

A near zero waste valorisation vision for bauxite residue through experimental results

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Abstract

Bauxite residue from the aluminium industry is mainly composed of iron oxide, titanium oxide, silicon oxide and undissolved alumina together with a wide range of other oxides and minor content of rare earth elements, gallium, vanadium and scandium, which vary according to the country of origin of the bauxite. Experimental results for a zero waste valorisation vision for the bauxite residue are presented using hydrometallurgical and pyrometallurgical treatment, aiming at the recovery of the critical metals. Application of bauxite residue for acid mine drainage (AMD) solution treatment and carbon dioxide capture under high pressure in an autoclave were studied as one possibility for the valorisation of bauxite residue.

Key words: bauxite residue, zero waste, critical metals, valorisation

Introduction

Aluminum is a material with global production of 45 million tonnes in 2013 via Bayer Process [1]. Bauxite residue from the aluminium industry is one of the largest industrial by-products in modern society with global stock levels estimated at around 3.000 million tonnes at the end of 2010 [2]. The amount of bauxite residue produced by an alumina plant can vary from 0.3 to 2.5 tonnes of residue per tonne of alumina produced. It is primarily depending on the following parameters: alumina content of the bauxite ore, the type of aluminium oxide/hydroxide present (e.g. gibbsite, boehmite or diasporite), and the temperature and high pressure conditions used for dissolution of bauxite ores. A processing temperature of 140-150°C is generally used for bauxites ores high in gibbsite, and a temperature of 220-270°C for the European diasporic bauxites.

Castaldi et al. [3] have studied the structure of bauxite residue, where nearly 80 % consists of three of these phases: cancrinite, sodalite and hematite, as shown in Table 1.

Table 1: Typical mineralogical composition of the bauxite residue (in %)

Cancrinite [$\text{Na}_6\text{Ca}_{14}\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_{1,6}$]:	29.0-33.0
Sodalite [$\text{Na}_8(\text{Cl},\text{OH})_2\text{Al}_6\text{Si}_6\text{O}_{24}$]:	16.0-24.0
Hematite [Fe_2O_3]:	27.0-29.0
Boehmite [$\text{AlO}(\text{OH})$]:	5.0-6.0
Gibbsite [$\text{Al}(\text{OH})_3$]:	4.0-5.0
Anatase [TiO_2]:	5.0
Andradite [Ca-Fe-Al-Si oxides]:	4.0
Quartz [SiO_2]:	2.0

The bauxite residues contain scandium and gallium (Approx. 50-150 ppm) and up to an order of magnitude higher such as: vanadium and rare earths elements.

Binnemans et al. [4] discussed the possibilities to recover rare earths from bauxite residues, which commonly contain only low concentrations of rare-earth elements, but are available in very large volumes and could provide significant amounts of rare earths to European countries. The success rate is set to increase if the rare-earth recovery from these industrial waste streams is

a part of a comprehensive, zero-waste, "product-centric" valorisation scheme, in which applications are found for the residual fractions that are obtained after removal of not only the rare earths but also other critical metals such as scandium, vanadium and gallium and especially base elements: aluminium, titanium and iron. Unfortunately, the extraction of aluminum, iron and titanium from bauxite residue is limited due to insufficient amount of acidic solution from leaching caused by the polymerization of silica [5]. Kinetic studies have demonstrated that at constant temperatures, silica dissolution increases with increasing acid concentration, but it decreases when the temperature is increased and the acid concentration is reduced. This is due to the enhancement in the solubility of monomeric silicic acid formed during acidic leaching. The control mechanisms of silica dissolution have been described according to the shrinking core model by a chemical reaction stage, i.e. silica polymerization, followed by a diffusion stage, because of the silica gel adsorbed on the surface of the particles that limits the metal extraction. The recovery of iron, titanium, aluminum, rare earth elements were considered by many authors [6-1].

The main aim of this work is to present experimental results of a zero waste vision for the bauxite residue valorisation of metallic and mineral components through metallurgical methods. The carbonation of bauxite residue and treatment of acid mine drainage solution shall be considered in order to present possible application of bauxite residue without an additional treatment.

Proposed near zero waste valorisation vision for bauxite residue

First proposal: Pre-use of alkalinity for neutralization of AMD solution and conditioning for EAF smelting of bauxite residue

Due to its properties, bauxite residue can also be used as an input material in various processes. The high alkalinity enables it to be used for AMD neutralisation with the aim of recovering a water effluent stream which can be discharged or treated further for portable waster productions. For the neutralisation experiments two different types of bauxite residue were used, as shown in Table 2. This table shows that the Greek bauxite residue contains more iron oxide, alumina, calcium oxide and scandium but smaller content of silica, titanium oxide and sodium oxide than the German one. Bauxite residue is highly alkaline due to the sodium hydroxide from the Bayer process. For the neutralization experiments, the S:L ratios of 1:10 (100 g/lAMD) and 1:5 (200 g/lAMD) were chosen.

