

Title

High strength construction material from raw bauxite residue by one-step alkali activation

Keywords

Bauxite residue, red mud, inorganic polymer, alkali activated materials, leaching behavior

Authors

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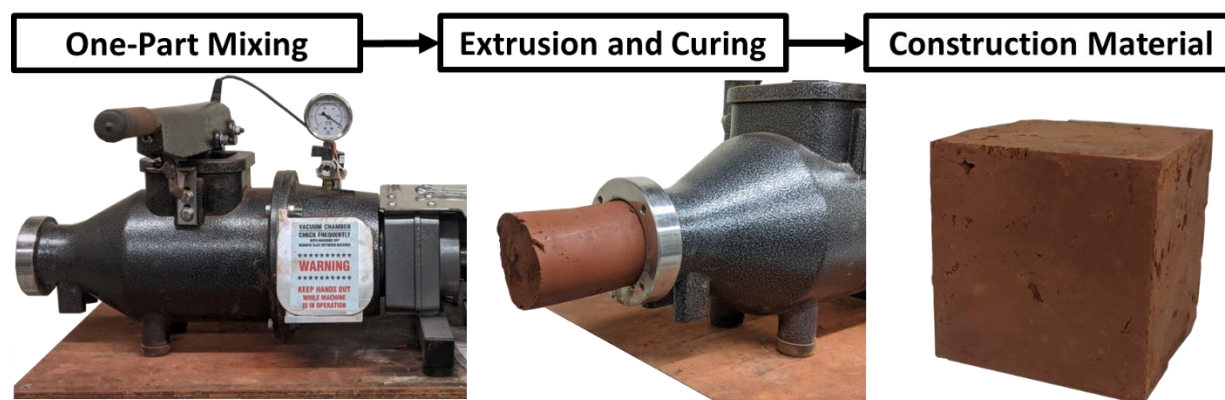
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Abstract

An alkali activated material composed of 77% raw, unmodified bauxite residue has been developed that meets the mechanical strength standards for construction materials. This can solve the circularity gap in aluminum production by providing a means to valorize bauxite residue in large volumes in the construction sector. This environmentally friendly building material leverages a novel one-step mixing process to dramatically increase the proportion of bauxite residue contained in the material without the need for calcination. The alkali activated material achieves over 30 MPa of strength after 3 days of curing, satisfying the ASTM standards for precast structural members. The microstructure has been characterized by mercury intrusion porosimetry and isothermal nitrogen adsorption. The leaching of metallic and nonmetallic pollutants from the material is substantially below the maximum allowable concentration in Quebec, Canada, the origin of the bauxite residue. This alkali activated material is a circular economy solution to valorize large contents of bauxite residue in construction applications such as retaining wall members, underground utility lines, and wastewater infrastructure while reducing the environmental impact of the aluminum industry.

Graphical abstract



1 Introduction

Bauxite residue is a globally accumulating waste product, and the development of a valorization technique is needed as a long-term solution to mitigate its production. The lack of valorization options for bauxite residue (BR) is a gap in the sustainability of the aluminum industry, recognized in the international 2022 Circularity Gap Report and by the Aluminum Stewardship Initiative, a global non-profit organization advocating for the sustainability in aluminum production [1, 2]. The global aluminum industry produces 150 million tons of BR per year, but less than 3% of the waste is utilized by current technology [3]. The field of construction is in sore need of greener construction materials with lower consumption of virgin raw materials and environmental impact [4, 5]. Replacing the virgin raw materials with BR simultaneously reduces the environmental footprint of both the construction and the aluminum sectors. However, the high alkalinity of BR severely limits the content that can be used in concrete without compromising the mechanical integrity by detrimental alkali-silica reactions [6, 7]. An alternative binder chemistry is required to utilize large concentrations of BR in construction materials.

Alkali activation of BR can produce construction materials with higher proportions of BR than is possible with Portland cement. Alkali activated materials (AAMs) have received heavy scientific scrutiny as an environmentally friendly alternative to cement. The principal challenge in producing BR-based AAM is maximizing the BR content while meeting the ASTM standards for construction materials which require the compressive strength to exceed 28 MPa. A plethora of studies have investigated the optimal chemical and phase compositions to meet this requirement [8–10]. However, comparatively few studies have evaluated process-property relationships for the alkali activation of BR as a means of achieving this goal. In this study, a new mixing methodology is demonstrated that utilizes a pugmill compressive mixer traditionally used only for the production

of ceramic pottery. In a novel discovery, compressive mixing synergizes strongly with the alkali activation of BR and allows the production of high-strength AAMs containing 77% BR. This methodology eliminates the need for the energy-intensive process of calcination and triples the proportion of BR compared to other fly ash-based BR AAM techniques [11, 12]. The strength development, microstructure, and leaching behavior of this new BR AAM have been characterized to assess the viability of the AAM as a construction material.

