

Bauxite Residue Reuse through Combined Operations: Industrial Pilot Modules

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Abstract

Bauxite residue' (BR) refers to the insoluble solid material, generated during the extraction of alumina (Al_2O_3) from Bauxite ore using the Bayer process. As the global demand for primary aluminium metal increases so does the BR production, currently in excess of 150 million tonnes per year (worldwide). This is generated at some 60 active alumina refining plants. In addition, there are at least another 50 closed legacy sites, so the combined stockpile of bauxite residue at active and legacy sites is estimated at between three and four thousand million tons. MYTILINEOS' since 1991 has been pioneering research on BR handling and reuse, focusing initially on massive low value applications such as use as a raw material for cement clinker production, iron production, bricks and tile production, soil and road substrate and others. From such approaches, only re-use in the cement sector has found industrial application leading to a current recycling of a 10 % of the annual BR production in various cement plants in Greece and Cyprus. To increase the BR reuse potential, MYTILINEOS and NTUA investigate BR-centric processes aiming to recover iron, aluminium, sodium and scandium from BR in a near-zero waste and break-even processing flowsheet which could be applied in a context of industrial symbiosis. To this end, lab-scale and industrial pilot scale research are combined to produce reliable data that will allow a comprehensive techno-economic evaluation that can lead to a viable solution. This paper will present several stand-alone processes and provide insight on the possibilities of interconnecting them.

Keywords: Bauxite residue, Metal recovery, Industrial pilot.

1. Introduction.

In the Bayer process for aluminium oxide production, bauxite ore is treated with caustic soda, causing the aluminium hydroxides/oxides (approximately 50 % of the bauxite ore mass) to be solubilized, while the remaining solid fraction is a by-product of the process, the Bauxite residue (BR). BR is produced as a red slurry (hence the common term "red mud") and contains iron minerals and other non-alumina bearing bauxite minerals as well as the liquor desilication product

(calcium and sodium alumino-silicate precipitates) from the Bayer circuit. It is estimated that for each tonne of alumina produced 0.9- 1.5 tonnes of solid residue is generated depending on the initial bauxite ore grade and alumina extraction efficiency. As the global demand for aluminium metal increases, so does the BR production. Current estimates indicate quantities in excess of 150 million tonnes per year (worldwide). This is generated at some 60 active Bayer plants. In addition, there are at least another 50 closed legacy sites. The combined stockpile of bauxite residue at active and legacy sites is estimated at between three and four thousand million tonnes.

Nowadays, many plants use high pressure filtration as a final step of slurry treatment, (the most efficient method of alkali recovery), in which the bauxite residue is pressed to remove the maximum remaining liquor and produce a compact filtercake with a moisture content of 25-30 %. The resulting filtercake, called "Filtered Bauxite Residue" (or ferroalumina), can be trucked or put on a conveyor belt, allowing for easy transport and further processing. The liquid filtrate from the filter-press, containing a small amount of caustic soda, is recycled to the washing lines, effectively re-entering the Bayer circuit [1].

The most significant difference between bauxite residue as a slurry and bauxite residue as a filtercake is the fraction of water and soda content in the final residue. The characteristics of filtered bauxite residue, (75-77 wt.% solids, 1-3 wt. % Na₂O) compared to bauxite residue slurry (30-50 wt. % solids, 4-6 wt. % Na₂O), drastically enhance its properties and its transportation either for disposal or for use (e.g., in cement industry or iron industry).

The large volume of waste produced during the Bayer process has been of concern to alumina producers since the early days of its adoption. In cases where land availability is becoming limited, the ever-growing demand for BR disposal space ultimately threatens the longevity of established alumina refineries. Stopping BR disposal or gradually reclaiming the legacy BR disposal sites is vital both for the industry and the society.

2. BR Re-Use potential.

The list of areas where bauxite residue could be used covers almost all areas of inorganic material science with particular focus on the recovery of elements present in the bauxite residue. Even Bayer himself in his 1892 patent describing the Bayer Process proposed the potential for iron recovery. Seeking effective solutions has attracted many researchers from industry, universities, institutes, and entrepreneurs to develop applications including construction of cement, bricks, roads etc., soil remediation as well as base metals and CRM metallurgical extraction.

