SYNTHESIS OF INORGANIC POLYMERS FROM VITREOUS SLAGS PRODUCED BY EAF SMELTING OF BAUXITE RESIDUE

Tobias HERTEL[1], Buhle XAKALASHE[2], Bernd FRIEDRICH[2], Yiannis PONTIKES[1]

[1] KU Leuven, Department of Materials Engineering, 3001 Leuven, Belgium

[2] RWTH Aachen University, IME Institute of Process Metallurgy and Metal Recycling, 52056, Germany

tobias.hertel@kuleuven.be, bxakalashe@ime-aachen.de, bfriedrich@ime-aachen.de, yiannis.pontikes@kuleuven.be

Introduction

Bauxite residue (BR), the main residue stream of the Bayer process, is currently produced at a rate exceeding 150 million tonnes per year.[1] Most of the BR produced is stockpiled due to limited industrial application. A promising bulk application of BR seems to be in the construction sector, but due to the low reactivity, the residue cannot be considered as a reactive binder material, such as conventional cements or inorganic polymers. Consequently, its industrial use stays rather low.[1,2] In view of improving the reactivity of BR, a chemical and thermal modification of BR had been proposed in order to produce a semi-vitrified precursor, which can be alkali-activated and eventually hardens as an inorganic polymer (IP) monolith.[3] Another valorisation route for BR is the recovery of metals, for instance, Fe, which can be recovered by smelting at high temperatures.[4] The downside of such a selective valorisation route is the residual waste which is created. In some cases the conditioning of the mineral by-product for downstream application has been reported.[5,6]

In this study, an integrated two-step process is presented for a zero-waste valorisation of BR. In the first step, BR is smelted with additives in an electric arc furnace (EAF) to remove metallic Fe and to produce simultaneously a vitreous slag. The slag produced is activated using an alkaline solution to produce an inorganic polymer. The mechanical properties and microstructure of the final product were then determined.

Experimental Methods

The BR was supplied by MYTILINEOS S.A. Aluminium of Greece and dried prior to chemical (XRF - S8 tiger, Bruker) analysis. A blend of 71.4 wt% BR, 7.1 wt% lignite coke (containing 87 wt% carbon) and 21.4 wt% silica sand (containing 98 wt% SiO_2) was

mixed prior to smelting. The blend was based on thermodynamic calculations (FactSage V.7.0) with a view to producing a low melting vitreous slag and metallic Fe. The mixed blend was subsequently fed into a pre-heated and water cooled 100 KW DC EAF operated at an average power of 4 KW. The material was contained in a graphite crucible to avoid slag contamination with the refractory material, and the smelting temperature was around 1500 – 1550°C *i.e.* approximately 100 – 150°C above the liquidus temperature. The isothermal step was set to 1 h. At the conclusion of the smelting tests, the molten material was poured into a bucket filled with water for fast cooling of the molten material (water-quenching). The solid material was subsequently dried for 24 h at 105°C. The dried material was separated into slag and metal, and weighed. The slag was milled in a vibration disk mill for 12 min to achieve a specific surface area of about 4000 cm^2/g according to the Blaine air permeability method (EN 196-6). The chemical analysis of the slag was evaluated by XRF and XRD (D2 Phaser, Bruker). Coulometric carbon analysis (Coulomat 702 SO/CS) was carried out to investigate the residual carbon content of the slag. IP specimens (2 x 2 x 2 cm^3) were synthesised with a liquid to solid ratio of 0.4 using a Na-silicate solution (molar ratios of SiO_2/Na_2O = 1.6 and H_2O/Na_2O = 16). Samples were sealed and cured for 24 h at 40°C and for further 13 d at ambient conditions, prior to strength testing and further characterisation.

The samples were tested for compressive strength on an Instron 5985 testing device using a 100 kN load cell and a crosshead speed of 2 mm/min. Microstructural characterisation was carried out using secondary electron microscopy (SEM - XL30 Phillips). Structural characterisation was carried out using attenuation total reflectance Fourier transformed infrared spectroscopy (ATR-FTIR, Alfa, Bruker) in a measurement range of 4000 – 400 cm^{-1}.

Results and Discussion

A satisfactory reduction of iron from BR was achieved, reflected in the low residual iron content (expressed as Fe) in the slag (see Table 1). The residual iron in the slag represents about 15 wt% of the total iron in BR (considering the loss on ignition). It must be noted that this residual iron represents both the iron oxide (predominantly FeO) and some entrained metallic iron.

The slag produced is enriched in alumina, titania and especially in silica which can be attributed to the fluxing strategy. The silicates form networks in the slag system which favours the formation of a glassy structure. The quantification of the XRD results confirm the mineralogical transformation of BR during the smelting and cooling process where a crystalline BR is transformed mainly into an amorphous

phase (approx. 95 wt%) after the recovery of iron, next to approx. 3 wt% plagioclase $((Na,Ca)(Al,Si)_4O_8)$ and traces of residual entrained iron.

