Reactivity Assessment of Bauxite Residue-Rich Slags

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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 $\theta/2\theta$ 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 pulse device according to EN 12504-4 [13]. The ultrasonic pulse measurement started from the moment the fresh material was cast in a cylindric silicone mould, which was around 4 min after mixing, and lasted up to 48 h. The ultrasonic probes operated at a frequency of 30 kHz. The device transmitted every 10 s a sonic pulse (P-wave) that travelled through the sample and was captured by the receiver. The travel distance of the pulse between the transmitter and receiver was 40 mm, which is the width of the sample. From the travel time, the velocity v of the compression wave and E-modulus (Edyn) were calculated according to the Newton-Laplace equation, Equation (1), with k-factor 0.876 and density (ρ) between 3.2-3.6 g/cm^3.

$$\mathrm{Edyn} = \mathrm{k}\mathrm{v}^2\rho \tag{1}$$

where:

k	k-factor 0.876
v	Velocity, m/s
ρ	Density, g/cm^3

The obtained milled slags were used for inorganic polymer production using a K-silicate solution with a SiO_2/K_2O ratio of 1.72 and a water content of 65 %. The samples were prepared with a 1:2 ratio of binder: M31 sand (Sibelco) to limit internal forces and defects caused by shrinkage phenomena. The binder to solution ratio was 0.45 to obtain a workable consistency. The mortars were mixed for two minutes before casting in moulds of 20x20x20 mm^3. The moulds were covered in plastic and left for curing for 24 h at 20 °C. Afterwards, the samples were demoulded and cured at 20 °C wrapped in plastic until testing. For each mortar 12 cubes were prepared, and each slag was tested in duplicate, amounting to 24 cubes per activated slag. The prisms were tested at 1 day, 7, 28 and 90 days of curing on uniaxial compressive strength at a rate of 0.3 kN/s.

3. Results

3.1 Characterization of the Materials Used in the Study

The chemical composition of the materials used for producing the slags is depicted in Table 1. The mix design of the slags and targeted compositions are found in Table 2 and Table 3.

Table 1. Chemical composition of the raw materials used in the study.

wt%	Bauxite residue	Milled bricks	Fly ash
LOI	10.7	0.3	3.7
Fe_2O_3	40.7	4.5	6.3
SiO_2	9.2	74.1	9.6
Al_2O_3	18.2	13.5	8.3
CaO	9.1	0.6	50.2
Na_2O	4.7	1.0	0.2
K_2O	0.1	3.4	0.8
MgO	0.3	1.1	2.3
P_2O_5	0.1	0.1	0.2
SO_3	0.4	<0.1	9.6
TiO_2	5.7	1.0	0.7
Cl	<0.1	-	<0.1
Ba	<0.1	<0.1	<0.1
MnO	<0.1	<0.1	<0.1
Others	0.7	0.2	0.2

Table 2. The mix design of the four slags.

(wt%)	Slag 1	Slag 2	Slag 3	Slag 4
Bauxite residue	75.0	50.0	75.0	75.0
Milled clay bricks	12.5	25.0	25.0	0.0
Fly ash	12.5	25.0	0.0	25.0
Carbon black	1.1	0.8	1.1	1.1
LOI	8.5	6.4	8.1	9.0

Table 3.The targeted chemical composition.

(wt%)	Slag 1	Slag 2	Slag 3	Slag 4
FeO	28.6	20.6	28.3	28.7
SiO_2	18.3	27.4	25.4	11.2
Al_2O_3	16.4	14.6	17.0	15.7
CaO	13.2	17.3	7.0	19.4
Na_2O	3.7	2.7	3.8	3.6
K_2O	0.6	1.1	0.9	0.3
MgO	0.6	1.0	0.5	0.8
P_2O_5	0.1	0.1	0.1	0.1
SO_3	1.5	2.6	0.3	2.7
TiO_2	4.5	3.3	4.5	4.4
Cl	<0.1	<0.1	<0.1	<0.1
Ba	<0.1	<0.1	<0.1	<0.1
MnO	<0.1	<0.1	<0.1	<0.1
Others	0.2	0.1	0.2	0.2

The slags are similar in terms of density, between 3.2 and 3.6 g/cm^3 (Table 4).

Table 4. Density values of the slags.

	Slag 1	Slag 2	Slag 3	Slag 4
g/cm^3	3.5	3.2	3.3	3.6

Table 5. Milling time needed to obtain a Blaine fineness above 5000 cm²/g and the measured Blaine fineness.

	Slag 1	Slag 2	Slag 3	Slag 4
Milling time (h)	5	4	4	4
Blaine (cm^2/g)	5500	5400	5100	5200

The Blaine fineness of all the slags was above 5000 cm²/g after milling, as shown in Table 5. The chemical compositions and amorphous content of the obtained slags are listed in Tables 6, respectively. The composition of the obtained slags is very similar to the targeted chemical compositions. The FeO content is, however, higher than calculated, due to the partial dissolution of the steel crucible in the slag during smelting at 1375 °C, thus enriching the slag in iron. Slag 2 has the highest amorphous content, followed by Slag 3, Slag 1 and Slag 4, respectively.

