

# Large-scale Valorization of Bauxite Residue for Inorganic Polymers

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## Abstract



A process is suggested in this paper to valorize bauxite residue (BR) on a large-scale. The resulting material is a binder that can be used, depending on its properties, in the production of bricks and tiles, or as an aggregate which can be safely stored in landfills or used in concrete or asphalt. The strategy is to develop a precursor that upon mixing with alkalis will lead to an inorganic polymer. To achieve the above, thermodynamic calculations were carried out. It was found that reducing conditions and additional silica promote the formation of an Fe<sup>2+</sup>-rich liquid phase during heating, which is expected to result in an amorphous phase upon solidification. In practice, this implies minor additions of silica and carbon to the bauxite residue, and firing at temperatures of about 1200 °C to produce a semi-glassy precursor. Experimental work verified the above hypothesis and indeed a highly reactive alkali activated binder was formed. Mixing this binder with “fresh” filter-pressed BR at a ratio 3:7 led to a hard, water-insoluble, reddish composite that can find different applications. An industrial implementation seems to be straightforward since existing installations can be adapted and only minor additions have to be carried out.

**Keywords:** Bauxite Residue; valorization; inorganic polymer; aggregate; firing.

## 1. Introduction

Bauxite residue (BR), also referred to as ‘red mud’, is generated during the digestion of bauxite in the Bayer process, exceeding a yearly production of 150 Mt [1]. The global inventory of BR is estimated to be above 2.7 Gt in 2007 [2]. BR is still considered as a problematic waste stream of alumina production, and as a result, one of the potential uses of it entails incorporating it in existing industrial processes. The main driving forces for the valorization of BR are the lack of storage volume in the disposal areas, as well as the long-term liability such storing incurs. The composition of BR with substantial amounts of Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and critical minor elements makes it attractive as a raw material for the recovery of valuable major metals or rare earth elements (like scandium) [3,4] but also in ceramics [5] or in building materials [6].

In addition to the use of BR as source for Al and Fe in ordinary Portland cements (OPC) or in low-energy binders, such as calcium sulfoaluminate (CSA) cements, attempts have been made to valorize BR in inorganic polymers (IP). The strength development of these alternative cementitious binders is based on polymerization reactions in alkaline media [7]. BR has been used in IP binder systems in combination with reactive materials such as metakaolin [8] or ground granulated blast furnace slag (GGBFS) [9]. Generally, an addition of BR to these reactive precursor materials leads to decreasing properties of the binder, with the result that the BR fraction in these binders is kept low to reach satisfying mechanical properties. Chemical and also partially thermal modifications of BR have been carried out by Hairi et al. who transformed it into a reactive material by using raw or tempered (500 °C) BR and mixing it with different additions like amorphous silica fume (6-26 wt%) and alumina (0-20 wt%) [10].

In contrast to the presented studies, the aim of this work is to use as much as BR as possible without using costly additives or other reaction promoters. The concept is to thermally and chemically modify BR and create a substantial amount of amorphous phase resembling other non-ferrous slags. It has been shown in the past that non-ferrous slags with a deviation from the traditional aluminosilicate chemistry, for example copper slag, can lead to IP [11]. Main characteristics of these iron-rich precursors is iron in oxidation state +II and with a high amorphous fraction [12]. The chemistry of BR is comparable with other iron-rich precursors, however the degree of crystallinity differs. Also, most of the iron in BR is trivalent. In the present work a process is presented which aims at a large-scale valorization of BR into a novel construction material. The focus of the study is whether a modified BR has the potential to form an inorganic polymer binder, and if that binder combined with fresh BR can deliver a final composite matrix suitable for certain applications.

## **2. Experimental Methods**

### **2.1. Characterization of the raw material**

The starting material of all experiments was filter pressed BR cake, provided by Aluminium of Greece (AoG). BR was dried for 72 h at 105 °C. The chemical composition was determined by semi-quantitative X-ray fluorescence (XRF). Thermogravimetric analysis (TGA) was performed up to 1000 °C using a heating rate of 5 °C/min in Ar atmosphere to determine thermal behavior. The mineralogy was determined by quantitative X-ray diffraction analysis (QXRD). The procedure is described elsewhere [13].

### **2.2. Thermodynamic calculations**

The thermochemical software FactSage 7.0 was used in combination with the FACTPS (pure substances), FToxid (oxide compounds/solutions) and FSstel (steel intermetallic compounds/steel alloy solutions) databases. The focus of the thermodynamic calculations was on the development of a liquid phase fraction during a heat treatment to 1200 °C by adding varying amounts of carbon (to reduce the predominant Fe<sup>3+</sup> originating from hematite into Fe<sup>2+</sup>) and silica in a mix with BR. As an alternative to silica, different calcia additions were modeled. In industrial practice, silica and calcia correspond to sand and limestone additions, which are easily available, low-cost resources.

### **2.3. Modification of BR**

Based on the results of the thermodynamic calculations (FactSage), a mix of BR, carbon (graphite powder) and silica (microcrystalline SiO<sub>2</sub>) in a weight ratio of 88.56:1.44:10 was mixed for 10 hours. Subsequently, firing was performed in a closed alumina crucible using an induction furnace with a SiC external crucible as susceptor. The atmosphere in the crucible was kept inert by flushing Ar (60 L/h) through a gas inlet which was integrated in the crucible lid. The forming gas species were released via a gas outlet. The sample was heated with a heating rate of 5 °C/min, followed by an isothermal step of 1 h at a maximum temperature of 1200 ± 30 °C. To suppress crystallization of the liquid phase during solidification, the semi-molten slag was quenched in water by tilting the furnace. The obtained precursor ('Pr\_A') was dried at 105 °C until a constant weight was reached.

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