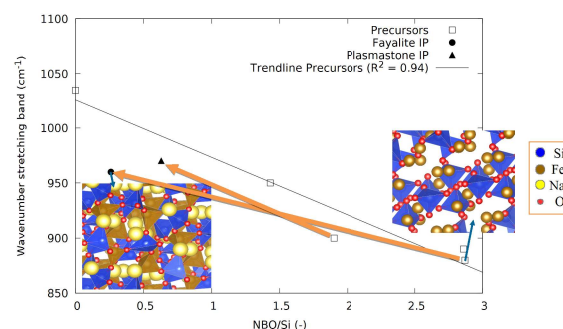


Figure 3: Relation between Si-O stretching band position and NBO/Si in the samples. The structures represent fayalite and its IP

Discussion

All samples show the Si-O stretching ($\pm 850\text{--}1050\text{ cm}^{-1}$) and rocking bands ($\pm 400\text{--}500\text{ cm}^{-1}$), Figure 1. The treated bauxite residue (treated BR) shows extra bands around $600\text{--}700\text{ cm}^{-1}$, corresponding to iron oxide phases¹⁰. The broadness of the bands in the spectra is in agreement with the amount of amorphous/glassy phase in the residues, which follows the trend plasmastone⁹ \approx synthetic Fe-Si-Ca-O > fayalite⁷ > treated BR¹⁰. The sharper features in the spectrum of the fayalitic slag correspond to different stretching modes of crystalline fayalite¹³. The Si-O stretching band decreases in wavenumber when the Si-O bond is strained or increases in length, e.g. by substitution of Si in the network (with Al/Fe)^{4,14} or the increase in non-bridging oxygens (NBO)^{4,15}. The mass of the counter-vibrating atom was shown to have a less significant influence¹³ and therefore, the precursor slags exhibit a good relation between the position of the Si-O stretching band and the NBO per silica atom, shown in Figure 3.

In Figure 2, the Si-O stretching band seems to shift from the slag to the IP from approximately 900 cm^{-1} to 950 cm^{-1} . This can be attributed to the slag dissolution, which leads to a decrease in the intensity of the initial band and the formation of a new band associated with the IP network. This new material is expected to be more Si-rich, in view of the silicates present in the activating solution. However, calculating the addition of silica and comparing this with the stretching band position, this is not sufficient for explaining the difference between the slag and IP. Additional factors can slightly affect the final outcome: the amount of non-bridging oxygen sites increases as the Na⁺ (or K⁺) increase, the choice of Na⁺ vs K⁺, next to the content of H₂O and silicates, which influence the degree of dissolution and polycondensation. A phenomenon that can help to explain the large extent of the difference between the slag and IP band position is the oxidation of Fe²⁺ to Fe³⁺ (observed by ⁷ and ⁹), disregarding the kind of structure the Fe ends up in. Assuming the participation in the silicate network (from ongoing work), this structural change is illustrated on Figure 3.

Conclusions

For iron-silicate precursors (with Fe in the 2+ state), a relation is observed between the amount of NBO/Si and the position of the Si-O stretching band, while the broadness of this band corresponds to the amorphicity of the material. The synthesis of the IP results in a decline of the intensity of the Si-O stretching band of the slag and the formation of a new band, at higher wavenumbers ($\pm 950\text{ cm}^{-1}$). This is because the slag was dissolved, more Si was added to the system, the Fe was oxidized and some other, minor factors.

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