Reactivity Assessment of Bauxite Residue-Rich Slags

Elise François[1], Felicite K. Kingne[2], Silviana Onisei[3], Youen Diquélou[4], Rui M. Novais[5] and Hubert Rahier[6]

1. Researcher
4. R&D manager
ResourceFull, Leuven, Belgium
2. Researcher
3. Post-doctoral researcher
6. Professor
Vrije Universiteit Brussel, Dept. Physical Chemistry and Polymer Science, Brussels, Belgium
5. Assistant Professor
Dept. of Materials and Ceramic Engineering/ CICECO-Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal
Corresponding author: silviana.onisei@vub.be

Abstract

Although multiple valorisation routes have been proposed and patented for bauxite residue, BR, its use is currently limited to less than 3 % of the annual >150 million tonnes being produced. One of the reasons is BR's low reactivity in a cementitious environment. In this paper, a method for increasing the reactivity of bauxite residue after vitrification is used and the resulted produced slags are tested as inorganic polymer precursors. Four different slags were prepared by mixing varying amounts of BR, clay bricks (CB), and fly ash (FA). The mixtures were melted at 1375ºC and then quenched in water. The slags were milled to reach a similar Blaine value of about 5000 cm^2/g. The reactivity of the binders, associated with the polymerization degree of the glass phase, was assessed by monitoring the heat flow. Results demonstrate highest reactivity for Slag 4, followed by Slag 1, 2 and 3. The fresh inorganic polymer (IP) pastes were cast in an ultrasonic device to estimate the evolution in mechanical properties and the setting time at 20°C and 65 % relative humidity. The fastest slag to set was Mix 4 after about 17 minutes, followed by Slag 1, 2 and Mix 3, all after about 2.5 h. Inorganic polymer samples were also produced, and their compressive strength was measured for 1, 7, 28 and 90 days. The strongest sample was made with Slag 2 (75 BR, 12.5 FA and 12.5 CB wt %) with a compressive strength of more than 100 MPa after 90 days. Slag 3, with the lowest amount of CaO and lowest Al/Si ratio, had the lowest mechanical performance.

Keywords: Bauxite residue, Iron rich slag, Calorimetry, Reactivity assessment, Inorganic polymers.

1. Introduction

The highly alkaline residue, BR, is generated in the Bayer process of alumina production. About 1 to 1.5 tonves of the residue are produced per ton of alumina, depending mainly on the nature of the bauxite ore and the process parameters [1]. Although multiple valorisation routes for use as cementitious material have been proposed and patented for BR, its use is currently limited to less than 3 % of the annual >150 million tonnes being produced. One of the reasons is bauxites residue's low reactivity in a cementitious environment. In this paper, a method for increasing the reactivity of bauxite residue after vitrification is used and the produced slags are tested as inorganic polymer precursors.

Generally, the use of inorganic polymers as an alternative binder drew the attention because of their excellent properties, such as high compressive strength, resistance to acidic solutions and

thermal stability [2, 3], in combination with their relatively lower CO_2 footprint [4]. Iron-rich precursors, for example copper [5], lead [6] or ferro-nickel slags [7] have shown already a potential for the synthesis of inorganic polymers and the re-use of industrial wastes. Characteristics of these precursors include among others, a partially vitrified structure and ferrous iron [8]. Chemically considered, these slags do not differ significantly from BR, apart from the mineralogy and the oxidation state of iron. This led to the assumption that a chemical adaptation followed by thermal processing can turn BR into a suitable precursor for IP, as has been shown by others [9, 10] that the process of transforming the BR slag into a reactive slag precursor is feasible.

In this paper four different mixtures will be produced based on bauxite residue, mixed with other residual resources, namely clay bricks and fly ash. Clay bricks contain a substantial amount of aluminosilicates, while especially aluminum and silicon are lacking in BR, thus addition of clay bricks could help to increase these. Fly ash can bring in some calcium, which is known to increase the reaction rate. These mixtures will be molten and quenchd to obtain an amorphous slag, as it is known that the degree of reactivity is related to the amorphous fraction. The mixtures will then be tested on their reactivity and mechanical properties. Although this procedure consumes a lot of energy, needed for melting the ingredients, it has the big advantage that a mixture can be obtained with constant quality. For certain applications this is of utmost importance.