In Europe, alumina refineries operate in Bosnia Herzegovina, France, Hungary, Germany, Greece, Ireland (AAL), Romania (ALUM), Spain and Ukraine, while significant BR deposits from refineries that have stopped their operations (legacy sites) exist in Italy, France (RT), Germany, Hungary and other countries. The current BR production level in the EU is 6.8 Mtpa (million tonnes per year); while the cumulative stockpiled level is a staggering >250 million tonnes (dry matter).

When seen as a potential mineral resource for reuse [2], the annual EU BR production, amounts to:

- With an average iron oxide content of 40 wt. %, it can be considered as an equivalent of 3.4 million tonnes of iron ore available in Europe. This would result in a 4 % decrease in iron ore imports and a 18 % increase in European iron ore production.

- With an average alumina content of 20 wt. % and an inherent clay-like behaviour, BR is a valuable raw material for various building applications; Recycling the alumina and soda (2-4 wt. %) of the BR back to the alumina refinery will lead to practically 100 % extraction efficiency of alumina from bauxite ore.
- Bauxite Residue and especially European BR (originating from European bauxites) contains significant amounts of iron, aluminium, silicon and titanium oxides as well as smaller concentrations of critical and/or industrially important elements such as V, Cr, Ga, Rare Earth Elements (REEs) (mainly Ce, La, Y, Nd), and Sc. The Greek BR (originating mainly from Greek bauxites) contains ~1 kg REEs/tonne and this concentration has a variation of only 8 % over a period of 15 years' of assessment. Extracting the REE from MYTILINEOS's annual BR production can meet the needs of approximately 10 % of the European REE demand.

3. BR Re-Use practice.



Figure 1. Applications tested at MYTILINEOS for direct reuse of BR as raw material.

MYTILINEOS' since 1991 has been pioneering research on BR handling and reuse, focusing initially on massive low value applications such as use as a raw material for cement clinker production, iron production, bricks and tile production, soil and road substrate and others (see

Figure 1). From such approaches, only use in the cement sector has found industrial application both in Greece and internationally.

Globally, it is estimated that up to 3 - 4 million tonnes of BR were reused in 2020 out of the total 150-160 million tonnes generated, i.e., 3-4 %. This reuse, for the most part, takes place in India and China and refers to:

- Cement clinker production: 2,400,000 to 2,900,000 tonnes;
- Raw material/additives in iron and steel production: 800,000 to 1,500,000 tonnes;
- Roads/landfill capping soil amelioration: 250,000 to 500,000 tonnes;
- Construction materials (bricks tiles, ceramics etc.): 1,000,000 to 1,400,000 tonnes;
- Glass ceramics, glass fibres: 100,000 to 120,000 tonnes
- Other (refractory, adsorbent, acid mine drainage, catalyst etc.): 300,000 tonnes

3.1 Use in Ordinary Portland Cement.

Over the past decade, Ordinary Portland Cement (OPC) producing plants in Belarus, China, Ukraine, India, Russia, Romania, Georgia, Moldova, Cyprus and Greece have used ‘as-is’ dried BR as a raw material for their clinker productions. It is estimated that over 3 million tonnes of BR are currently used in the production of clinker, in at least 6 to 10 plants in the former Soviet Union area, more than 40 plants in India, 3 plants in Greece and 1 plant in Cyprus. In all cases BR is used to substitute 0.8-3.5 % of the clinker raw meal as a source for iron and alumina. Key barriers in this practice are BR moisture, soda and chromium levels as well as the logistics of the operation. In most reported cases the application of BAT technologies in BR handling, such as filter-pressing, has been a catalyst in providing an easily transportable dry matter with a low soda content. This provides a BR that can be accepted as an alternative raw material for cement plants. However, logistic costs still limit this practice to approximately 1000 km from the BR production site. BR transport takes place by ship or train in the other reported cases.

