Transforming Bauxite Residue into an Alternative Cement via Vitrification, a Scalable Solution?

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Abstract

Bauxite residue (BR) has in principle a great potential to be used in the construction (concrete) industry considering its large availability. However, an implementation is hindered in Europe, mainly due to its classification as a waste, its alkaline nature, low reactivity and small particle size. Vitrification has been identified as a potential solution for transforming BR into a reactive, high value-added and safe product. In this work, the reactivity of BR, as a precursor for cementitious materials, was increased by partially melting a mix consisting of BR (> 70 wt%) and additives at 1200-1300 °C, followed by quenching. This route resulted in an iron-depleted, reactive Al_2O_3-SiO_2-CaO-FeO-Na_2O amorphous phase and iron-bearing crystalline phases. Taking the work further, upscaling of the vitrification process was carried out with a focus on the impact of the chemical variability of the bauxite residue, energy demand of the heat treatment and milling of the material. A total of 5 t of BR and minor additives (C, SiO_2 and $CaCO_3$) were pelletised and mixed, and further processed at 1200-1300 °C in a top-blown rotary converter with subsequent fast cooling. After milling, the vitrified BR was mixed with an alkaline solution and sand to produce inorganic polymers mortars that reached compressive strength up to 100 MPa. These results verified the successful transformation of BR into a reactive material at a demonstration scale. We believe that the present work, which goes beyond the laboratory scale, provides arguments for reconsidering the prescriptive cement standards and waste status of the residue, and might eventually contribute towards a successful future industrial implementation.

1. Introduction

Bauxite residue (BR) valorization is still limited to less than 3 % of the annual 150 Mt produced [1]. Multiple routes have been proposed and patented; however, currently no technology led to a major breakthrough. Major reasons are the alkaline nature, being classified as waste and small particle size, and from a technical point of view its low reactivity, e.g., in a cementitious environment [2]. In general, most valorization efforts have looked into metal extraction (Fe, Fe-Si alloys, Al, Ti, REE), soil and road stabilization and construction materials [1]. However, in general the materials that bauxite residue would replace are readily available and this often in higher grades [1, 3–5]. Therefore, in order to make BR more attractive for new and existing valorization routes, it has to have a net benefit to incentivize use. In addition, the valorization route has to target net zero-CO_2 (or equivalent) emissions by 2050 [6].

Given the large volumes of available BR, the construction sector is the most likely option for large-scale valorization. At the moment, the main application for the residue is as iron and alumina source for the production of conventional cement [1]. The valorization is limited due the relatively low cement production in Europe, the logistics involved and the abundance of alternative raw materials for the European cement plants [5]. In addition, the strict control of the Na_2O content, due to the increased risk for the alkali silica reaction, limits its valorization to smaller volumes

[7,8]. This risk also exists if the raw BR is used in a cementitious mixture [8]. Although the use of BR is still limited, the cement industry has to move to a more sustainable future, which is only feasible if more waste resources are used, alternative binders technologies are available (including little to no cement) or carbon capture and storage becomes widely and cheaply available [9]. In this work we focus on the first two points in which BR is used to produce precursors for inorganic polymers. Compared to normal cement based binders, inorganic polymers result after mixing of a precursor and an alkali solution also in an easy to shape binder, gluing aggregates (sand and/or gravel) together.

In order to be able to produce such binder from BR, it has to be thermally- or chemically activated. Therefore, research has focused on the use of vitrification. At temperatures ≥ 1100 °C, the material is transformed in a partial melt, and when fast cooling is applied, the melt is preserved in an amorphous phase. Once the vitrified BR (VBR) is milled, the Al_2O_3-SiO_2-CaO-FeO-Na_2O amorphous phase is easily soluble in alkaline environment, resulting in a stable binder with compressive strengths up to 130 MPa after 28 days for inorganic polymers, which is for a cement (CEM I) based mortar in the range of 50-70 MPa [10–14]. The initial investigated application was inorganic polymers, however it was shown in [13] that also its use in blended cement shows great potential. In previous works [10, 12–14], the optimal temperature and composition of the mix were investigated for different residues. With only SiO_2 and C addition for the reduction of Fe^{3+} to Fe^{2+}, compressive strengths up to 43 MPa were achieved [10]. By increasing the temperature to 1200-1300 °C and the addition of CaO (e.g., as $CaCO_3$), compressive strength could be increased to 130 MPa with shrinkage as low as 1.5 mm/m in inorganic polymers [12]. Further work identified that Na_2O is responsible for a strong decrease in the melting temperature and significantly increased reactivity and strength development [14]. The high alkalinity, opposed to conventional cement manufacturing, is actually beneficial for the vitrification process and performance of the final product. Figure shows a simplified flowsheet of the whole process. The left part of the process has potential to be easily integrated in an alumina plant using existing infrastructure [10].