Table 2: Composition of the bauxite residue samples wt.-% or ppm (Sc)

Origin	Fe ₂ O ₃	Al ₂ O ₃	CaO	SiO ₂	TiO ₂	Na ₂ O	Cr ₂ O ₃	Sc
Germany	35.3	15.7	6.7	14.0	11.4	8.9	0.2	86
Greece	44.0	23.0	10.2	5.5	5.6	1.8	0.3	122

Acidic water can damage the plants by corrosion and pose an environmental threat. The aim of the following experiments was to neutralise 500 ml of waste water containing the metallic ions such as iron, copper, and rare earths using bauxite residue.

During the experiments, pH values were recorded over the time to analyse the kinetics of the precipitation process. Table 3 shows the initial and final pH values of the neutralization experiments. The initial pH value of the AMD solution is 1.973 ± 0.031 . Using bauxite residue for the neutralisation of the AMD-solution, pH-value was increased from 1.973 to one in the range between 4.41 and 5.87. At the conclusion of the neutralisation process, filtration was carried out to separate the solid fraction from the neutralised liquid stream.

Table 3: The neutralisation of acid mine drainage solution

Greek Bauxite residue	Initial pH value	Final pH value
100 g, 20°C, 1st	1.983	5.873
100 g, 20°C, 2nd	2.008	5.948
50 g, 60°C, 1st	1.959	4.410
50 g, 60°C, 2nd	1.968	4.936

Figure 1 presents the dried solid after filtration originating from the German bauxite residue and the Greek bauxite residue. The precipitation of AMD water has not changed the colour of the bauxite residues significantly

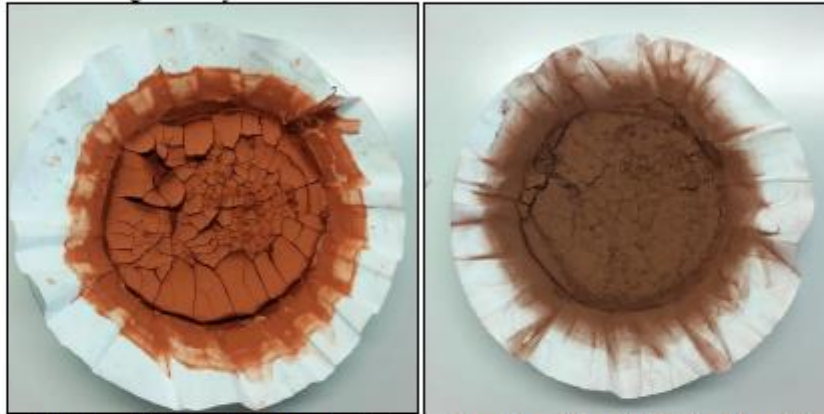


Figure 2: Dried solids after filtration, left: German bauxite residue, right: Greek bauxite residue

The dried solid from the Greek bauxite residue is darker in colour due to its higher content of iron as shown in Table 2. These dried solids could be introduced to a smelting process, which is a superior approach to current industrial AMD neutralisation practices that produce a waste sludge. The low pH dried solids together with precipitates from the AMD neutralisation process would be well suited for the smelting process. Iron will be recovered into the pig iron phase while the ignoble elements will be enriched in the mineral phase for downstream recovery as shown in Figure 2.

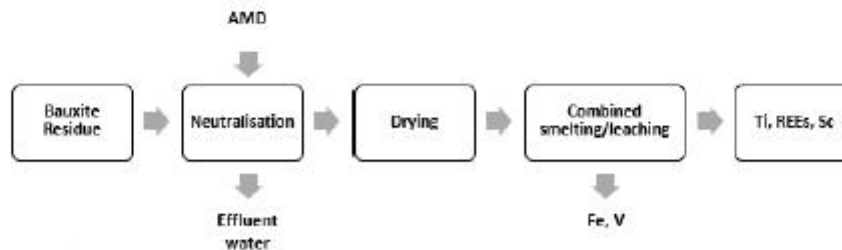


Figure. 2: Pre-use of alkalinity of bauxite residue for neutralization of AMD and for removal of alkalines contained in bauxite for downstream EAF smelting and leaching for the recovery of valuable elements.

Our first experimental studies based on untreated bauxite residue [7, 8, 9] confirmed that the recovery of Al, Ti, REE, Fe and V is possible, as shown in Fig. 3.

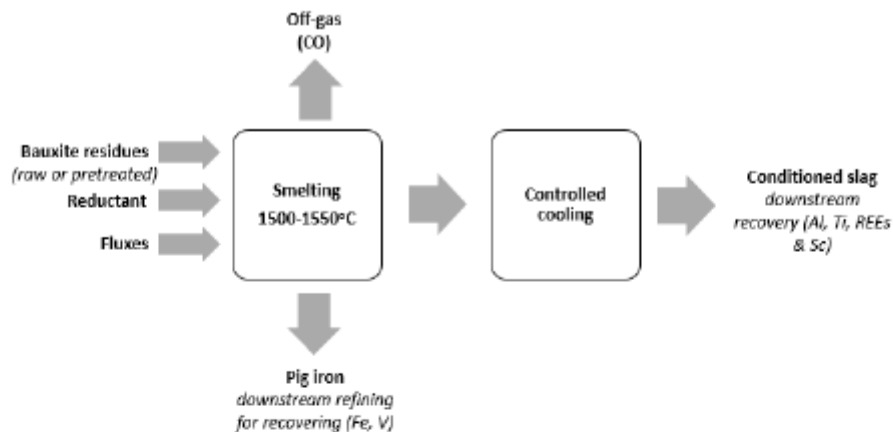


Figure 3: Reductive smelting of bauxite residue using lignite coke as the reductant and acidic to basic fluxes for low temperature smelting and the production of conditioned slag.