Since the complete adoption of filterpressing at MYTILINEOS (2012), more than 330 000 tonnes of Greek BR have been used as Fe and Al additive for clinker production and the reuse is gradually growing. Currently MYTILINEOS transports by sea, close to 100 000 tonne per year of filterpressed BR to four different Cement plants where BR substitutes up to 2.5 % of the feed raw material for clinker production without interfering with the final product specification. The main goal of MYTILINEOS over the next years is to effectively utilise more than 300 000 tonnes of BR annually, providing a reliable iron and alumina source for cement producers in the close vicinity of Greece.

4. BR processing for added value products.

Several processes have been proposed, but never implemented, for the simultaneous recovery of the major metals from bauxite residue (towards a “zero waste” objective). Concerning cost and risk, a detailed cost/benefit analysis of one or more specific process proposals is needed not only to establish economic viability, but also to deal with the whole volume of the produced residue. To increase the BR reuse potential MYTILINEOS has invested over the last decade in collaborative research with several European institutes and companies. The goal of this research is to obtain a near-zero waste and break-even processing flowsheet which could be applied in a context of industrial symbiosis. This ‘Mud2Metal’ concept [3], shown in Figure 2, has led to the development of numerous EC-funded research projects such as SCALE, ENSUREAL, RemoAL, ReActiv and others, through which industrial pilot scale technology demonstrations have taken place at MYTILINEOS.

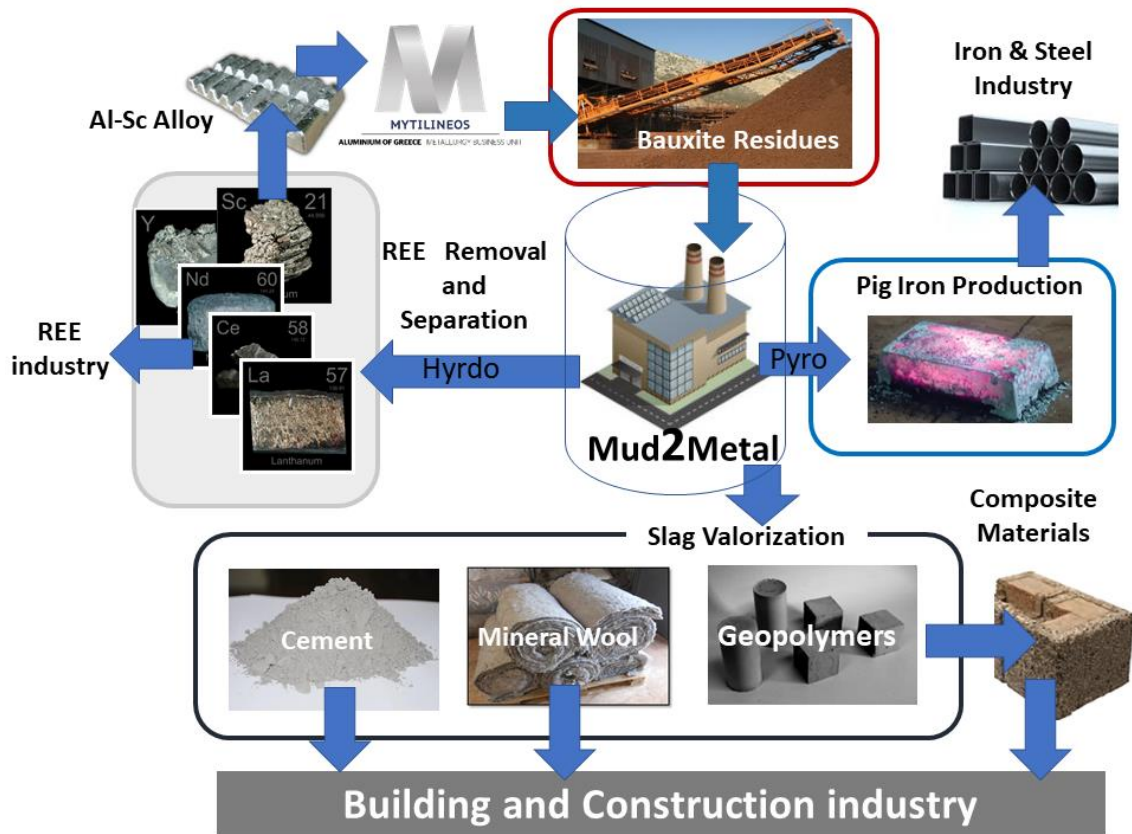


Figure 2. The Mud2Metal concept for holistic valorisation of BR into added value products.