In this work, we go beyond laboratory scale and explore the potential upscaling of the vitrification process. In a first step, the BR composition is modified to reach the optimum chemistry as described in [12] by mixing BR, C, $CaCO_3$ and SiO_2. The final product is characterized in terms of compressive strength. Additionally, the research required to provide this technology as a promising alternative to cement manufacturing will be discussed.

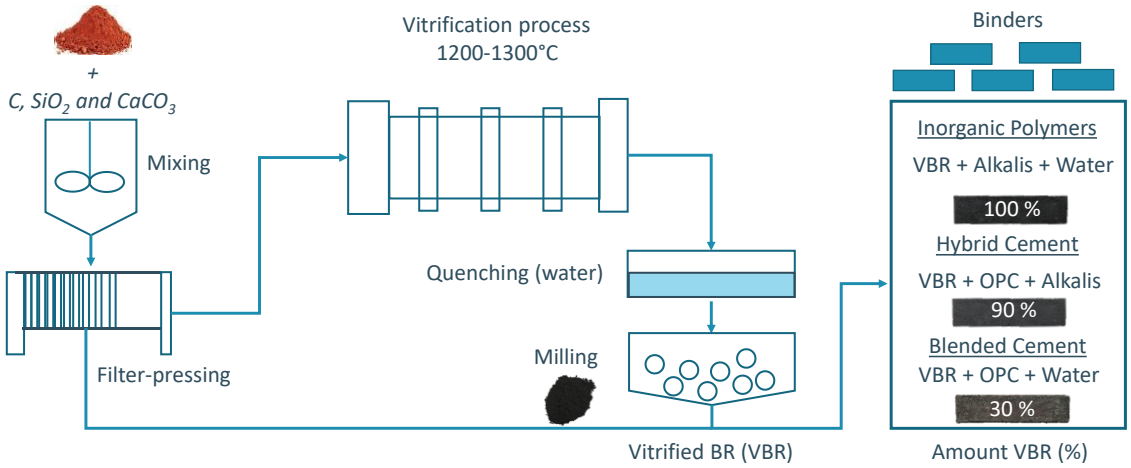

Figure 1: Simple flowsheet showing the unit operations to obtain a milled VBR and the potential products. In this work, only inorganic polymer binders are discussed.

2. Methodology

2.1 Characterization and Modeling

BR was received from Alum Tulcea with a moisture content of around 35 wt%. The material was first dried at 300 °C for 24 h. The chemical analysis of the residues was performed using a Bruker S8 Tiger Wavelength Dispersive X-ray fluorescence spectrometer (WDXRF) following a lithium borate and lithium bromide fusion with 10 wt% BR sample at 1050 °C to form fusion beads. Thermal analyses were performed on the dried material using a TA SDT Q600 in order to determine the amount of bound water and carbonates, and to calculate the loss on ignition (LOI) at 1000 °C. Thermodynamic calculations were performed using FactSage 7.0 to identify the optimal operation conditions in the pilot scale [15]. For these calculations, a pO_2 of 10^{-9} atm was assumed, which was found to be a realistic value in practice [11].

2.2 Processing of Raw Materials

Five tonnes of BR were processed before the vitrification step with the modular upscaling containers which were developed in the Recover project (EIT Raw Materials, https://recover.technology/). Firstly, 0.5 t of raw BR was mixed with additives and extruded into a pellet (Figure 2) with subsequent drying at 300 °C. This extruded pellet was used as initial feed to the furnace described in section 2.3. Secondly, 5 t of BR was dried at 300 °C and mixed with the additives in a high shear mixer for 2 min. The homogenized powder mix was discharged into paper bags of about 25 kg per bag. This was charged in the furnace after partial melting of the initial pellet feed was achieved. For future upscaling trials, a double layered mixing tank is now in operation, which mixes the BR slurry with additives and is pumped using compressed air in a filter press. After filter pressing, the material is pressed out to produce pellets and is dried under elevated temperature or vacuum.

Figure 2: Steps of processing in the pilot plants in order to obtain VBR.

2.3 High Temperature Experiments

The previously described pellets and homogenized dried BR powder mix were processed in a top blown rotary convertor at RWTH Aachen (IME), which is equipped with an the off-gas system and a methane burner in top lid. The furnace operated with a rotation at approximately 2-4 rpm. After partially melting the material at 1200-1300 °C, the furnace was tilted and the melt was

discharged towards the granulation setup, which consisted of a launder and a 1000 L water tank (Figure 3). The material was afterwards dried until a constant mass was reached and subsequently milled in attritor ball mill until a fine powder with a Blaine (according to EN 196-6 [16]) of 5800 cm^2/g was reached.