2 Experimental procedures

Alkali activated materials (AAMs) were prepared from bauxite residue using a one-step mixing procedure. Filter-pressed bauxite residue (BR) was produced in Quebec, Canada, and received in its raw, wet state from Rio Tinto. The water content in the BR was measured to be 25.4%. Fly ash from Titan America, tradename ProAsh®, was used as a supplementary binder. The chemical composition and density of the BR and fly ash used are given in Table 1. Anhydrous, reagent-grade calcium hydroxide (slaked lime) was added to moderate the calcium content. A combination of anhydrous, reagent grade sodium metasilicate and sodium hydroxide were used as alkali activators. The components were added in the quantities specified in Table 2 to the mixing chamber and mixed without any drying, pretreatment, premixing, or modification. All the components were mixed simultaneously in a single step in a Peter Pugger® brand pugmill operating at 15 rpm. After mixing for twenty minutes, the resulting paste was extruded out of the pugmill, shaped, and cured, as shown in Figure 1. To comply with ASTM standard C109 [13], the paste was cast into 5 cm stainless steel molds and sealed to prevent moisture loss. Curing was conducted at 60°C in a saturated humidity chamber. The compressive strength was measured after 1, 3, and 7 days under constant loading of 1 kN/sec, as per ASTM C109.

Table 1: Chemical composition of the bauxite residue and fly ash raw materials

Equivalent oxide composition (%), dry	Bauxite residue	Fly ash
Al ₂ O ₃	74.7	21.4
SiO ₂	6.7	55.3
Na ₂ O	0.01	1.0
Fe ₂ O ₃	16.0	10.2
CaO	0.03	3.4
Moisture content (%)	25.4	-
Specific gravity	2.79	2.65

Table 2: Composition of the alkali activated material

Component	Quantity (g)
Raw bauxite residue	5000
Grade C fly ash	933
Calcium hydroxide (slaked lime)	217
Sodium metasilicate	283
Sodium hydroxide (lye)	36

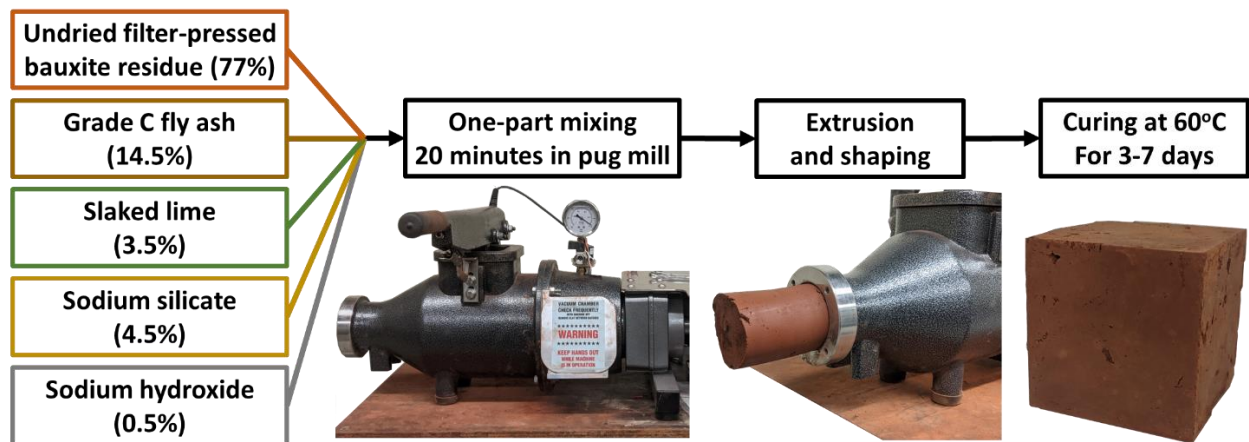


Figure 1: One-step mixing, extrusion and curing process used for the production of high-strength alkali activated materials containing 77% unmodified, filter-pressed bauxite residue.

