

THE USE OF ATR-FTIR SPECTROSCOPY IN THE ANALYSIS OF IRON-SILICATE INORGANIC POLYMERS

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Introduction

Fourier transformed infrared (FTIR) spectroscopy has seen intensive use in the structural analysis of silicates. Especially when the material is amorphous/glassy, disabling the applicability of X-ray diffraction, the information gained from FTIR spectroscopy is highly important. 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}.

A glass of pure SiO₂ shows only 3 bands in the FTIR spectrum, associated with 3 kinds of vibrations: stretching vibrations ($\pm 1100\text{ cm}^{-1}$) and two modes of bending vibrations, out-of-plane bending ($\pm 500\text{ cm}^{-1}$), commonly referred to as “rocking”, and in-plane bending ($\pm 800\text{ cm}^{-1}$), commonly just referred to as “bending”¹. In aluminosilicate IP, “geopolymers”, the evolution of the spectrum when adding the alkaline activator to metakaolin is mainly seen as a shift of the stretching band to lower wavenumbers^{4,5}. Other features tend to appear, which can be associated to water in the IP system (bands at $\pm 3600\text{ cm}^{-1}$ and $\pm 1650\text{ cm}^{-1}$) or the formation of carbonates (bands at $\pm 1500\text{ cm}^{-1}$ and $\pm 850\text{ cm}^{-1}$)⁶.

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^{7,8,9}, plasmastone^{10,11}, treated bauxite residue¹². The overview aims to expose similarities and differences between particular slags, which can increase the understanding of the spectra and ultimately, the structure of the materials under study.

Experimental

The slags and IP were investigated by 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.

Results and Discussion

Metakaolin¹³ is used as a reference. The slags in Figure 1a are all semi-crystalline with chemical composition mainly FeO, SiO₂ and minor contents of Al₂O₃ and CaO (see referred documents). All samples show the Si-O stretching ($\pm 850\text{--}1050 \text{ cm}^{-1}$) and rocking bands ($\pm 400\text{--}500 \text{ cm}^{-1}$). The in-plane bending band ($\pm 700\text{--}800 \text{ cm}^{-1}$) is not clear for every sample, which is commonly observed for silicates with a high content of network modifier elements¹. The treated bauxite residue (treated BR) shows extra bands around 600–700 cm^{-1} , which is attributed to iron oxide phases in this particular residue¹². 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 plasmastone¹¹ \approx synthetic Fe-Si-Ca-O > fayalite⁹ > treated BR¹². The sharper features in the spectrum of the fayalitic slag correspond to different vibrational modes of crystalline fayalite¹⁴. 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)^{4,15} or the increase in non-bridging oxygens (NBO)^{4,16}. Because of the latter, slags incorporating more network modifying elements have the band at a lower wavenumber.

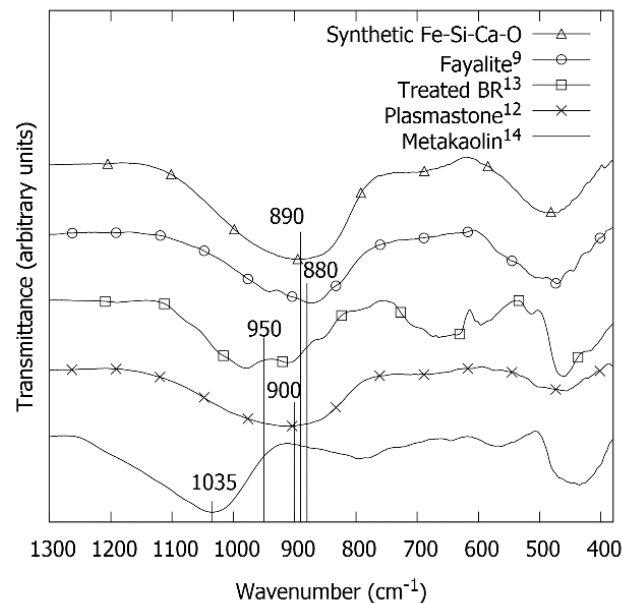


Figure 1: Infrared spectra of the studied precursors with indication of the position of the Si-O stretching band