Figure 3: Left- Granulation of the partial melt; Right- The fine granulated material after quenching.

2.4 Production of the Inorganic Polymer

Inorganic polymer mortars were produced by mixing 550 g of VBR with 275 g of a sodium silicate activating solution (SiO_2/Na_2O=2.0, 65% H_2O) and CEN sand (1350 g), which has a particle size distribution as described in the EN 196-1 [17]. This procedure only deviates from the EN 196-1 regarding the amount of binder and liquid over solid, which is used due to the increased density of the VBR (3.4 g/cm^3). A reference OPC sample was prepared using CEM I 52.5 N CE CP2 NF according to EN 196-1. After 24 h the inorganic polymer samples were demoulded, wrapped in plastic foil and stored at ambient temperature. The OPC reference was stored in a climate chamber with a humidity > 90 % at ambient temperature, which corresponds to the optimal curing conditions. The compressive and flexural strength for the wrapped samples were tested using an Instron 5985 testing machine with a load rate of 2 and 1 mm/min, respectively.

3. Results and Discussion

Table Table 3 shows that the BR is characterized by a high iron and alumina content. The LOI is measured on the residue, which is dried at 300 °C and is mainly originating from the loss of bound water (11 wt%) and carbonates (1.4 wt%). The targeted composition for upscaling is taken from previous work done at laboratory scale and only takes into account the CaO and SiO_2 content [12]. The mineralogy of the BR is not shown here, as the chemistry of the BR is the parameter that determines the final product performance.

Table 3**: Chemistry of the BR with standard deviations, based on the measurement of 10 independent samples.**

	Fe_2O_3	CaO	SiO_2	Na_2O	Al_2O_3	TiO_2	LOI (1000 °C)
BR	49.2 ± 0.5	4.7 ± 0.1	13.3 ± 0.2	7.3 ± 0.2	21.4 ± 0.5	3.8 ± 0.1	12.4 ± 1.4
Target	-	14.2	18.3	-	-	-	-

3.1 Upscaling of the Process

For upscaling the process and final product, there are 2 important requirements: 1) Performance of the final product and 2) relatively low viscosity of the partial melt in the vitrification step. The high performance (> 100 MPa) can be achieved by adjusting the chemistry of the VBR as described in [12] in combination with fast cooling of the partial melt. The relatively low viscosity of the melt is required to be able to free flow it to the granulation setup. This viscosity of the melt can be achieved by having sufficient amount of melt (> 70 %) [18]. Second, the addition of CaO decreases the viscosity due to depolymerization in the melt [19].

The designed mix of BR and additives was converged to the target chemistry through the addition of $CaCO_3$ and SiO_2. The final mixture consisted of 77 wt% BR (dry), 15 wt% $CaCO_3$, 6 wt% SiO_2 and 1.9 wt% coke. If the moisture content of the raw BR (35 wt%) is taken into account, the amount of BR valorized in the mixture is 83 wt%. Through FactSage, the calculated amount of melt was 82 wt% at 1200 °C with a liquidus temperature of 1270 °C. The operational boundaries were drawn using FactSage and are visualized in Figure 4. The optimal chemistry identified at the pilot trial is indicated by the heart symbol in Figure 4. If SiO_2 is added, the amount of melt and viscosity would increase. However, a surplus of SiO_2 would result in a viscous partial melt, which is not suitable for granulation. Therefore additional $CaCO_3$ is added close to the area where gehlenite ($Ca_2Al_2SiO_7$) starts precipitating. If excess CaO is added, gehlenite would start precipitating and the performance of the final product will be lowered due to a decrease of Ca, Al and Si in the glass, and later amorphous phase [13,14]. In the furnace experiment (see methodology section), the melt remained liquid enough for at least 5 min to be able to have a continuous granulation. After granulation, the water content of the VBR was only 2.6 %, so no significant drying was required.