After reductive smelting between 1500°C and 1550°C, as shown in [6, 7, 8, 9], the iron was separated to a metallic phase and the slag phase was treated in order to recover aluminium, titanium, rare earth and scandium. Additional conditioning of the bauxite residue with basic oxygen furnace slag and bottom ash as fluxing agents in the smelting process in order to recover the valuable metals with exclusive use of secondary resources as slag formers is presented [7, 8, 9]. The final products based on aluminium, titanium, rare earth elements and scandium were obtained after a hydrometallurgical treatment using leaching, filtration, and precipitation as shown in [6, 8, 9, 11]. The leaching process was through dry digestion with sulfuric acid or a combination of sulfuric acid and hydrogen peroxide below 100°C in order to avoid the formation of silica gel, which blocks the extraction of rare earth elements. Scandium phosphate was obtained as the most valuable product.

Second proposal: A near zero waste valorisation vision for bauxite residue after smelting through experimental results for cement industry

The first step for the bauxite residue treatment was the removal of iron and production of slag suitable for the subsequent treatment in order to obtain rare earth elements and fulfil the near zero waste criteria (as shown earlier in Fig. 3). After an acidic leaching aiming to recover of titanium, rare earth elements and scandium under an atmospheric pressure, the solid residue shall be carbonated under high pressure in an autoclave, as shown at Fig. 4.



Figure 4: A near zero waste valorisation vision for bauxite residue after smelting through experimental results for cement industry

The chemical and mineralogical composition of bauxite residue after hydrometallurgical and pyrometallurgical treatment allows an effective use in the field of carbon capture and utilization.

The benefit of bauxite residue carbonation is the long-term storage of CO₂ generated in industrial processes. An addition to this environmental benefit is that residue carbonation delivers economic and social benefits by reducing the area required for residue storage. Generally, carbonated residue is less dusty and can be re-used in road base and in building materials in the cement industry thus achieving the vision of near zero waste valorisation of bauxite residue.

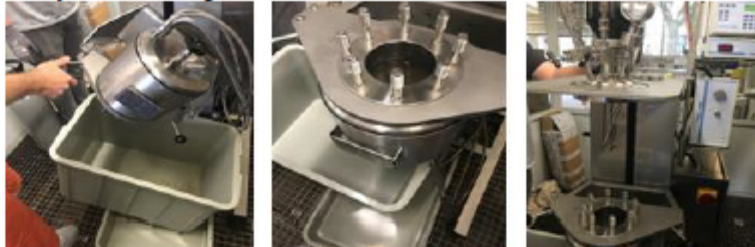


Figure 5: High pressure Büchi autoclave used for the carbonation of bauxite residue [12]

The first trials of the carbonation of the bauxite residue were performed using 200 g of bauxite residue (fraction under 180 µm) in 1L Büchi autoclave at 175 °C with 600 rpm in two hours in the presence of additives in (mol/L): 0.64 NaHCO₃, 0.06 H₂C₂O₄, 0.003 C₆H₈O₆, as shown at Fig. 5. We started with an initial pressure of 50 bar CO₂ (closed system in equilibrium) and reached 75 bar total pressure after heating. The calculated carbonation value of Greek bauxite residue was amounted 39 % in two hours in the presence of additives and 28 % without additives under above mentioned conditions, what is the first promising result in comparison to the carbonation efficiency of the olivine under 63 µm (about 31 %). The carbonation of the slag after a smelting of the bauxite residue with the influence of the particle size shall be studied in our future work in order to compare it with original bauxite residue without smelting and other materials such as flying ash, a ladle slag and olivine.

Conclusion

The bauxite residues were used for the recovery of iron, aluminium and titanium and critical elements such as vanadium and rare earth elements using a combination of pyrometallurgical and hydrometallurgical methods. The first proposal of near zero waste strategy uses a neutralisation of the acid mine drainage solution, with bauxite residue as starting material as a potential conditioning step in order to remove of the contained alkalines which is favourable for EAF smelting of the dried sludge material. This approach is superior to conventional AMD neutralisation practises as there is no production of a waste sludge. The second proposal represents a pyrometallurgical treatment of slag after iron recovery or a direct hydrometallurgical process using a bauxite residue with a final carbonation process for the cement industry. The aforementioned solutions present promising means towards achieving a near zero waste valorisation vision for bauxite residue. There is limited information related to the mineralogy of the different rare-earth phases in bauxite residue and in downstream solid streams during processing. Knowledge of these phases could help the development of new more efficient treatment processes with a high extraction efficiency.

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