4.1 Scandium Extraction



Figure 3. Left: Leaching Pilot unit at MYTILINEOS; Right: II-VI SIR Pilot unit installed at MYTILINEOS.

Under the H2020 SCALE project, NTUA and MYTILINEOS demonstrated the leaching and extracting of Sc from BR at its industrial pilot plant (see Figure 3). More than 9 tonnes of BR were processed with dilute sulfuric acid solution producing 10 m³ of leach solution, which was processed with II-VI proprietary SIR ion-exchange technology to produce a crude Sc concentrate with 22 wt. % Sc [4]. With the given technology, processing the annual BR production at

MYTILINEOS would lead to 62 tonnes of Scandium concentrate being produced. This concentrate can then be upgraded into 22 tonnes of Sc₂O₃ and later into 733 tonnes of AlSc₂ master alloy. The latter is currently priced at 100-150 USD/kg, given its unique properties in strength, corrosion resistance and weldability which allow utilization in aerospace and 3D printing application.

The leached BR (LBR) retains approximately the same mass but is now depleted in soda and enriched in gypsum. This makes it a more attractive raw material for OPC cement production. According to cement producers, in relation to BR utilized today, they could absorb up to twice the amount of LBR per year.

4.2 BR De-Alkalinization / Soda recovery

The presence of soda (Na₂O) in the BR is a limiting factor to its utilization in cement and iron production (soda destabilizes blast furnaces' refractory lining) as well as contributes to the difficult handling and transport of the BR which is characterised as caustic material. Soda, on the other hand, is the main consumable in the Bayer process, as such, it is an asset to the alumina refinery. Utilizing the technology recently reported by RUSAL [5], soda can be recovered from BR through thermochemical leaching with a CaO solution. Under the H2020 RemovAl project, MYTILINEOS has demonstrated this technology by processing more than 500 kg of BR in its Hyrdo Pilot plant. The Na₂O content in the solid BR has been reduced from 3.5-0.4 % and a 13 g/l Na₂O solution has been produced. This solution can be directly recycled to the alumina refinery. The De-alkalinized BR can be used in cement and iron production and is also being examined by NTUA as a precursor for Supplementary Cementitious Material (SCM) production in the recently launched ReActiv project.

4.3 Iron extraction- EAF smelting

The pyrometallurgical recovery of iron from the BR is the next logical step for the development of a holistic utilization flow sheet for BR. It valorises approximately half of the BR stream and, at the same time, allows the customization of the properties of the remaining material (slag) in such a way that it can be further processed for valuable metal extraction (Al, Ti, Sc, ...) or use in the construction sector.

Under the ENEXAL project, MYTILINEOS and NTUA have demonstrated the potential to transform the BR into pig iron through Electric Arc Furnace (EAF) processing. The pig iron produced was suitable for the secondary steel industry as a 15 wt. % scrap substitute in EAF processing [6]. Larger BR pig iron utilization as scrap substitute would be disruptive to the steel mill operations as the minor elements of the BR pig iron would produce steel outside of the required specifications.

Table 1. BR Pig Iron produced in ENEXAL and average steel scrap elemental composition.

Element (%)	Fe	C	Mn	Si	P	S	Ni	Cr	V	Cu
BR Pig iron	92.30	4.25	0.09	1.89	0.22	0.05	0.21	0.57	0.41	-
Average Steel scrap	98.56	0.09	0.06	0.01	0.02	0.06	0.12	0.11	0.01	0.37

This technology is being revisited in the H2020 RemovAl project with the aim of producing added value pig-iron for use in FeSi production as well as fine tuning the produced slag for use in other applications. These uses include cement production, mineral wool production and alumina extraction (Figure 4).



Figure 4. BR pig iron production at MYTILINEOS Pyro-Pilot Plant.

