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.

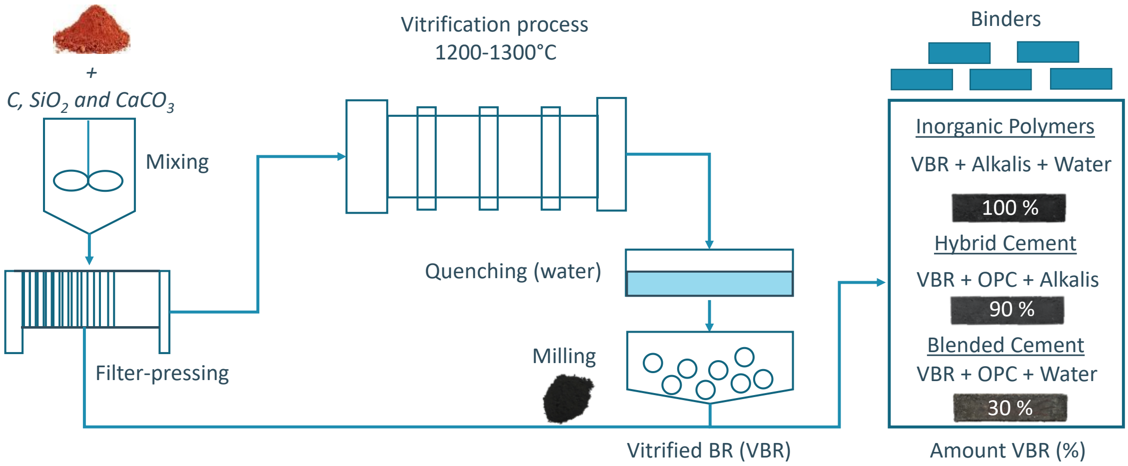

Figure 1: Simple flowsheet showing the unit operations to obtain a milled VBR and the potential products. In this work, only inorganic polymer binders are discussed.

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6. References

1. Ken Evans, The history, challenges, and new developments in the management and use of bauxite residue, *J. Sustain. Metall.* 2 (2016) 316–331. https://doi.org/10.1007/s40831-016-0060-x.
2. Tobias Hertel, Yiannis Pontikes, Geopolymers, inorganic polymers, alkali-activated materials and hybrid binders from bauxite residue (red mud) – Putting things in perspective, *J. Clean. Prod.* 258 (2020) 120610. https://doi.org/10.1016/j.jclepro.2020.120610.
3. Chenna Rao Borra et al., Smelting of bauxite residue (red mud) in view of iron and selective rare earths recovery, *J. Sustain. Metall.* 2 (2016) 28–37. https://doi.org/10.1007/s40831-015-0026-4.
4. Frank Kaußen, Bernd Friedrich, Reductive smelting of red mud for iron recovery, *Chemie-Ingenieur-Technik*. 87 (2015) 1535–1542. https://doi.org/10.1002/cite.201500067.
5. Efthymios Balomenos, Could “red mud” be the answer to some of Europe’s critical-metal supply concerns?, *Policy Br. EU.* (2018) 1–9. http://kuleuven.sim2.be/wp-content/uploads/2018/04/REDMUD-Brief-6.5.pdf.
6. European Commission, The European green deal, *Eur. Green Deal.* (2020). https://doi.org/10.2307/j.ctvd1c6zh.7.
7. Yanxiu Wang et al., Recovery of alkali and alumina from bauxite residue (red mud) and complete reuse of the treated residue, *J. Clean. Prod.* 188 (2018) 456–465. https://doi.org/10.1016/j.jclepro.2018.04.009.
8. Farshad Rajabipour et al., Alkali-silica reaction: Current understanding of the reaction mechanisms and the knowledge gaps, *Cem. Concr. Res.* 76 (2015) 130–146. https://doi.org/10.1016/j.cemconres.2015.05.024.
9. Thomas Czigle et al., Laying the foundation for zero-carbon cement, McKinsey. (2020).
10. Tobias Hertel, Bart Blanpain, Yiannis Pontikes, A proposal for a 100 % use of bauxite residue towards inorganic polymer mortar, *J. Sustain. Metall.* 2 (2016) 394–404. https://doi.org/10.1007/s40831-016-0080-6.
11. Tobias Hertel et al., Correlating the amorphous phase structure of vitrified bauxite residue (red mud) to the initial reactivity in binder systems, Submitted to *Cem. Concr. Res.* (2021).
12. Michiel Giels, Tobias Hertel, Yiannis Pontikes, High performance mortars from vitrified bauxite residue; the quest for the optimal chemistry and processing conditions., Submitted to *Cem. Concr. Res.* (2021).
13. Michiel Giels et al., Designing highly reactive precursors from bauxite residue: can the RILEM R3 test assist?, in: *7th Int. SLAG Valoris. Symp.*, 2021: pp. 89–92.
14. Michiel Giels et al., Transformation of bauxite residue into highly reactive precursors for inorganic polymers and blended cement, feasible in the Alumina industry?, in: *3rd Int. Bauxite Residue Valoris. Best Pract. Conf.*, 2020: p. 9.
15. C.W. Bale et al., FactSage thermochemical software and databases - recent developments, *Calphad Comput. Coupling Phase Diagrams Thermochem.* 33 (2009) 295–311. https://doi.org/10.1016/j.calphad.2008.09.009.
16. EN 196-6, Methods of testing cement - Part 6: Determination of fineness, 2010.
17. EN 196-1, Methods of testing cement - Part 1: Determination of strength, 2016.
18. Zhuangzhuang Liu, Effect of solids on the rheology of heterogeneous silicate melts, *Thesis KU Leuven*. (2017).
19. Bjorn Mysen, Pascal Richet, *Silicate glasses and melts*, 2005.