

**KU LEUVEN**

Proceedings of the  
THIRD INTERNATIONAL

# SLAG VALORISATION SYMPOSIUM

THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

19-20 March 2013  
Leuven, Belgium

**Editors** Annelies Malfliet, Peter Tom Jones, Koen Binnemans, Özlem Cizer, Jan Fransaer, Pengcheng Yan, Yiannis Pontikes, Muxing Guo, Bart Blanpain



# SYNTHESIS OF INORGANIC POLYMERS FROM METALLURGICAL RESIDUES

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## Abstract

*Twenty-one metallurgical residues with a wide range of chemical and mineralogical composition have been investigated aiming to identify the most promising precursors for the synthesis of inorganic polymers. The study involved dissolution experiments in NaOH solution as well as synthesis of samples where water absorption and compressive strength were measured. The results range, from samples that do not harden to samples having compressive strength exceeding 40 MPa. There is no evident relationship between the values of Si and Al dissolved in the NaOH solution and the compressive strength; there is however a rather clear connection between water absorption (indicative of open porosity) and strength. These findings could be of interest for a number of metallurgical industries and open a novel valorisation path for some of the residues.*

## Introduction

Geopolymers are typically X-ray amorphous aluminosilicate materials that consist of a random three-dimensional tetrahedral network of aluminate and silicate units, with charge balance being achieved by the presence of alkali metal ions.<sup>1</sup> They are conventionally formed by alkali hydroxide or alkali silicate activation of a solid precursor at near-ambient temperatures. The resulting geopolymer cures to form a hard, durable material that can be used as an alternative to Portland cement for applications in adverse environments such as high temperature or, alkaline environments or for the encapsulation and disposal of hazardous wastes. Unlike geopolymers (where the binding phase is almost exclusively aluminosilicate), inorganic polymers (IP) can exhibit different chemistries and are seen as a wider family of materials. Indeed, it was recently demonstrated that also Fe-Al-rich amorphous silicates are interesting precursors for the synthesis of IP.<sup>2</sup> The goal of this work is to go beyond typical raw materials and present data that are relevant for metallurgical industries.

## Materials and Methods

The materials used for experiments derive from different metallurgical processes and can be organised as follows: slags from steel and stainless steel production (AMI, AMII, AMIII, AMIV, AMV, AMVI, MHV); residues from landfill, originally coming from metallurgical processes (MHI, MHII, MHIII, MHIV); and finally slags from other pyrometallurgical (UMI, UMII, MC, HRI, HRII) and hydrometallurgical processes (NRI, NRII, ALCI, ALCII, ALCIII). The chemical composition of residues was determined with XRF (Philips PW2400). Mineralogy was determined by quantitative X-ray powder diffraction analysis (D500, Siemens). The dissolution experiments were conducted in polypropylene bottles with 10 M NaOH solution, at a solid/liquid ratio of 40 w/w. The samples were stirred in a horizontal shaking table for 24 h at  $25\pm 0.5^\circ\text{C}$ , filtered afterwards through a  $0.4\ \mu\text{m}$  filter paper and finally acidified with  $\text{HNO}_3$  to a pH lower than 2. The main elements in the solutions (Si, Al, Ca, Fe, Mg, Pb, Zn, Cr, Ti) were analysed by ICP-OES. Samples were produced in order to validate if the slags can be transformed into monoliths. The starting powders were milled in a Retsch disk mill to  $<80\ \mu\text{m}$ . The activating solution was composed of 50 wt% 10 M NaOH and 50 wt% Na-silicate solution ( $\text{SiO}_2$  25.5–28.5 wt%,  $\text{Na}_2\text{O}$  7.5–8.5 wt%, density 1.35–1.38 g/mL). The powders were mixed with the activating solution in a bench mixer for different times -from a few seconds to 15 min because of very different reactivity of materials- and poured in  $2.5 \times 2.5 \times 2\ \text{cm}^3$  plastic moulds. Different solid/liquid ratios were used, varying from 2.0 to 5.0, to achieve comparable viscosity of the mixtures. Moulds were sealed and samples were cured at ambient conditions. Compressive strength and water absorption were measured after 28 days.

## Results and Discussion

### Characterisation of Materials

The XRF analyses of the materials used in the experiments appear in Figure 1. All twenty one residues contain  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , with the  $\text{SiO}_2$  content varying from 3.6 wt% to 86.7 wt%. The  $\text{Al}_2\text{O}_3$  content varies from 0.9 wt% to 38.1 wt%. FeOx (no analysis done on the  $\text{Fe}^{+2}/\text{Fe}^{+3}$  ratio) is a major component in ten of the residues (HR II, AM III, UM II, UM I, AM I, MH I, ALC I, NR II, MC and MH IV), ranging from 27.5 wt% to 76.52 wt%. CaO is a major oxide for eleven residues (UM II, UM I, AM I, NR I, MH V, HR I, AM IV, AM II, AM V, AM VI, AM III) from 20.5 wt% to 47.7 wt%. The other main metal found in the residues (expressed as oxides) are MnO, MgO,  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$ , ZnO. Two of the residues contain also major quantities of sulphur (NRI, NRII). In terms of mineralogy, depending on the process the residues are produced, they are quite distinct. Detailed discussion of the latter will be presented in a forthcoming publication.

