

ACTIVATION OF FAYALITE SLAG TOWARDS INORGANIC POLYMERS

Antigoni KATSIKI¹, Arne PEYS², Yiannis PONTIKES², Hubert RAHIER¹

¹ Department of Materials and Chemistry (Physical Chemistry and Polymer Science), Vrije Universiteit Brussel, Pleinlaan 2, Brussels, Belgium

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

antigoni.katsiki@vub.ac.be, arne.peys@kuleuven.be, yiannis.pontikes@kuleuven.be, hubert.rahier@vub.ac.be

Introduction

Copper production results in major amounts of slag, at a rate of 2.2 tons slag per ton of produced copper,¹ with fayalite (Fe_2SiO_4) being the dominant phase. In terms of applications. Thus, it is indeed a residue that needs to be exploited. Alkali activation of fayalite slag is already known and described in literature.^{1,2} However, the acidic activation of fayalite slag with H_3PO_4 remained unexplored. Phosphate cements are two component systems, consisting of a hardening liquid and a solid phase and they are known to be fast reacting systems.³ Laboratory trials were done by activating the fayalite slag with low concentration phosphoric acid solution (H_3PO_4), monopotassium phosphate solution (KH_2PO_4), as well as the combination of them (unpublished results). It was found that the addition of potassium phosphate to orthophosphoric acid causes an increase of the setting time of the cement, thus allows better control.⁴ However, despite their acceptable rheology, due to their extremely short pot life (approximately 15 min), the inability of long mixing, the excessive heat release, and the moderate workability, the production of large samples was not possible. Considering the aforementioned, as well as the importance to use the slag residue, it is of great importance to address the above challenges and take advantage of that fast reacting system. This could be done by working towards an alternative and innovative manufacturing solution, such as 3D printing.

Materials and Methods

Fayalite slag received from a Belgian industry was used as the powder precursor. Two different grain sizes were used, to investigate the influence of the particle size on the reactivity and workability of the produced cementitious materials. The powder was milled with a Wiener S attritor mill, for 1 and 16 hours respectively. A wide range of compositions, with different liquid to solid ratios were synthesised on small scale and tested with isothermal calorimetry (TAM Air, TA Instruments), at 20°C. To evaluate the effect of the two different grain sizes of the powder, the same compositions were always used for all the different combinations of hardening liquids.

Fayalite slag, pure phosphoric acid (85%), and distilled water were mixed at an l/s mass ratio of 1.38, with a high shear mixer for about 2 min to obtain a homogeneous slurry. The ratio of fayalite slag to quartz sand by mass that was chosen for the preparation of mortars was 1:1. The aqueous slurry was directly poured into cylindrical plastic containers of 60 mm x 32 mm and the specimens were sealed to prevent evaporation of water. Unfortunately, it was not possible to synthesise specimens with fayalite slag after 16 hours of milling due to the extremely short pot life. More specifically, the reaction between the activating solution (H_3PO_4 with KH_2PO_4) and the milled FS powder occurred almost instantly, while mixing the components.

After casting, the cylinders were stored for one day at room temperature and were unmoulded the next day. Curing continued for seven days at room temperature and they were subsequently tested under compression by using an Instron 5900R. FTIR spectra (32 scans, resn. 4 cm^{-1} , range $4000 - 400\text{ cm}^{-1}$) were collected starting from fresh paste up to 7 days after synthesis, using a Bruker EQUINOX 55 FTIR Spectrometer with smart ITR. The influence of the curing time, as well as of the particle size of the slag on the final structure of the material were the main points studied. Finally, the microstructure of the starting slag powder, of the phosphate cement paste, as well as of the crushed mortar specimens was analysed with a Phenom Pro desktop scanning electron microscope (SEM).

