High Temperature Processing Options for the Valorisation of Bauxite Residue towards New Materials

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Abstract

The paper describes different processing schemes to transform bauxite residue (BR) into new binders for building applications, while recovering, depending on the chosen route, base metals. The flow chart consists of several unit operations. The first step is the chemical modification, by mixing BR with additives, such as C, SiO_2, and/or B_2O_3. Different blends are sintered or vitrified at temperatures ranging from 900 to 1200 °C. When silica and carbon are added, typically a semi-vitreous slag is generated, which can be either alkali-activated or used as a pozzolana in blended cements. Upon addition of B_2O_3, C and SiO_2, the formation of easy to recover metallic Fe is observed, while the Fe-depleted slag is a highly reactive precursor for an alkali-activated binder. The suggested options have been tested and demonstrated successfully at a laboratory scale. In order to evaluate the feasibility in a closer to real-life scenario, an upscaling pilot-plant project has been launched. This also contributes to a precise and realistic environmental and economic assessment, which is essential before commencing industrial implementation.

Keywords: Bauxite residue, alkali-activated binder, semi-vitreous slag, bauxite residue valorisation, pozzolana.

1. Introduction

Bauxite residue (BR) is the alkaline digestion residue of the alumina producing Bayer cycle. The annual generation rate worldwide exceeds 150 Mt [1] and the accumulated inventory is more than 4 Gt, stored at various disposal areas [2]. The chemical composition of BR, consisting mainly of iron oxides, aluminium hydroxides and titanates, turns the material into an interesting candidate for different applications, such as the recovery of base metals and rare earth elements [3,4], the use in ceramics [5,6] or in cementitious materials [7]. Next to the enormous amount of research papers published, there are already examples of processes incorporating BR at an industrial level, demonstrating the potential of using BR. Nevertheless, its current use sums up to merely 1 – 3 % of the yearly generated (mass of) BR. Concerns, such as uncertainty if the quality of the residue is constant, and thus of resulting products, public perception, the availability of well-established raw materials at low price and the strict legislation in some countries, rating BR hazardous due to its alkalinity, act as barriers against a successful market penetration of BR-based products [1,8].

A reuse of BR in building materials seems to be a promising route, since it is used as bulk at a large scale. Next to cements, the use as an inorganic polymer precursor or as a pozzolana in blended cements are possible routes. Inorganic polymers (IP) can be used as alternative building materials, which in contrast to the hydration of cement, gain their strength by polymerisation, after alkali dissolution, of a reactive, silica-rich material. Most often, Al-rich silicates are used (e.g. metakaolin or fly ash) but Fe-silicates are also reactive precursors [9]. The main advantages of IP are that various industrial residues can be used as raw materials and that the mechanical properties are often superior to those of conventional cements/concretes. In addition to the above, resistance to chemicals and to fire is often attained [10,11]. Pozzolanas (aka pozzolanic materials) are non-hydraulic, meaning that there is no reaction by blending them solely with water. However, the reactive silica and alumina (pozzolanas are typically aluminosilicates) react with portlandite ($Ca(OH)_2$), one of the cement hydration products (reaction 1), to produce strength-giving calcium silicate hydrate phases (reaction 2), calcium aluminate hydrates (reaction 3) or calcium aluminosilicate hydrates, such as strätlingite ($Ca_2Al_2SiO_7 \cdot 8\ H_2O$) [12,13].

$$Ca_3SiO_5 + H_2O \rightarrow x\text{CaO-}y\text{SiO}_2\text{-}z\text{H}_2\text{O} + Ca(OH)_2 \qquad (1)$$
$$Ca(OH)_2 + SiO_2 + H_2O \rightarrow x\text{CaO-}y\text{SiO}_2\text{-zH}_2\text{O} \qquad (2)$$
$$Ca(OH)_2 + Al_2O_3 + H_2O \rightarrow x\text{CaO-}y\text{Al}_2\text{O}_3\text{-}z\text{H}_2\text{O} \qquad (3)$$