4.4 Iron extraction - Microwave roasting

An innovative technology that is being used for the extraction of iron from BR is Microwave assisted reductive roasting. Microwave radiation can heat up a mixture of BR and metallurgical coke, thus leading to iron reduction experiments with very fast reaction time. The iron produced is then recovered through wet magnetic separation. Under the H2020 RemovAl project, this process is optimized to maximize the liberation of the iron species and avoid non-Fe phases in the magnetic concentrate. With the use of salts as fluxing agents during the microwave roasting, an iron recovery of more than 80 % is achievable [7].

Under the same project, another critical challenge in microwave processing is tackled. The challenge of scaling up from a lab scale static microwave reactor to a continuous one suitable for industrial processing. Experiments on a lab prototype microwave rotary furnace have showed the reduction of hematite inside the BR to magnetite at around 750 °C and to metallic iron at 1000 °C. The aim now is to scale up this process in a pilot scale microwave rotary furnace capable of processing several kilograms of BR per hour.

4.5 Iron extraction - Alkaline pulp electrolysis

Under the H2020 SIDERWIN project, NTUA investigates the electrolytic extraction of Fe from BR. Low temperature electrolysis of iron ore in an alkaline environment is a breakthrough technology for the future carbon free iron production from hematite concentrate. Bauxite Residue is a potential alternative raw material for the Siderwin process [8], but there are significant differences with pure hematite concerning the solution behaviour and the electrochemical mechanism. When 50 % w/w NaOH, 10 % w/w Bauxite Residue pulp at 110°C , 500 RPM stirring rate and current density 138Am⁻², was applied, the resulting Faradaic Efficiency was 73 % . Whereas, when pure hematite was used under the same conditions, the Faradaic Efficiency reached 83 % . At higher current densities however, the efficiency for BR drops significantly in contrast with hematite's behaviour (Figure 5)

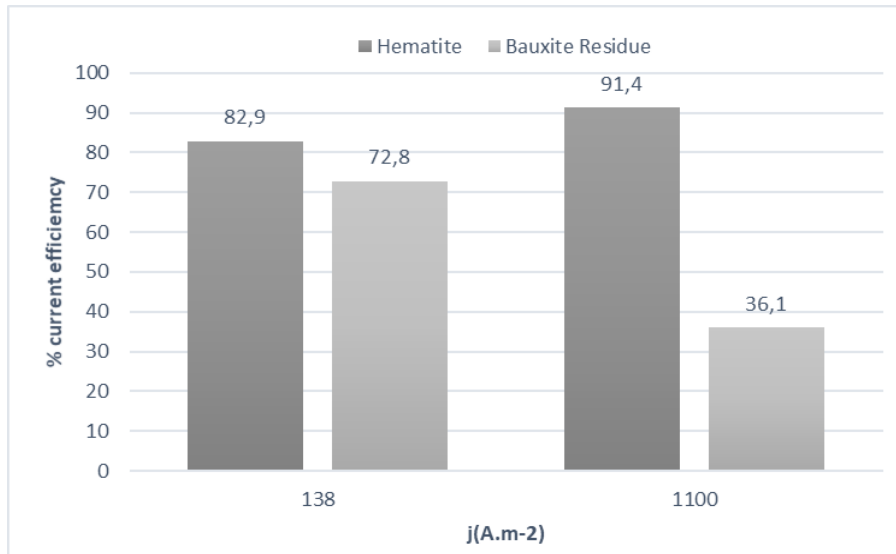


Figure 5. Current efficiency as a function of current density for Hematite and Bauxite Residue.

Relative to a hematite concentrate, the impurities that BR contains may be critical to the electroactivity of the systems. Processing of BR to remove impurities and long-term electrolysis experiments will be tested in subsequent work to optimize this promising process.