The microstructure of the AAM was characterized using mercury intrusion porosimetry and isothermal nitrogen adsorption. The AAM was dried and gently fragmented into 5-10 mm pieces

for microstructural analysis to avoid undue distortion of the microstructure. The macropore size distribution, total porosity, permeability, and density were measured using a Micromeritics Autopore® porosimeter. The volume of mesopores was characterized by the Barret-Joyner-Halenda method and the specific surface area was calculated by Brunauer-Emmet-Teller theory with a Micromeritics Gemini® analyzer. The leaching behavior of the AAM was assessed in accordance with EPA method 1311 and Quebec method CTEU-9 [14, 15]. The AAM was ground and sieved below 75 microns. For method 1311, the ground sample was combined with a 2.88 pH solution of acetic acid at a weight ratio of 1:20 and mixed for 18 hours. For method CTEU-9, the ground sample was mixed at a ratio of 1:4 with a 7.0 pH solution of deionized water for 7 days. Mixing was conducted in polypropylene vials, at 30 rpm, in the manner specified by both leaching standards. After mixing, the leachate solutions were filtered with 0.45-micron glass filters. A portion of each solution was acidified to pH of 1 using nitric acid and analyzed for trace metals with a ThermoFisher Scientific® inductively coupled plasma mass spectrometer. The remaining portion of each solution was analyzed for fluoride content using an ion-specific electrode.

3 Results and discussion

The pugmill mixing procedure produced alkali activated materials (AAMs) with exceptionally high strength. The specimens exceed 30 MPa, as shown in Figure 2(a), after only 3 days of heated curing; gaining more than 90% of their final strength in this time. The strength of the AAM satisfies the 28 MPa required by ASTM standards for several applications as precast structural components including concrete barriers (C825 [16]), retaining wall members (C915, C1776 [17, 18]), underground utility, wastewater and storm drain structures (C858, C913, C1504 [19–21]), manhole sections (C478 [22]), septic tanks (C1227 [23]), and brick masonry (C62 [24]). This presents a

variety of applications for environmentally friendly structural materials composed primarily of BR.

A key advantage of the pugmill methodology is the use of BR in its raw, filter-pressed state, as received from the aluminum production facility. The pugmill methodology does not require the BR to be dried and milled to bolster reactivity. This deviates significantly from conventional methodologies and allows all the mixing to be conducted in a single step without additional pretreatment stages; greatly simplifying the production process. The only similar study in the literature to use undried BR limited the BR content to 24% [12]. With the new methodology, the proportion of BR can be tripled to 77% while maintaining high strength. The compressive strength is five times greater than comparable studies of BR-fly ash AAMs prepared with traditional two-part mixing methodologies which achieved only 5 – 7 MPa when containing 70-80% BR [25, 26]. This demonstrates the synergy between the compressive pugmill mixing and the stronger alkali activation reactions in the BR without the need for additional processes to improve the reactivity, such as milling and calcination.