2. Materials and Methods

Four different slag chemistries were prepared by melting BR in combination with other residual streams. The aim was to increase the SiO_2 and CaO content in the BR in order to optimise the fraction of molten material and to obtain a more amorphous and reactive glass upon quenching [11, 12]. The addition of SiO_2 was in the form of milled clay bricks, rich in SiO_2 (74.1 wt %) and Al_2O_3 (13.5 wt %). To increase the CaO content of the slag, a calcium rich fly ash was used, i.e., CaO content of 50.2 wt %. To increase the molten phase in the liquid slags, which necessitates Fe^{2+} for the chosen temperatures, carbon was added in the form of carbon black. The as-received wastes and the slags were characterized before use. The mineralogical composition was evaluated by X-ray diffraction (XRD) recorded using a θ/2θ diffractometer (PANalytical X'Pert Pro, NL), equipped with a fast RTMS detector (PIXcel 1D, PANalytical), with Cu K radiation (45 kV and 40 mA, 5-80 °2θ range, with a step scan of 0.02 °2θ, and time per step of 200 s). Full quantitative phase analyses (FQPA) were assessed for quantifying both crystalline and amorphous phases in the slags, using the combined Rietveld-reference intensity ratio methods, using 10 wt % of a-Al_2O_3 (NIST SRM 676a) as an internal standard. The sample's chemical composition was determined by X-ray fluorescence spectroscopy (Philips X'Pert PRO MPD spectrometer). The amount of carbon black added in the mixtures was calculated as 1.5 wt % of the BR content. Before melting, the different raw materials were blended as a slurry using a Hobart mixer, ensuring homogeneous mixtures. Subsequently, the slurry was dried at 60 °C for 48 h. The obtained dry mixtures were then melted in an induction furnace at 1375 °C using a steel crucible. The atmosphere in the furnace during melting was maintained at 40/20 CO/CO_2 (l/h) to ensure a reducing environment, further promoting the formation of a liquid phase. The molten slags were quenched in water after one hour residence in the furnace at 1375 °C. The rapid cooling of the molten slag results in an amorphous and thus more reactive material. The wet slag was subsequently dried at 100 °C for 48 h. The samples were then milled in a ball mill for 4 to 5 h, depending on the hardness of each sample. The density of the slags was measured with an Ultrapys 5000 Micro, Anton Paar. The reactivity of the slags with a Na-silicate activating solution (molar ratio of SiO_2/Na_2O of 2.0 and H_2O content of 65 wt %) was investigated by isothermal heat flow calorimetry of paste samples recorded at 20.0±0.2 °C for 72h using a TAM Air calorimeter (TA Instruments). The samples were internally stirred using the Admix Ampoules in order to monitor the initial heat flow and the initial reactions. The liquid to solid (L/S) was kept constant to 0.45. The dynamic E-modulus (E-mod) development was measured with an ultrasonic

3.3 Mechanical Properties of the Produced Slags

The compressive strength data are shown in Figure 4. At the ages of 1 and 7 days, the inorganic polymer prepared with Slag 4 shows the highest strength values, followed by Slag 1, Slag 2 and Slag 3, respectively. After 28 days, this sequence is not observable anymore. At later ages, Slag 1, 2 and 4 perform similarly. Slag 3 has overall the lowest strengths results. This is the slag with the lowest CaO content and Al_2O_3/SiO_2 ratio.

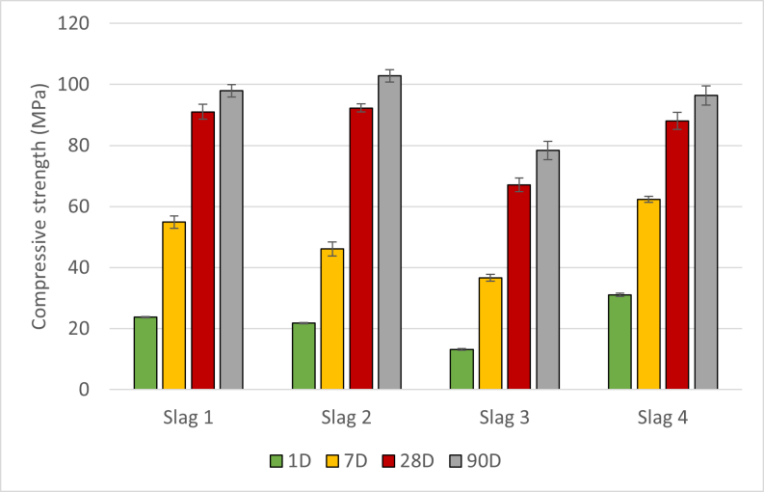

Figure 4. Compressive strength values at 1, 7, 28 and 90 days.

