

INVESTIGATING THE PROPERTIES OF IRON IN INORGANIC POLYMERS WITH ^{57}Fe MÖSSBAUER SPECTROSCOPY

Alexios P. DOUVALIS¹, Arne PEYS², Silviana ONISEI², Yiannis PONTIKES²

¹ Department of Physics, University of Ioannina, 45110 Ioannina, Greece

² Department of Materials Engineering, KU Leuven, 3001 Heverlee, Belgium

*adouval@uoi.gr, arne.peys@kuleuven.be, silviana.onisei@kuleuven.be
yiannis.pontikes@kuleuven.be*

Introduction

Inorganic polymer (IP) materials are promising alternatives for cementitious binders because of their lower environmental impact¹, which originates from the facts that less CO₂ is released during the production of the precursor, and also importantly, industrial residues can be used. These residues are not only ground granulated blast furnace slag or fly ash, which are commonly used in blended cements, but also Fe-rich slags from the non-ferrous industry, that have been proven to form IPs with mechanical properties exceeding those of Portland cement². The investigation of the structure of IPs from these Fe-rich slags has seen difficulties, mainly because traditional experimental techniques in IP science do not provide all the information on the involvement of Fe in the silicate network³.

^{57}Fe Mössbauer spectroscopy is a common technique to investigate Fe in silicate minerals⁴ and glasses⁵ and is recently proposed to investigate Fe-rich IPs of volcanic origin⁶. Using this technique, a clear distinction can be made between the different oxidation states of iron, in particular the Fe²⁺ and Fe³⁺ states that are observed in silicate glasses. Such an example is the work of Onisei *et al.*⁷, where the transformation of the Fe²⁺ state of the precursor slag to a Fe³⁺ state in the IP was revealed. By performing ^{57}Fe Mössbauer spectroscopy studies, the present paper provides an overview of the state, properties and the role that iron plays in the formation of the IP network of binary FeO_x-SiO₂ (Bi) and ternary FeO_x-CaO-SiO₂ (Te) systems. Some preliminary results from the study at different time stages of the reaction between the precursor slag and the activating solution using this technique are also presented.

Experimental

The precursor slags were synthesised by melting and quenching pure oxides in an induction furnace under reducing atmosphere. Bi/Te IPs were synthesised using a solution with molar ratios SiO₂/Na₂O of 1.2 and H₂O/Na₂O of 22. The kinetic study was performed using SiO₂/Na₂O of 1.6 and H₂O/Na₂O of 20. The chemical compositions of the precursor slag samples were determined using a Philips PW 2400 X-ray

fluorescence (XRF) spectrometer in semi-quantitative mode. The Bi/Te precursor slags contained (in wt%) FeO (73)/(48), SiO₂ (27)/(35) and CaO (0)/(17), while the precursor slag used for the kinetic reaction experiments contained FeO (47), SiO₂ (34), CaO (12), Al₂O₃ (5) and MgO (2). The crystalline and amorphous contents of the samples were estimated using a Bruker D2-Phaser X-ray diffraction (XRD) system.

⁵⁷Fe Mössbauer spectra were recorded in transmission geometry at 77 K using a constant acceleration spectrometer equipped with a ⁵⁷Co(Rh) source kept at RT and a liquid nitrogen Mössbauer cryostat. The spectrometer was calibrated using metallic α -Fe and the reported isomer shift (IS) values are given relative to α -Fe at RT. For reaction time intervals up to 6 hours the sample holders contained a spread drop of paste from the activated mixtures frozen in liquid nitrogen (77 K). Crushed fine-powder sample holders were used for the hardened samples reacted for more than 12 h, as well as for all other slag and IP samples, which were cured for at least 24 h. The recorded spectra were fitted using a least squares minimisation software⁸.

Results and Discussion

The main features of the Bi/Te slags' ⁵⁷Fe Mössbauer spectra are the dominant contributions of quadrupole split Fe²⁺ states (Figure 1). For the Bi slag only one major Fe²⁺ contribution is evident, while for the Te slag the spectrum contains at least two different major Fe²⁺ contributions. These spectra present also minor Fe³⁺ state contributions, which are more intense in the Te slag. The absorption areas of the Fe³⁺ states are increased significantly after polymerisation. This verifies that the inorganic polymerisation process involves the oxidation of iron from Fe²⁺ to Fe³⁺. However, the total absorption area of the Fe³⁺ states for the Te IP sample is significantly larger than that for the Bi IP sample. This indicates that the presence of Ca ions is associated to pronounced oxidation of Fe²⁺ to Fe³⁺. Moreover, the resonant absorption lines of the Fe²⁺ states for the Bi slag are quite sharper than those of both Fe²⁺ states of the Te slag, denoting the existence of distribution of neighbouring ion environments around these ions in the latter sample. On the other hand, the XRD analyses suggest that the amount of crystalline phases present in the Bi slag is significantly larger than that of the Te slag sample, which is almost completely amorphous. The same trends are followed in the case of the corresponding IP samples as well.