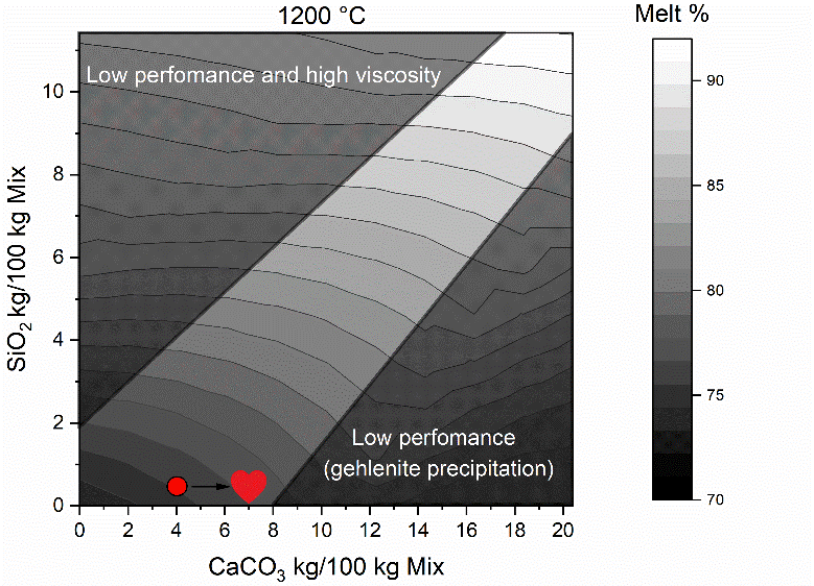

Figure 4: Calculated amount of melt at 1200 °C. The optimal region for operation lies in the zone between the 2 dark shaded triangles.

3.2 Inorganic Polymers

Inorganic polymers were prepared by mixing the milled VBR with a sodium silicate solution (SiO_2/Na_2O = 2.0, 65 wt% water) and sand (CEN). This resulted in a dense mortar with a compressive strength up to 100 MPa and a flexural strength of 11 MPa (Figure). The sample shows the highest strength increase within the first 7 days, which is correlated to its high early

reactivity. Mainly the calcium and sodium contributes to the rapid strength development [12,13]. Compared to a standard OPC-based binder, the compressive strength increase for the inorganic polymers is also significantly higher between 2 and 28 days, however flexural strength remains quite similar. The flow of the inorganic polymer mixture is with 217 mm on the flow table test, also higher than 200 mm for the OPC reference, which is important for casting and compaction of the mixture.

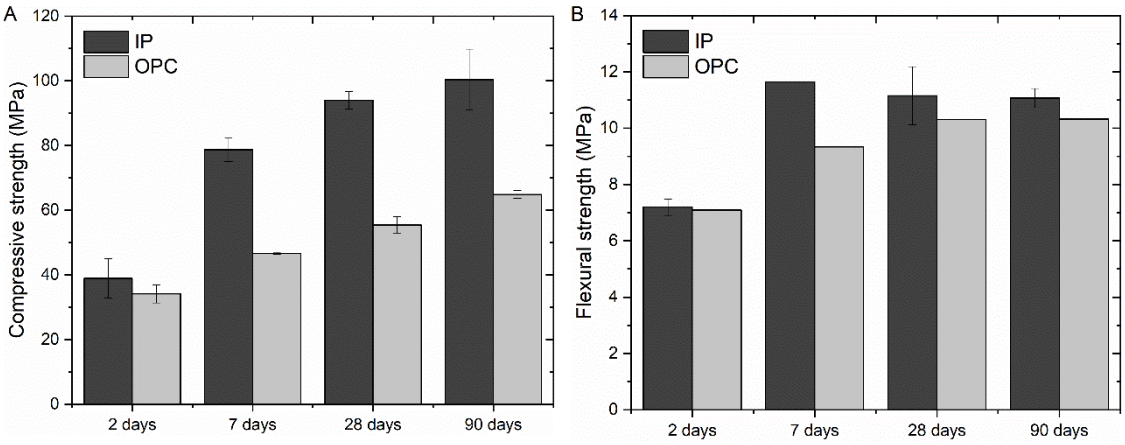

Figure 5: Compressive and flexural strength of the inorganic polymer and OPC reference. Error bars indicate the standard deviation.

3.3 Wider Implications

The work in laboratory and pilot scale demonstrated that BR can be successfully transformed into a product (VBR) usable for alkali-activated binder materials (e.g. inorganic polymers). Incorporation of VBR in blended cement is currently investigated. Future research will focus on the upscaling of BRs from multiple European refineries, which (BRs) have been proven to give promising properties on laboratory scale. However, a full (ongoing) analysis has to review the cost of vitrification and milling. Implementation of new green technologies, like the use of H_2 in combination with electric heating through induction or microwave, are of interest.

4. Conclusion

The work in both laboratory and pilot scale demonstrated that vitrified bauxite residue, processed using vitrification, is an attractive, alternative cementitious product for the construction industry. With an optimized mix design, BR can be partially molten and granulated at relatively low temperatures at about 1200 °C (in comparison to conventional cement production at about 1450 °C). The highly reactive amorphous phase is beneficial for the production of alkali-activated inorganic polymers with compressive strength reaching up to 100 MPa. The decrease in available SCMs (fly ash and blast furnace slag in particular, due to the envisaged energy transition), can be an opportunity for alternative materials, such as VBR (in inorganic polymers or blended cement). However, the prescriptive cement standards and the classification of bauxite residue as a waste is one of the major barriers remaining at the legislative level. Policy actions towards implementation of performance based standards and declassification of the waste status and are required to facilitate the eventual implementation of such a valorization route.

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