Results and Discussion

A comparison between the two different FS powders (after 1 hour and 16 hours of milling respectively), activated by diluted phosphoric acid solution is shown in Figure 1. In the collected spectra, a broad band in the $3700\text{--}2500\text{ cm}^{-1}$ region is related to stretching vibrations of adsorbed water and bending vibrations at 1650 cm^{-1} . The second important broad band is situated in the $1255\text{--}800\text{ cm}^{-1}$ region and is referring to Si-O vibrations from fayalite or newly formed products. In comparison to previous work with the same fayalitic slag, bands observed at 943, 865, and 826 cm^{-1} , correspond to fayalite crystals.¹ However, the band at $\pm 1045\text{ cm}^{-1}$ and shoulder at $\pm 1200\text{ cm}^{-1}$ cannot be associated to this slag. As phosphates commonly have a band in this region⁵, this band can be attributed to P-O vibrations. It should be noted that for both pastes, the shoulder disappears with increasing aging, while, the characteristic bands around 1045 and 945 cm^{-1} end up to a single broad band at 945 cm^{-1} after seven days of curing. This broad single band could be ascribed to the low mobility which molecules have after hardening. As mentioned before, the shoulder at $\pm 1200\text{ cm}^{-1}$ disappeared and the band at $\pm 1045\text{ cm}^{-1}$ became sharper and shifted towards smaller wavenumbers. The difference in reaction rate, by using the two different types of FS powder, is not clear from IR though.

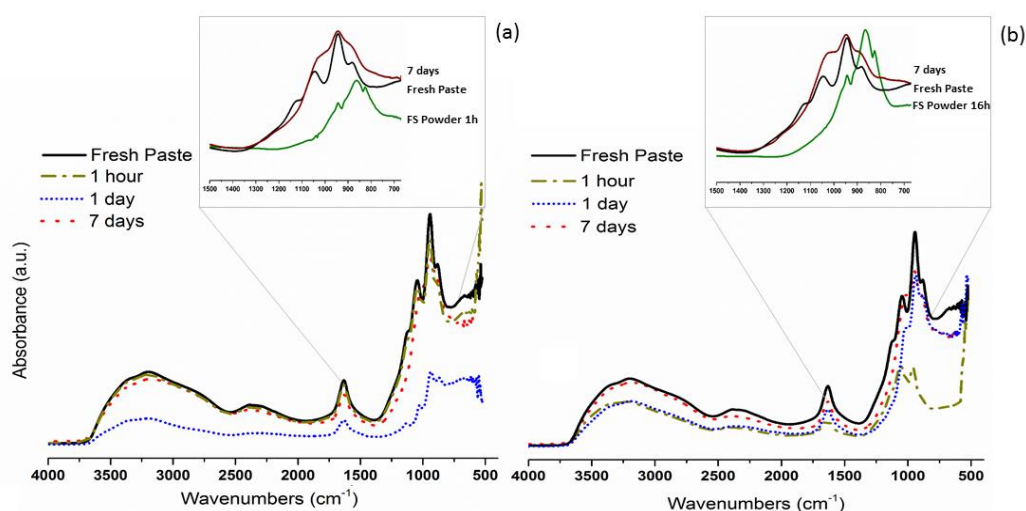


Figure 1: Comparison of the FTIR spectra of pastes activated by phosphoric acid solution with (a) fayalite slag after milling for 1 hour and (b) after milling for 16 hours. The I/s mass ratio which was used is 1.38

Through calorimetry, a first impression of the range of the chemical compositions which could provide a good reactivity, workability, as well as acceptable mechanical properties was obtained. The average compressive strength obtained for FSPA mortars by using the slag after one hour of milling, with an I/s mass ratio of 1.38 and curing at room temperature was $17 \text{ MPa} \pm 2$, which is a promising result considering the fact that the binder is not fully optimised yet. It can be stated that slower reaction occurred by using the slag powder after one hour of milling due to the smaller active surface of the particles. The mixture was in a liquid state and after approximately 15 min changed rapidly to a hardened mass. Because of this behaviour, it was only possible to fabricate three specimens per mixture. However, in additive manufacturing perspectives, this is not a limited parameter.