The Mössbauer parameter (MP) values of the Fe²⁺ states in the Bi samples, both in the slag and the IP, [IS_{slag&IP}=1.26(2) mm/s, QS_{slag&IP}=3.05(2) mm/s, QS: quadrupole splitting], indicate ferrous ions in a fayalite-type (Fe₂SiO₄)⁴ structure. For the corresponding values of the Fe²⁺ states in the Te samples, one component [IS₁^{slag&IP}=1.28(2) mm/s, QS₁^{slag}=2.63(2), QS₁^{IP}=2.81(2) mm/s] can be attributed to ferrous ions in a fayalite-type structure, while the second component [IS₂^{slag&IP}=1.12 mm/s, QS₂^{slag}=2.02(2), QS₂^{IP}=2.12(2) mm/s], due to its lower IS and QS values, could concern ferrous ions residing either in a distorted Ca-to-Fe substituted fayalite-type (Fe_{2-x}Ca_xSiO₄)⁹, or in a relative to the pyroxene-type (Fe_{2-x}Ca_xSi₂O₆)⁴ structure. Due to

the broadening of the absorption resonant lines, the environment of these Fe^{2+} ions could be regarded to have to a large extent a short range crystal structure periodicity, *i.e.* to adopt a glass structure.

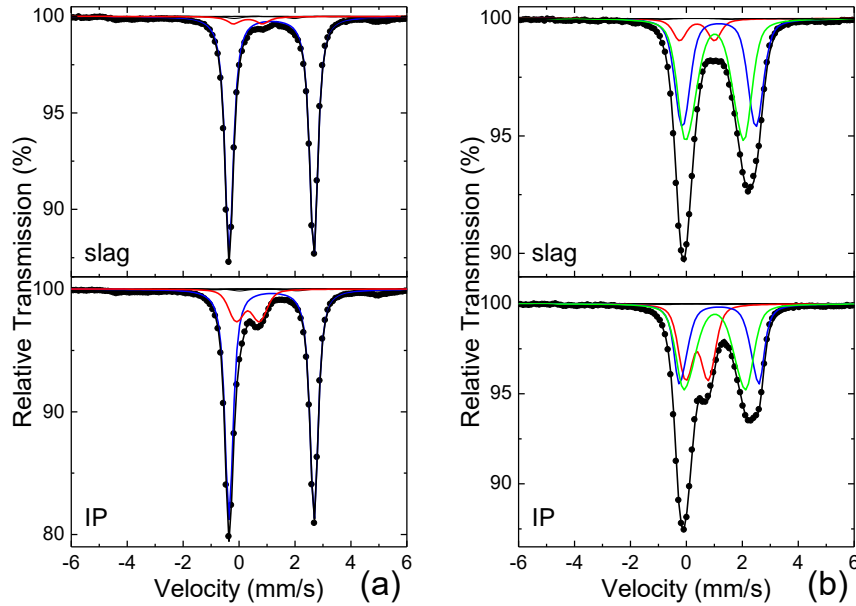


Figure 1: Characteristic ^{57}Fe Mössbauer spectra of the precursor slags and the resulting IP samples of the binary (a) and ternary (b) systems recorded at 77 K

The IS values of the Fe^{3+} states for the Bi and Te samples range between 0.42(2) mm/s and 0.49(2) mm/s. There is a significant drop for the QS values of these states from the slag to the IP forms, both for the Bi [$\text{QS}^{\text{slag}}=1.04(2)$ mm/s, $\text{QS}^{\text{IP}}=0.82(2)$ mm/s] and for the Te [$\text{QS}^{\text{slag}}=1.24(2)$ mm/s, $\text{QS}^{\text{IP}}=0.82(2)$ mm/s] samples. This transition reflects the changes in the immediate local environment of these ions in the course of the polymerisation procedure, and suggests a drop of their coordination number of neighbouring ions^{4,5,6}, most probably from 6 in the slag to 5 or 4 in the IP structure. Based on this result, it is thus suggested that the ferric ion could behave like silicon in the IP binder, *i.e.* it could act as a network former.

The above remarks deduced from ^{57}Fe Mössbauer spectroscopy signify that, Ca ions play an important role in the structure and morphology of the studied materials, both for the slag precursor as well as for the IP formation, in the sense that their addition affects the state and environment of the Fe ions in their structure and favours the development of the glass phase.

Characteristic Mössbauer spectra of the precursor slag and the activated pastes taken after 6 h, 12 h, 1 day, 2 days, 3 days, 1 week, 2 weeks, 3 weeks and 4 weeks curing are shown in Figure 2. It is evident that further oxidation of iron from Fe^{2+} to Fe^{3+} starts to appear as a significant contribution in the spectra after an interval of about 6 to 12 h, but accelerates further with time up to 24 h, while it seems to have a slower rate for longer curing times.