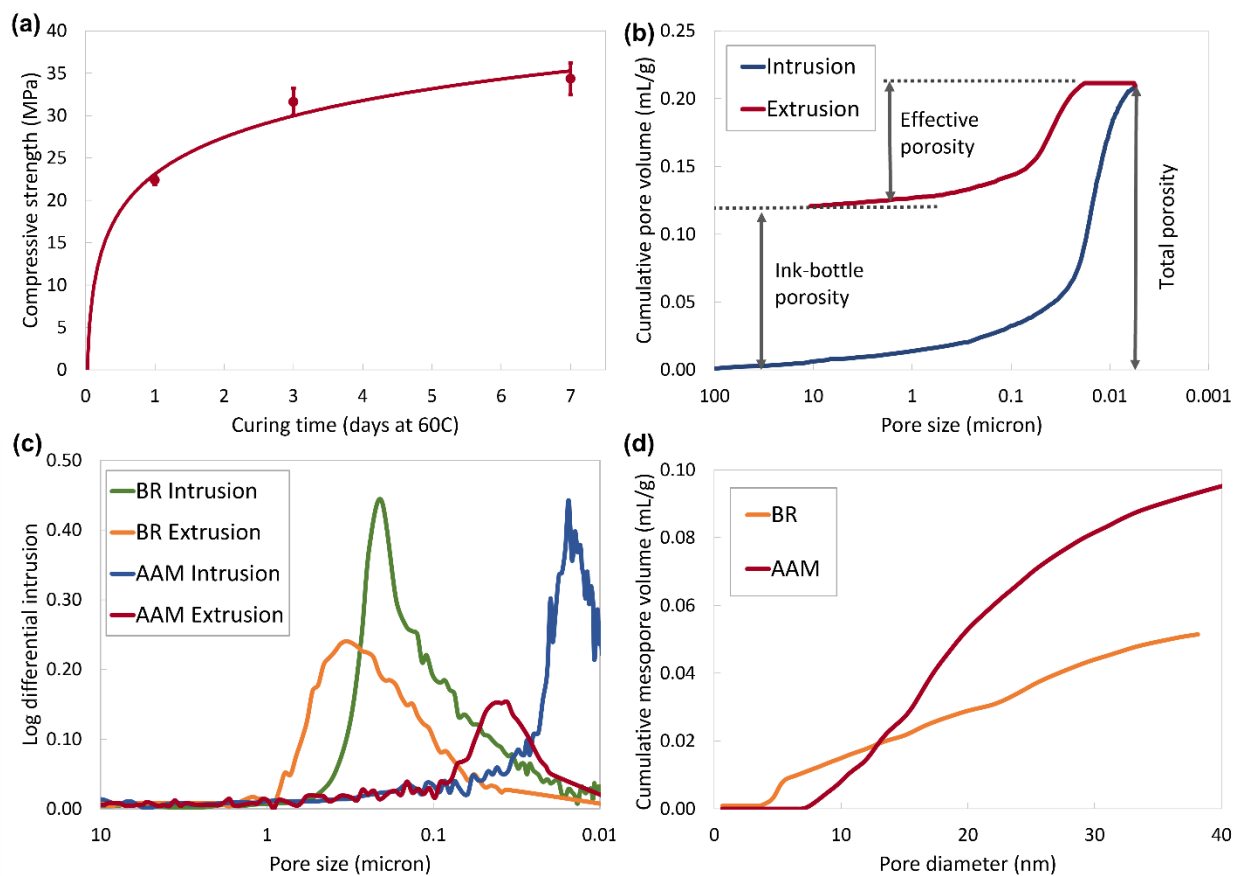


Figure 2: (a) The compressive strength in MPa of the alkali activated material (AAM) during heated curing. (b,c) Mercury porosimetry showing (b) the intrusion and extrusion of the AAM in mL/g and (c) the pore size and neck size distributions in microns of the AAM and bauxite residue (BR). (d) The mesopore volume in mL/g of the AAM measured using isothermal nitrogen adsorption.

To characterize the microstructure of the material, the AAM was analyzed by mercury porosimetry and nitrogen adsorption. The mercury intrusion and extrusion of the AAM, shown in Figure 2(b), reveal a strong ink-bottle effect. This indicates a high degree of constriction between the true pore diameters and connective pore necks. While the total porosity of the AAM is 34%, the effective

porosity is less than half of this because of this constriction. The pore size distribution, illustrated in Figure 2(c), is monomodal. The extrusion of the AAM specimen reveals that the median pore size is 40 nm, and the intrusion shows that the pores are linked by necking points of diameter 15 nm. The pores are significantly smaller than raw BR which has pores of 300 nm and less constriction. The increased mesopore volume of the AAM is confirmed by isothermal nitrogen adsorption, shown in Figure 2(d), which shows that it is more than twice that of raw BR. The microstructural properties calculated from the porosimetry are listed in Table 3. The permeability is increased by more than one hundred-fold, making the AAM a borderline semi-pervious material [27].

Table 3: The properties of the alkali activated material after seven days of curing at 60°C compared to raw bauxite residue.

Property	Bauxite residue	Alkali activated material
Compressive strength (MPa)	-	34.4
Total porosity (%)	39.3	34.3
Effective porosity (%)	28.6	14.9
Permeability (millidarcy)	0.02	5.63
Bulk density (mg/L)	1.54	1.64
Skeletal density (mg/L)	2.54	2.49
Specific surface area (m ² /g)	22.8	24.9

The valorization of bauxite residue presents a unique challenge due to its ecotoxicity [28]. Prior studies have shown that alkali activation is effective at stabilizing trace toxins in BR, making the AAM safe for use [29–31]. However, no prior study has investigated the leaching of AAM which contained high contents (>50%) of BR. In this study, an accelerated acid leaching test (EPA 1311) and a water-based leaching test (QC CTEU-9) were conducted to determine the safety of this unique AAM containing 77% BR [14, 15]. A summary of the results is shown in Figure 3,

alongside the maximum allowable concentrations for resurgent surface water in Quebec, Canada, where the BR was produced [32]. The alkali activation was successful in stabilizing the trace pollutants in the BR, making them unavailable for leaching. The results under both acidic and neutral leaching conditions were similar and varied based on the specific pollutant. In general, the EPA 1311 procedure yielded lower leaching due to the lower sample / solution ratio. In all cases, the leaching of the AAM was significantly below the maximum allowable concentration, demonstrating that the AAM can be used as a construction material without risk of ecotoxicity.