SEM images of the fayalite slag powder after 1 hour of milling, the paste of the phosphate cement with mass ratio $r=1.38$, as well as of the mortar of phosphate cement with same ratio, are presented in Figure 2. Regarding the microstructure of the binder (Figure 2b), it is characterised by a homogeneous, condensed structure. For both paste's and mortar's micrographs, unreacted FS particles were sparsely distributed in the specimens. The presence of micro-cracks and rough surface, which exist in the mortar's micrograph, can be related to the fact that unpolished fragments were used for analysis. Thus, the structure contained cracks which were created through the compressive strength measurements. It is important to be mentioned that this is only a preliminary study on this newly developed system. More in-depth analysis and optimisation on the rheology, thermal behaviour and mechanical properties of the material have to be done.

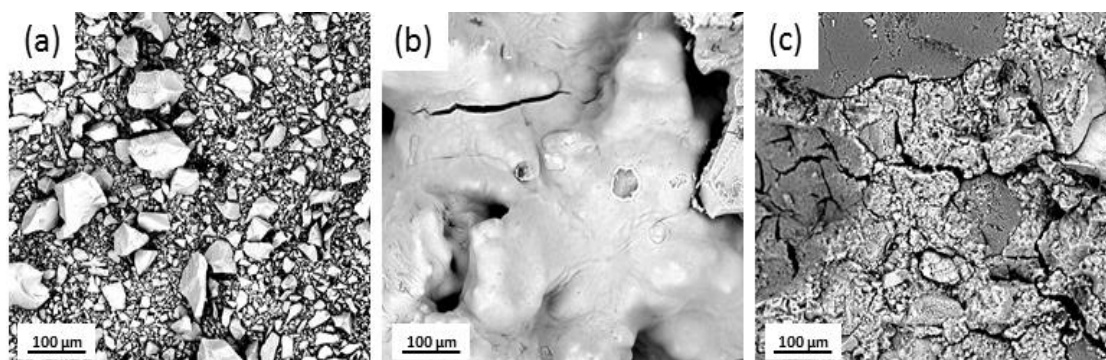


Figure 2: SEM cross-section of the: (a) FS powder after 1 hour of milling, (b) paste of phosphate cement with $r=1.38$, after 1 hour milling, (c) mortar of phosphate cement with $r=1.38$, after 1 hour milling

Conclusions

Inorganic polymers based on fayalite slag were fabricated, under acidic activation, at a first stage research, and presented good mechanical properties at room temperature. The compressive strength of the newly developed cement was > 15 MPa, reaching up to a maximum of 19 MPa. The work demonstrated the importance of the particle size of the raw precursor, as well as its influence on the workability of the mixture. It has been proven that by starting from a rather coarse powder, it is possible to produce specimens, with an acceptable pot life. Further development of the material will require a more in-depth analysis of the rheology, thermal behaviour, and microstructure.

References

1. M. Marangoni, L. Arnout, L. Machiels, L. Pandelaers, E. Bernardo, P. Colombo and Y. Pontikes, "Porous, Sintered Glass-Ceramics from Inorganic Polymers Based on Fayalite Slag", *J Am Ceram Soc*, **99** (6) 1985-91 (2016).
2. S. Onisei, K. Lesage, B. Blanpain and Y. Pontikes, "Early Age Microstructural Transformations of an Inorganic Polymer Made of Fayalite Slag", *J Am Ceram Soc*, **9** (35661) 1-9 (2015).
3. A. S. Wagh and S. Y. Jeong, "Chemically bonded phosphate ceramics: I. A dissolution model of formation", *J Am Ceram Soc*, **86** (11) 1850-1855 (2003).
4. Ľ. Medvecký, R. Štulajterová, J. Briančin and J. Ďurišin, "The effect of modification of KH_2PO_4 hardening liquid with H_3PO_4 and chitosan on setting reactions and compressive strength of calcium phosphate cement", *Mater Sci Eng C*, **29** 2493-2501 (2009).
5. L. Berzina-Cimdina and N. Borodajenko, "Research of Calcium Phosphates Using Fourier Transform Infrared Spectroscopy", *Infrared Spectroscopy – Materials Science, Engineering and Technology*, 123-148 (2012).