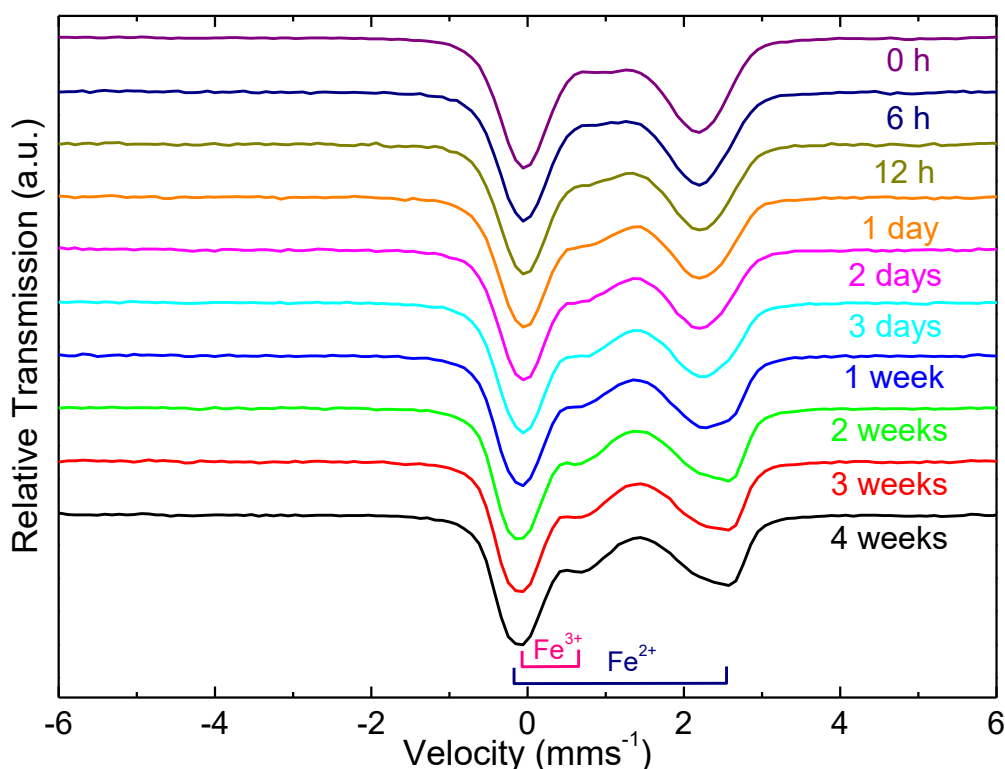


Figure 2: Raw Mössbauer spectra of activated mixtures recorded after different reaction time intervals

References

1. A. Peys, L. Arnout, B. Blanpain, H. Rahier, K. Van Acker and Y. Pontikes, "Mix-design parameters and real-life considerations in the pursuit of decreasing the environmental impact of inorganic polymers", *accepted for publication in Waste Biomass Valorization* (doi: 10.1007/s12649-017-9877-1).
2. L. Kriskova, L. Machiels and Y. Pontikes, "Inorganic Polymers from a Plasma Converter Slag: Effect of Activating Solution on Microstructure and Properties", *J Sustain Metall*, **1** (3) 240-51 (2015).
3. S. Onisei, K. Lesage, B. Blanpain and Y. Pontikes, "Early Age Microstructural Transformations of and Inorganic Polymer Made of Fayalite Slag", *J Am Ceram Soc*, **98** (7) 2269-77 (2015).
4. J. M. D. Coey, "Mössbauer Spectroscopy of Silicate Minerals", G. J. Long (ed) "Mössbauer Spectroscopy Applied to Inorganic Chemistry Volume 1", Springer, New York (1984).
5. B. O. Mysen, "The structural behavior of ferric and ferrous iron in aluminosilicate glass near meta-aluminosilicate joins", *Geochim Cosmochim Ac*, **70** (9) 2337-2353 (2006).
6. P. N. Lemougna, K. J. D. MacKenzie, G. N. L. Jameson, H. Rahier and U. F. Chinje Melo, "The role of iron in the formation of inorganic polymers (geopolymers) from volcanic ash: a ⁵⁷Fe Mössbauer spectroscopy study", *J Mater Sci*, **48** (15) 5280-5286 (2013).
7. S. Onisei, A. P. Douvalis, A. Malfliet, A. Peys and Y. Pontikes, "Inorganic Polymers Made of Fayalite Slag: Effect of Activating Solution and Curing on the Microstructures and the Behavior of Fe", to be submitted.
8. A. P. Douvalis, A. Polymeros and T. Bakas, "IMSG09: A ⁵⁷Fe ¹¹⁹Sn Mössbauer spectra computer fitting program with novel interactive user interface", *Journal of Physics: Conference series*, **217** (1) 012014 (2010).
9. A. M. Bychkov and A. V. Polosin, "Fe ions in mineral melts", *Abstracts of the Lunar and Planetary Science Conference*, **20** 131 (1989).