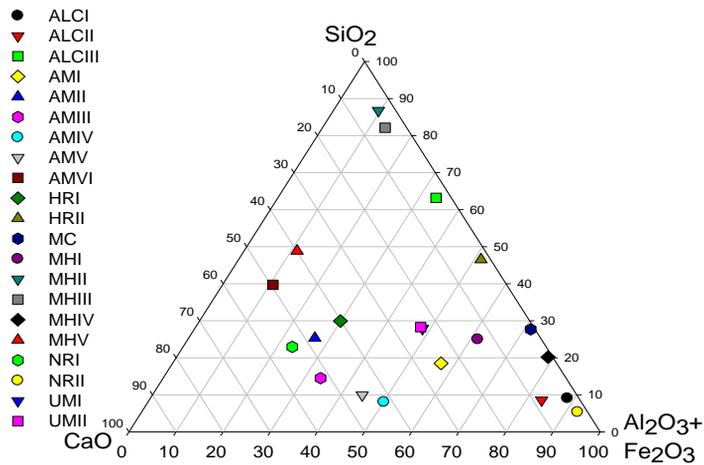


Figure 1: Chemical composition of residues studied

### Reactivity Test

The process of geopolymerisation starts with the dissolution of Al and Si from alkaline solution forming the  $M_x(AlO_2)_y(SiO_2) \cdot nMOH \cdot mH_2O$  gel.<sup>1</sup> Subsequently, setting proceeds with the gel reorganising, polymerising and hardening into geopolymers. As a result, an understanding of the extent of dissolution is fundamental for unravelling geopolymerisation. Figure 2 shows the concentration of Si and Al in the solution after the reactivity test for the materials studied compared to fly ash and metakaolin, which have been studied extensively<sup>3</sup>.

The results show that the release of Si and Al in all the residues studied is smaller compared to metakaolin but frequently comparable to fly ash.<sup>5</sup> However, unlike metakaolin and fly ash, the ratio of Si and Al released is highly variable. With respect to Ca and Fe, they are only found in small concentrations in the solutions most probably due to their precipitation as hydroxides. For residues rich in Zn, Pb or S, it

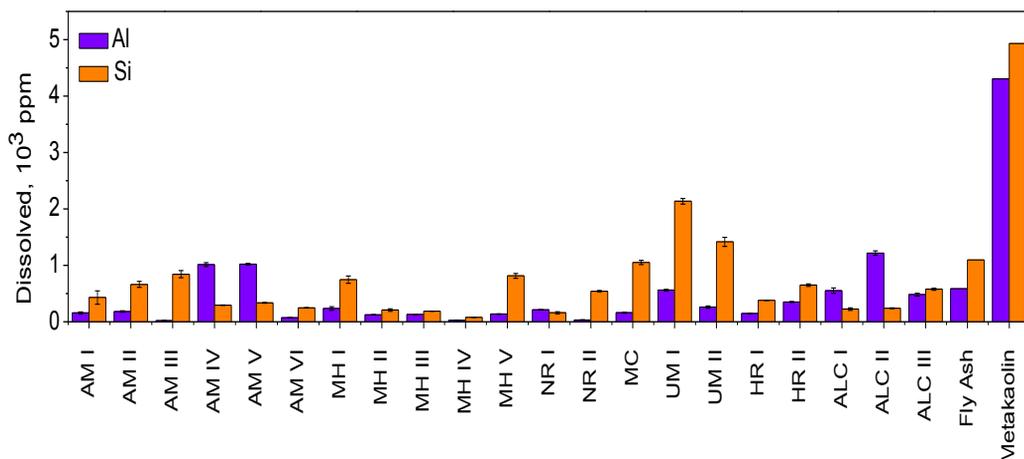


Figure 2: Concentration of Si and Al in the solution after the reactivity test for the materials studied. Data for fly ash and metakaolin are from H. Xu, *et al.*<sup>4</sup>

was found that part of these elements goes into solution. In conclusion, due to the release of a number of elements, it is expected that the final inorganic polymers will also show a complex chemical arrangement in their network.

### Physical Properties of Inorganic Polymers

Eight of the residues tested did not set when mixed with high alkaline activator; i.e. all hydrometallurgical residues (ALCI, ALCII, ALCIII, NRI and NRII) and three of the samples from landfill mining (MHII, MHIII and AHIV). The other residues have compressive strength values between 6.2 MPa (AMI) and 47.5 MPa (UMII); more than 50% of the sample achieved values over 20 MPa. There is no evident relationship between the values of Si and Al dissolved in the alkaline solution. There is however, a clear connection between the water absorption (indicative or open porosity) of the samples and their compressive strength. Thus, the samples with the highest water absorption values of 18% (AM V), 16.8% (AM VI) have the lowest compressive strength (9.4 MPa and 7.8 MPa) and the sample with lowest water absorption 3.2% (UM II) has the highest compressive strength (47.5 MPa).

### Conclusion

The potential of twenty-one metallurgical residues for becoming IP was investigated. Samples have very distinct chemical and mineralogical characteristics. Results from reactivity tests show that the release of Si and Al in all the residues is smaller compared to metakaolin but in a number of cases comparable to fly ash. None of the residues from the hydrometallurgical processes give IP monoliths. Indicative compressive strength data show that IP produced from pyrometallurgical processes give the higher values. There is a clear connection between the water absorption of the samples and their compressive strength.

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