Table 6. Chemical composition of the produced slags and their amorphous content.

wt%	Slag 1	Slag 2	Slag 3	Slag 4
FeO	36.4	29.8	36.9	37.3
SiO_2	18.9	27.1	24.0	14.1
Al_2O_3	17.0	14.7	17.6	17.6
CaO	13.4	16.5	7.8	16.9
Na_2O	2.2	1.6	2.6	2.5

wt%	Slag 1	Slag 2	Slag 3	Slag 4
K_2O	0.6	0.9	0.7	0.4
MgO	0.5	1.1	0.4	0.7
SO_3	1.0	1.2	0.4	1.2
TiO_2	4.3	3.1	4.7	4.3
Amorphous content	81.0	98.3	86.8	66.7

3.2 Reactivity assessment

The reactivity of the binders, associated with the polymerization degree of the glass phase, was assessed by monitoring the heat flow. Isothermal calorimetry measures the heat flow, which relates to the reaction rate, coming from the reactions in the sample. In this way provides the time-frame in which the different reaction stages occur. Using isothermal calorimetry, it was shown that, chemically, iron-rich inorganic polymers seem to follow a 2-stage reaction pattern: dissolution and polymerization [14, 15]. Several heat flow events were observed from the dissolution and development of the inorganic polymer binder. Figure1, shows the 2 exothermic events which in geopolymers is often used to indicate the timing of the polymerization reactions [16]. The first event is observed rather as a shoulder and is related to wetting and the start of dissolution. It occurs immediately upon mixing for Slags 1, 2 and 3. For slag 4, this event is not seen separately from the second exotherm which is very large and overlaps with the first one as it occurs much earlier than for slags 1 to 3. After the start of the dissolution, the species that were dissolved can recombine via a polycondensation reaction. The main part of these reactions occurs between 10 min and 40 min after the mixing of the slags with the activating solution. The quickest one is slag 4 at 0.13 h with 36 mW/gslag, followed by 3 broader peaks at 0.5h, 0.4h and 0.7h for Slag 1, 2 and 3 respectively.

It has been shown that in the Fe-rich IPs the Fe^{2+} in the similar slags [17] is oxidized to Fe^{3+} during and/or after the synthesis. A contribution from this reaction is not distinguished here or in previous studies [17,18, 15]. The oxidation most probably occurs simultaneously with the dissolution or polymerization or occurs on a longer time-scale and it is not noticed as a separate phenomenon in the calorimetry measurements [17].

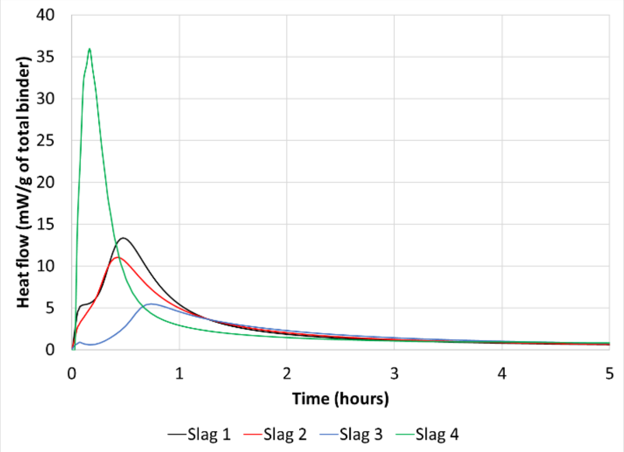

Figure 1. Isothermal Heat flow calorimetry of the inorganic polymer pastes for the first 5 hours.

The E-modulus development is an indication for the stiffness of the samples and is shown in Figure 2 (a) and (b). The overall development of the inorganic polymer samples is distinct to the one of a cement [19] where the stiffens occurs more steadily (smoothly) compared to inorganic polymer samples, where the stiffening starts in the first minutes after casting and continues in a sharp manner for the first 8 hours to 30 h. The first slag to stiffen was Slag 4 after about 15 minutes. This is expected and in accordance with what was observed at the preparation of the samples where a flash setting was observed, and with the calorimetry results. Slag 2 shows an increase of the stiffness after about 30 minutes, followed by Slag 2 at 50 minutes, and Slag 3 after about 2 hours. The E-modulus is increasing for another 10-20 hours, which is likely related to the development of the binder. All slags have a sharp decrease in E- modulus at 9 h for Slag 4, followed by Slag 1, 2 and 3 at 10, 12 and 30 h, respectively. This decrease is possibly related to the shrinkage of the paste.