Table 1: Chemical composition of BR and BR slag (determined by XRF)

Component (wt%)	Fe	SiO_2	Al_2O_3	CaO	TiO_2	Na_2O	Others	Loss on ignition
BR	30.4*	5.5	24.0	10.2	5.6	1.8	0.2	9.4
BR slag	7.0**	39.5	30.3	10.5	7.9	3.2	1.6	-

*expressed as Fe, present as Fe_2O_3 in BR

** expressed as Fe, present as FeO and Fe in BR slag

The carbon content was determined to 0.4 wt% indicating an almost full reaction of the added C. After milling, a specific surface area (Blaine method) of 3800 ± 200 cm^2/g was found. The microstructure of the IP binder is characterised by a dense matrix (Figure 1a and b) in which partially reacted slag grains are glued together by the binder.
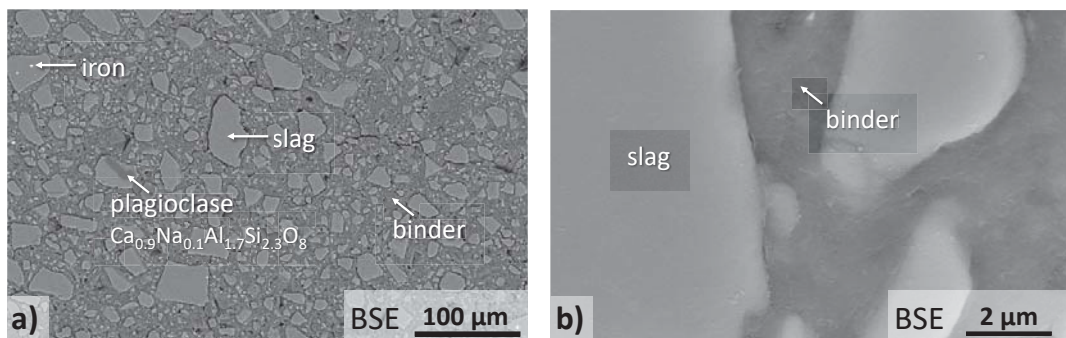

Figure 1: SEM-BSE image a) low magnification b) high magnification

FTIR results revealed that the typical broad Si-O stretching band in the region of 930 – 980 cm^{-1}, which is characteristic for these glassy silicate materials, shifts to higher wavenumbers after alkali activation, an effect of the addition of the silicates, *i.e.* dissolution of the slag and the formation of an IP binder.
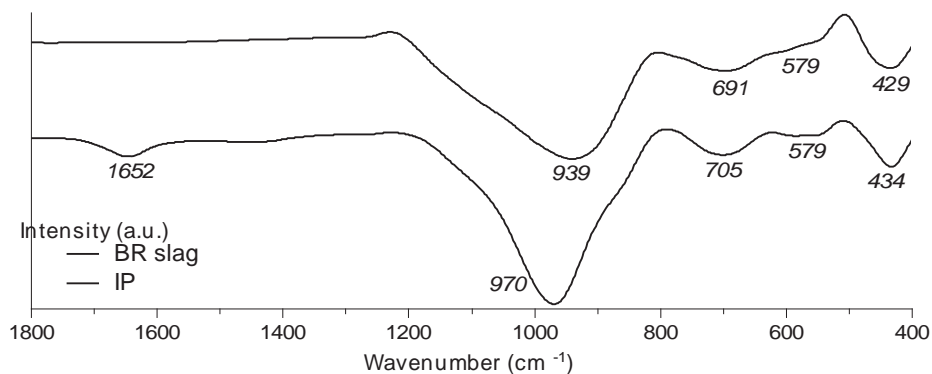

Figure 2: FTIR spectra of the BR slag and the IP

A compressive strength of the IP bricks produced of 76.6 ± 4.8 MPa was measured after 14 d of curing, which is significantly higher compared to Fe-rich IP produced earlier from BR;[3] this is primarily due to the significantly higher amount of glass phase in the precursor.

Conclusions

We have described a close-to zero-waste valorisation for BR *via* a two-step process. In the first step, iron removal was achieved through carbothermic reduction in an EAF with a satisfactory recovery of more than 80%. The combination of silica fluxing during the smelting of BR, followed by water quenching of the molten product has shown to favour the formation of a low melting and vitrified slag. The relatively low residual iron in the slag indicates that the slag was liquid enough to allow for a good slag and metal separation. The results demonstrated the high reactivity of the vitreous slag and the formation of a dense IP with satisfactory strength of about 75 MPa. In our opinion, such a relatively simple process could find application at an industrial scale, with a higher added value compared to alternative valorisation methods.

Acknowledgements

References

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