

The Solid-state “Bayer Process”-inspired Valorization Route: Adding a Sodium Alumino-silicate to the Precursor

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Abstract

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Despite the potential of re-use in many sectors, less than 3 % of the annually produced bauxite residue (BR) is in some way valorized, with the rest being usually stored in disposal areas. This work aims to increase the valorization of BR by producing dense monoliths through alkali-activation followed by hydrothermal curing in an autoclave, a process which is believed to be simple, robust and most likely of low CAPEX and OPEX. The solid precursors, BR and an alumino-silicate by-product from the spent potlining treatment by the Low Caustic Leaching and Liming process, named LCLL ash, were dry mixed in contents of 80 and 100 wt% of BR and 0 and 20 wt% of LCLL ash. Na-silicate was added as an alkaline activator, and the final blend was press-shaped at 50 MPa for 1 min to obtain prismatic specimens of 6x1.5x1.5 cm³. Curing took place in an autoclave at 220 °C for 24 h. X-ray diffraction showed that the hydrothermal curing promoted the dissolution of quartz and gibbsite, and the formation of zeolites (and zeolite-type phases), such as cancrinite and analcime. The compressive strength of the autoclaved specimens was six times higher than that of the specimens cured at room temperature, and the addition of LCLL ash significantly improved the strength gain (from 31 MPa in the sample containing only BR, to 40 MPa in the sample with LCLL ash). An upscaling of such process seems feasible, even within the premises of alumina plants, as the knowledge on such processing or the required infrastructure (e.g., autoclaves) is available within the industry. Final products can be tiles, bricks, or other building elements.

Keywords: Bauxite residue, Red mud, Dense monoliths, Autoclave curing, Alumina plant residues.

1. Introduction

The Bayer process is the principal industrial approach to produce alumina, characterized by the digestion of the bauxite ore with caustic soda and further precipitation of alumina (oxy)hydroxide [1]. A significant portion of the bauxite does not dissolve during the process and is usually discarded and stored in disposal areas, receiving the name of bauxite residue (BR) or red mud. The production of 1 t of alumina generates 1-1.5 t of bauxite residue [2], and as the production of alumina to produce aluminium increases, so does the generation of bauxite residue. According to the International Aluminium Institute (IAI) [3], the production of BR in 2017 was close to 160 Mt and is expected to increase to 220 Mt by 2040, resulting in a global inventory of 8 billion tonnes of BR. The residue is accumulated in disposal areas, and poses potential risks for ecosystems and human health due to the high alkalinity in combination with its fine particle size distribution [2,4]. Therefore, over the last decades, efforts have been made to find applications for this material.

Some of the most attractive areas for the use of BR are the following: construction materials [5–9], metals recovery [10], soil amelioration [9], road constructions [11], pigments and glass-ceramics [2]. Despite the numerous alternatives, however, only about 3% of the total mass of BR

available is used, with some of the major barriers being its high alkalinity and moisture content [2].

One possible and promising way of using bauxite residue is in the production of alkali-activated materials (AAM), which can benefit from the BR's chemical composition (Si, Al, Ca and Fe) and inherent alkalinity. AAM's are produced from a mostly amorphous precursor, usually an aluminum silicate, and an alkaline activator [12], resulting in a material with properties that can be superior to those of conventional binders [13], such as high early strength and resistance to chemical attack. Moreover, their production can result in a lower carbon footprint in comparison to conventional binders [14], as there is no need for calcination at elevated temperatures as in the case of Portland cement clinker. The major drawback related to the use of BR to produce AAM is its low reactivity, which is the reason why many researches have used BR merely as a minor addition (<20 wt%) to other precursors. Alternatives to overcome this challenge usually require the use of high temperatures (> 1000 °C), significant energy consumption and/or expensive/high-carbon footprint additions.

A conceivable and more environmentally friendly process is through hydrothermal curing at temperatures below 300 °C and under high pressure, which can increase the dissolution of the phases in the BR, and hence its reactivity. A successful example of this approach is the patent developed by Hertel and Pontikes [15], in which the inventors produced 100 wt% BR monoliths with compressive strengths up to 20 MPa. The bauxite residue was activated with sodium silicate solution and samples were put into shape using pressures of 19 and 50 MPa. Specimens were hydrothermally cured in autoclave at 220 or 260 °C and the respective steam pressures. After autoclaving, quartz and gibbsite, which were present in the precursor, showed a significant decrease in intensity in the XRD patterns, indicating that these phases dissolved under hydrothermal curing. The use of industrial clay and kaolin as additives increased the reactivity, resulting in better mechanical performance. A manuscript has been submitted based on the outcomes of the patent [16].

The aforementioned process was coined Solid-state "Bayer Process"-inspired Valorization Route, as, similarly to the Bayer process, it makes use of an alkaline agent to get the raw materials to react in an autoclave, with the major differences (apart from the resulting products) being the very low liquid content and the press-shaping of the monoliths. The process was put into practice in this paper using bauxite residue and a by-product from an aluminium electrolysis plant, aiming to investigate the synergy between residues from the same producer. The methodology consisted in mixing the raw materials and press-shaping specimens followed by hydrothermal curing in an autoclave at 220 °C for 24 h. The specimens were characterized before and after autoclaving in terms of mineralogy and compressive and flexural strength.

2. Materials and Methods

Bauxite residue and a by-product from the Low Caustic Leaching and Liming process, named LCLL ash, were supplied by Rio Tinto and used as raw materials in this research. The LCLL ash is a sodium aluminosilicate and more information on how it is obtained can be found elsewhere [17,18]. Both materials were dried at 105 °C until constant mass, deagglomerated using a disk mill (Pulverisette 13, Fritsch) and characterized in terms of chemistry, mineralogy and physical parameters.

Chemistry was determined by Wavelength Dispersive X-ray fluorescence (WDXRF) in a Bruker S8 Tiger (4 kW Rh system) and analyzed in the software Uniquant 5 (Omega Data System BV). Loss on ignition was determined by means of thermogravimetric analysis using a TA Instruments DSC SDT Q600 Thermogravimetric Analyzer, at a heating rate of 5 °C/min from ambient temperature to 1000 °C in N₂ atmosphere. Mineralogy was qualitatively accessed by X-ray

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