4.6 Alumina extraction

With the appropriate fluxing during the BR smelting process, a slag can be engineered where alumina oxides are selectively leachable in sodium carbonate solutions. This process is based on the Pedersen process for alumina production, in which, prior to leaching, the bauxite ore (or in this case BR) is reductively smelted in an Electric Arc Furnace (EAF) with lime and coke, to recover the metallic iron and produce a calcium aluminate slag [9,10]. In the leaching step, the slag is leached with a dilute sodium carbonate/sodium hydroxide solution to produce a calcium carbonate residue (called grey mud) and a pregnant sodium aluminate solution (PLS). Following a solid/liquid separation process, the pregnant solution enters the precipitation stage, where carbon dioxide gas is bubbled to lower the pH of the solution and precipitate aluminum as aluminum trihydroxide. carbon dioxide is dissolved in the sodium aluminate solution, which increases the hydrogen ion concentration, neutralizing the alkaline solution, reducing the pH and triggering the decomposition of the aluminate ion, resulting in the precipitation of aluminum hydroxide.

More than 500 kg of BR slag were produced at the MYTILINEOS EAF pilot under conditions that lead to the formation of rich calcio-aluminate slag of specific mineralogy. This slag was crushed and grinded below 500 μm and then 300 kg of it was leached at lab scale at NTUA and at pilot scale at MYTILINEOS Hydro Pilot plant with sodium carbonate solution.

Based on the results of laboratory leaching tests that were performed at 70 °C and 90 °C, for different leaching times the Al extraction mechanism was further explained [11]. Al extraction rates observed are the net result of two mechanisms. The first is a mechanism of direct dissolution of Al into the solution, due to the hydraulic character of calcium aluminate phases. The second mechanism of Al extraction is a causticization mechanism that becomes progressively more dominant, as the concentration of $\text{Al}(\text{OH})_4^-$ in the solution increases. As in the case of spent Bayer liquor causticization, the present leaching solution containing $\text{Al}(\text{OH})_4^-$ - NaOH – Na_2CO_3 reacts with the hydroxylated Ca sites on the slag particles producing calcium monocarboaluminate.

Calcium monocarboaluminate then reacts with the dissolved CO_3^{2-} ions, further dissolving $\text{Al}(\text{OH})_4^-$ and simultaneously precipitating CaCO_3 on the surface of slag particles. This action is responsible for the decelerating extraction rates. After approximately 15 minutes of leaching, further extraction is ceased, as the particles get completely coated with CaCO_3 .

At the pilot scale, the leaching of 300 kg of slag lead to the production of approximately 2.7 m³ of alumina bearing solution (10-12 g/l Al) and 244 kg of 'grey mud'. In total 68 % of the aluminium in the slag was leached into the solution.

The precipitation of aluminum trihydrate from the slag leach solution has been extensively studied at NTUA. The challenge during the precipitation stage was to avoid dawsonite ($\text{NaAlCO}_3(\text{OH})_2$) formation. Previous works [12,13] have shown both thermodynamically and experimentally that dawsonite can be precipitated if high amounts of carbonate ions are in the PLS and/or if prolonged carbonation occurs. Optimum experiments (run at 40 °C, 160 mL/min pure CO_2 flow rate, 200 rpm stirring and 24 hours aging) precipitated 84 % of aluminum and 99 % when seed was used. The precipitate was not gibbsite but bayerite, a polymorph of gibbsite. To successfully increase the particle size, 3 cycles of reusing the precipitated bayerite as seed for the upcoming precipitation were needed to reach a d_{50} of more than 45µm without any size separation techniques. After 10 cycles, large agglomerates are clearly observed (ranging from 20-85µm) which again are comprised of needlelike crystallites.

At pilot scale the CO_2 gas neutralization of the 2.7 m³ pregnant liquor solution, resulted in a 96 - 99 % bayerite recovery, producing 38 kg of product (Figure 6). Depending on the CO_2 purging rates used, impurities in the precipitated bayerite were as low as 0.55 wt. % Na_2O and 0.68 wt. % SiO_2 .



Figure 6. Bayerite precipitate from BR processing at MYTILINEOS.

Starting from BR and based on the results of the above-mentioned demonstrations, 1 tonne of BR would yield 300 kg of pig iron, 200 kg of hydrated alumina (bayerite) and 800 kg of grey mud. Grey mud (mainly calcite with calcium-silicates and calcium-titanate impurities) can be used in building and agricultural applications, or it can be leached to recover critical raw materials like Scandium.

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