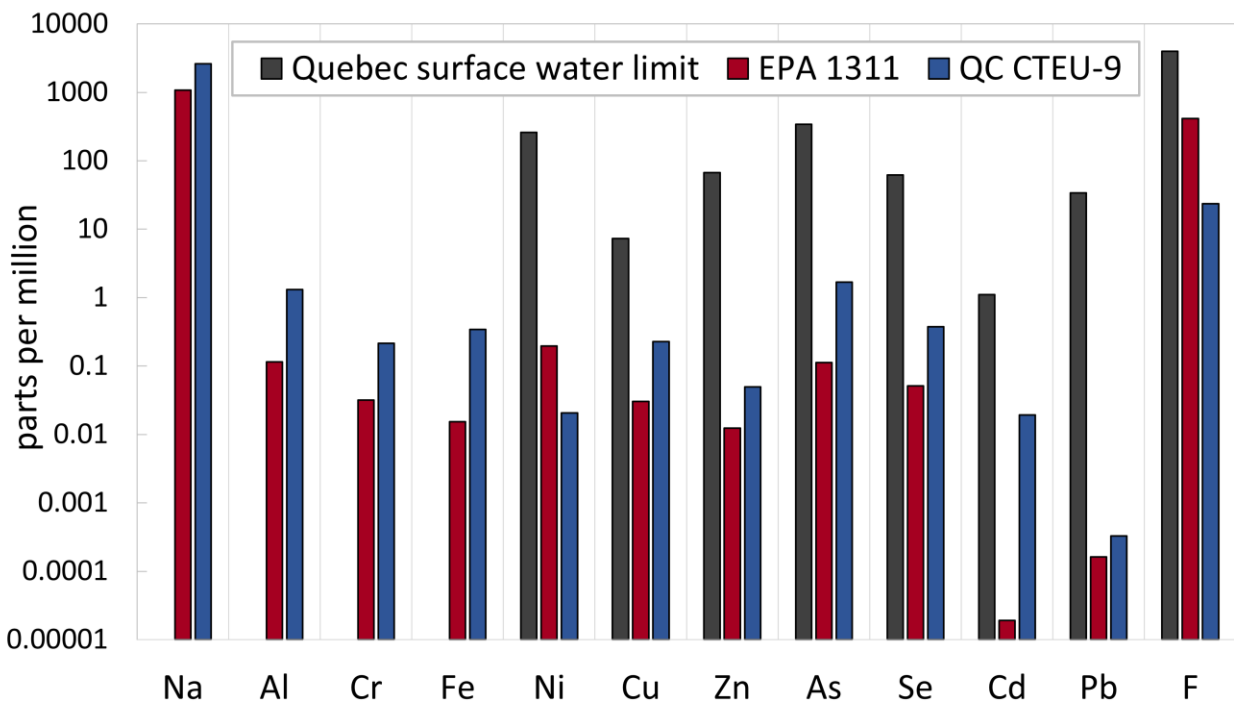


Figure 3: The water leaching (QC CTEU-9) and accelerated acid leaching (EPA 1311) behavior of the alkali activated material compared to the maximum allowable concentrations for resurgent surface water in Quebec in parts per million [32]. The limit for sodium, aluminum, chromium, and iron are not defined by the standard.

4 Conclusion

The bauxite residue (BR) alkali activated materials (AAMs) are an environmentally friendly construction material that addresses the circularity gap that exists in aluminum production and improves the sustainability of both the aluminum and construction sectors. With the novel pugmill mixing methodology demonstrated in this work, AAMs can be produced containing 77% unmodified BR, eliminating the need for costly and energy-intensive preprocessing steps. The AAMs reach 34 MPa in only three days of curing, meeting the ASTM requirements in numerous standards for retaining walls, brick masonry, and wastewater infrastructure. Leaching analysis confirms that the strong alkali activation effectively pacifies the ecotoxicity of the BR. With this new mixing methodology, BR AAMs are a circular economy solution to reduce the impact of the aluminum sector on the environment by valorizing large contents of BR as an environmentally friendly construction material.

5 Acknowledgements

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6 Conflict of Interests

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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