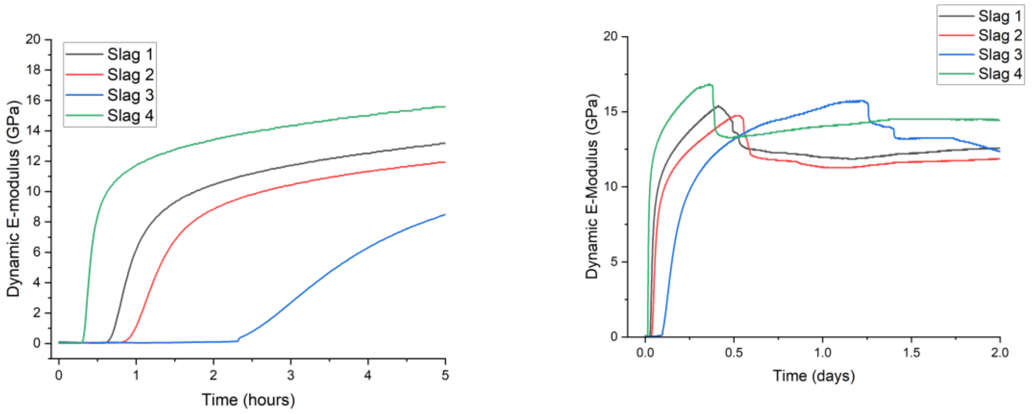

Figure 2. (a) the E-modulus development of the pastes for the first 5 hours. Panel (b) the later E-modulus development of pastes for 48 h long.

Despite the fact all attempts to correlate cumulative heat release, E-modulus and strength were not really successful, there appears to be a linear relation between heat evolution (not cumulative) and E-modulus at 24h (Figure 3(a)). It is doubtful if there is a physical meaning behind this, yet, it could be used as a way to deduce qualitative information at least for E-modulus (and ultimately compressive strength) via calorimetry measurements. Also, there might be a correlation between the cumulative heat release at 24 h and the compressive strength values at the same time Figure 3(b). However, with the existing data no correlation between the overall cumulative or/and E-modulus and final compressive strength results has been observed. Furthermore, if the chemistry is changing, the reactions will also change and not all reactions will have an equal contribution to strength development. More measurements are in progress and will be published in a future work.

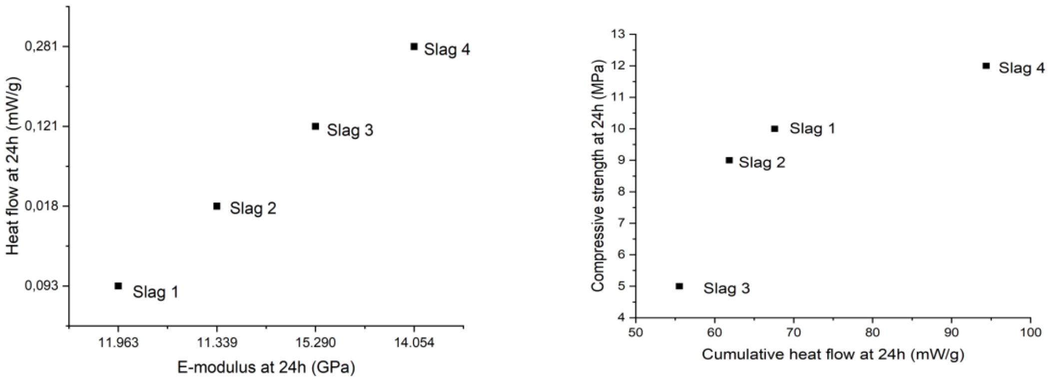

Figure 3. Possible correlation between (a) E-modulus and Heat flow at 1 day; (b) Cumulative heat and compressive strength at 1 day.

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.

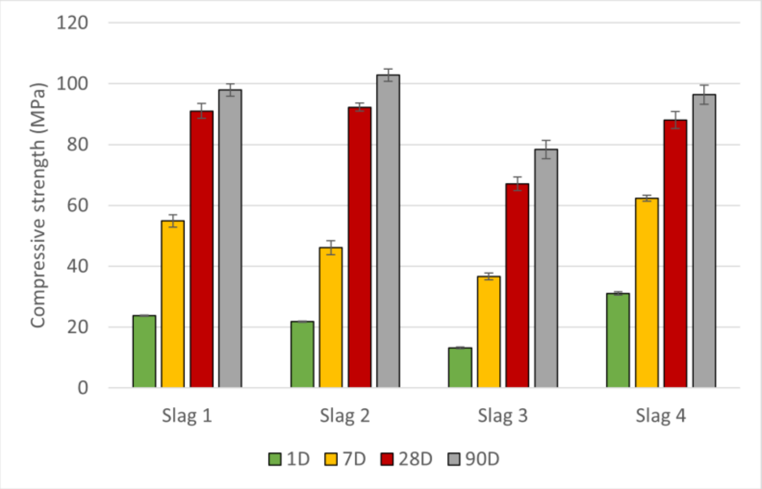

Figure 4. Compressive strength values at 1, 7, 28 and 90 days.

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.

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