4. Conclusion

Inorganic polymer samples were prepared with treated BR as the main component. The reactivity of the binders, associated with the polymerization degree of the glass phase, was assessed by monitoring the heat flow and E-modulus development. There is a possible correlation between the E-modulus value at 24h and the cumulative heat flow at the same time, results that could be used as a way to deduce qualitative information for E-modulus via calorimetry measurements. Also, there might be a correlation between the cumulative heat release at 24 hours and the compressive strength values at the same time. Inorganic polymer samples were also produced, and their compressive strength was measured for 1, 7, 28 and 90 days. The strongest sample was made with Slag 2 (75 BR, 12.5 FA and 12,5 CB wt %) with a compressive strength of more than 100 MPa after 90 days.

Acknowledgements

The authors gratefully acknowledge the grant from ERA-MIN 2: research & innovation and the collaboration with the SREMat group from KUL.

5. References

1. Ken Evans, The history, challenges, and new developments in the management and use of bauxite residue, *Journal of Sustainable Metallurgy* 2016, Vol. 2, 316–331.
2. Valeria F.F. Barbosa, Kenneth J.D. MacKenzie, ClelioThaumaturgo, Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: Sodium polysialate polymers 2000, *International Journal of Inorganic Materials* 2000, Vol. 2, 309–317.
3. Duxson, P. et al., Geopolymer technology: The current state of the art. *Journal of Material Science* 2007, Vol. 42, 2917– 2933.

4. Benjamin C. McLellan et al., Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement, *Journal of Cleaner Production* 2011 Vol. 19, 1080–1090.
5. Silviana Onisei et al., Early age microstructural transformations of an inorganic polymer made of fayalite slag, *Journal of American Society* 2015, 2269–2277.
6. Silviana Onisei et al., Synthesis of inorganic polymers using fly ash and primary lead slag. *Journal of hazardous materials* 2012, Vol. 205-206, 101–110.
7. Konstantinos Sakkas et al., Utilisation of FeNi-Slag for the production of inorganic polymeric materials for construction or for passive fire protection, *Waste and biomass valorization* 2014, Vol. 5, 403–410.
8. Yiannis Pontikes, Lieven Machiels, Silviana Onisei, Slags with a high Al and Fe content as precursors for inorganic polymers. *Applied Clay Science* 2013, Vol. 73, 93–102.
9. Tobias Hertel, Yiannis Pontikes, Geopolymers, inorganic polymers, alkali-activated materials and hybrid binders from bauxite residue (red mud) – Putting things in perspective, *Journal of Cleaner Production* 2020, Vol.258.
10. Michiel Giels et al., High performance mortars from vitrified bauxite residue; the quest for the optimal chemistry and processing conditions, *Cement and Concrete Research* 2022, Vol. 155.
11. Tobias Hertel, Bart Blanpain, Yiannis Pontikes, A proposal for a 100 % use of bauxite residue towards inorganic polymer mortar, 2016, Journal of Sustainable Metallurgy, Vol. 2, 394–404.
12. Michiel Giels et al., High performance mortars from vitrified bauxite residue; the quest for the optimal chemistry and processing conditions, 2022, *Cement and Concrete Research*, Vol. 155.
13. EN 12504-4 2004, Testing concrete - Part 4: Determination of ultrasonic pulse velocity, *European Committee for Standardization*, 91.100.30, 2004.
14. Silviana Onisei at al., Early age microstructural transformations of and inorganic polymer made of fayalite slag. Journal of the American Ceramic Society 2015, Vol. 98(7), 2269–2277.
15. Silviana Onisei et al., Synthesis of inorganic polymers from metallurgical residues, *Proceedings of the 3rd International Slag Valorisation Symposium* 2013 Leuven, Belgium, 355–358.
16. Hubert Rahier et al., Reaction mechanism, kinetics and high temperature transformations of geopolymers. *Journal of Materials Science* 2007, Vol. 42(9):2982– 2996.
17. Arne Peys et al., Molecular structure of CaO-FeO_x-SiO_2 glassy slags and resultant inorganic polymer binders, *Journal of the Americal Ceramic Society* 2018, Vol. 101(12), 5846-5857.
18. Lubica Kriskova, Lieven Machiels, and Yiannis Pontikes, Inorganic polymers from a plasma convertor slag: effect of activating solution on microstructure and properties, *Journal of Sustainable Metallurgy* 2015, Vol. 1(3):240–251.
19. Petr Misák et al., Ultrasonic NDT determination of initial and final setting time of cement paste, *MATEC Web of Conferences* 2020.