After the synthesis of the IP (synthesis conditions in the referred documents) changes in the spectra involved new features, as well as shifts of bands that were already observed in the slags (Figure 2). New bands show the presence of water at $\pm 1650\text{ cm}^{-1}$ and $\pm 3600\text{ cm}^{-1}$ (the latter not shown in Figure 2) and carbonates at $\pm 1500\text{ cm}^{-1}$ and $\pm 870\text{ cm}^{-1}$. Another band is observed at $\pm 1400\text{ cm}^{-1}$. As this band is also observed for a sample that was not in contact with air before the measurement (Figure 2a, cured in closed container), the formation of a carbonate is unlikely. This band might indicate the presence of hydroxyl groups in the material.

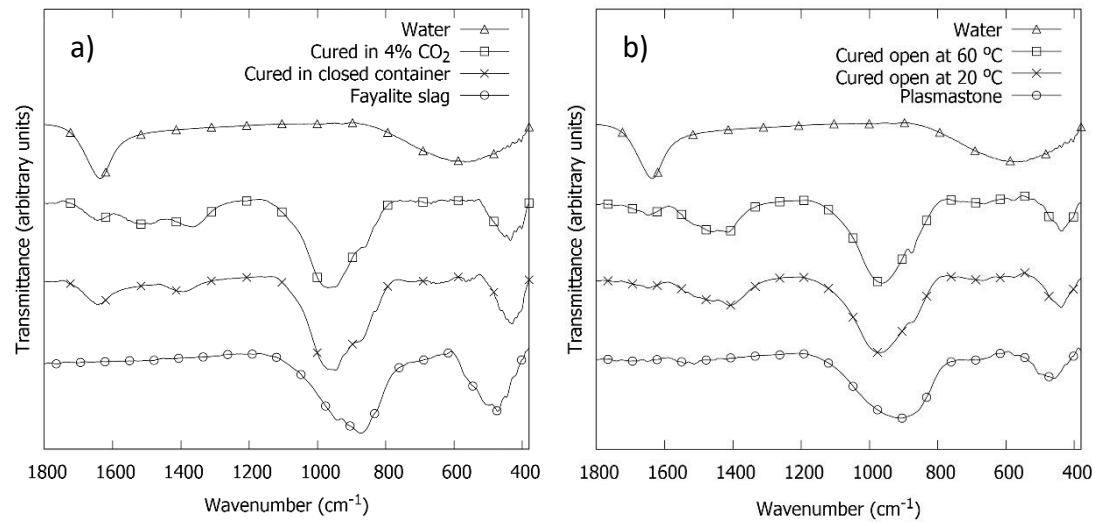


Figure 2: Infrared spectra of the fayalite slag (a)⁹ and plasmastone (b)¹¹ based IP, including precursors and water as reference

The Si-O stretching band shifts to higher wavenumbers 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 (demonstrating the formation of the IP). This new material is expected to be more Si-rich, in view of the silicates present also in the activating solution, and possibly, with a higher ratio of $\text{SiQ}^2/\text{SiQ}^1$ structural units compared to the initial precursor. Additional factors also affect the final outcome, only to mention a few: 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 H_2O and silicates, influences the degree of dissolution and polycondensation, and there is oxidation⁹ of Fe^{2+} to Fe^{3+} , with probable incorporation into network forming positions.

Conclusions

Like for silicate glasses and aluminosilicate geopolymers, structural information on iron-silicate inorganic polymers can be gained using FTIR spectroscopy. As such, they seem to comply with the general rules defined for glassy silicate materials. A relation can be found between the position of the Si-O stretching band and the chemical

composition of the inorganic polymer, while the formation of carbonates and the presence of water (free or bound) can be detected.

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