Despite these possibilities, using BR "as produced" in the above applications is not contributing to improved properties. In fact, BR shows low reactivity in hydraulic, pozzolanic and alkali-activated systems and behaves mostly as a filler. An exception to the above is BR generated via the sintering process, which contains hydraulic C_2S (Ca_2SiO_4), at levels even higher than 50 wt% [14]. To counterbalance this, in most of the cases dealing with the non-sintered (classical) Bayer process, BR is blended with another reactive raw material, such as metakaolin [11], fly ash [15,16] or FeNi slag [17]. The resulting mechanical properties are satisfactory, but they typically decline with an increasing content of BR in the solid raw mix. In rare cases, BR contributes to higher compressive strength (at least the first 28 days) [18], but this is most probably due to physical effects, in view of the fine granulometry, and maybe due to the alkali activation of cement; it is doubtful if it participates in the chemical reactions, as traditional pozzolanas (e.g. fly ash) would do. Moreover, in most works in the literature, aspects relating to the durability of these blended binders remain undiscussed.

In order to increase the reactivity of BR, thermal treatment has proven to be one of the suitable process options. Investigations [19] have proven that the calcination of BR in the range of 600 – 800 °C leads, for instance, to an increase in pozzolanicity in mixtures with Ordinary Portland Cement (OPC). A patent was filed by Votorantim Cimentos S/A and Companhia Brasileira De Alumínio studying the pozzolanic behaviour of a chemically and thermally modified BR by adding $CaCO_3$, such as limestone and a silica source, such as sand or clays, followed by firing in a temperature range of 1000 and 1500 °C [20]. Up to 30 wt% of the resulting material was blended with OPC. All requirements for pozzolanic materials were met. Thermal activation of BR also increases the solubility and its suitability as precursor for geopolymers/inorganic polymers [21]. The downside of a thermal modification of BR is the energy requirement associated with the operation of the furnace (possibly also dryer) and the corresponding emissions due to the burning of fuel and calcination. Additional costs caused by the use and transport of materials needed for transforming BR into a chemically reactive material, turn the often promising proposals into rather unattractive processes with respect to their economic and environmental impact.

In order to address the above mentioned downsides, integrated, near-zero-waste processes appear as a reasonable path forward. In these schemes, base and/or critical metals are recovered in an intermediate step before valorising the residual fraction typically towards building materials [22,23]. Potential additions are sourced from the vicinity of the alumina plant and/or BR disposal area and kept to a minimum. The drawback of such an approach is that it entails substantial risks: the integrated flow charts are rather complex, with substantial capex and opex, leading to a range of materials that are relevant for different markets (typically impossible to predict), each one having its own characteristics. An alternative approach is to develop processes that use the bulk of the material for a single application, i.e. building materials. Such a scheme is typically simple and robust, minimising operational uncertainties, yet, the value

This upscaling project also contributes to a precise and realistic environmental and economic assessment, which is essential in view of the envisaged industrial implementation. The selection of the most suitable flowsheet for an industrial implementation is, among other factors, dependent on the local availability and costs of additives, the quality of BR, for instance, its silica content, and the available infrastructure. Local industrial synergies might be conceivable, for instance, between the alumina and boron industry, when boron containing wastes potentially turn into a feedstock for the modification. The vicinity of alumina and cement plants would favour, for instance, the production of pozzolanic materials.

5. Conclusion

Several suggestions for a high temperature modification of BR towards valuable products are presented in this study. BR was successfully transformed into a precursor for inorganic polymers and a pozzolana and, depending on the additions, Fe was recovered in an intermediate step. After the successful demonstration in lab-scale, an upscaling project has been initiated in order to investigate the potential of the valorisation routes in a closer to real-life scenario. More data will be presented at the end of 2017, beginning of 2018.

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7 References

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