MUD2METAL: A HOLISTIC FLOW SHEET FOR THE BAUXITE RESIDUE VALORISATION

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Abstract

A vast amount of research effort has been spent on the effective utilisation of Bauxite Residue (BR). Although numerous projects and research efforts have attempted to utilise BR as a source for the production of a raw material (i.e. blast furnace for pig iron production) or to utilise it as a feedstock in another industry (i.e. raw meal in cement calciners and others), currently clear-cut cases of industrial utilisation of BR are rare and can only be applied on a fraction of the produced BR. This is largely because most solutions proposed, aim at using BR as a raw material substitute in a single established industrial process leading to uneconomic or potentially disruptive processes.

In this paper a new concept for holistic exploitation of the BR is discussed, where a multitude of niche and bulk application products are produced, leading to a near zero-waste, viable and environmentally benign process. Based on the combination of recent research results, the Mud2Metal conceptual flow sheet is analysed technologically, environmentally and economically.

Introduction

The Greek BR stream contains significant amounts of iron, aluminium, silicon and titanium oxides as well as smaller concentrations of critical and/or industrially important elements such as REEs (mainly Ce, La, Sc, Y, Nd), V, Cr and others. The high scandium content (135 ppm in Greek BR) in particular makes BR a valuable secondary resource.

Based on the results of the ENEXAL project, [1] where BR was transformed into pig iron and mineral wool, the Mud2Metal concept proposes to solve the BR disposal problem through technological innovations and products co-generation; a sustainable flow sheet can be developed which transforms BR from a waste into a multitude of high added-value products, as shown in Figure 1. Under this approach, the multitude of products secures both the economic viability of the flow sheet as well as the complete utilisation (near zero waste) of the BR produced by the Alumina industry. Iron alloy and cement are two products with huge market applications which can absorb the majority of the BR volume. In addition niche applications like REE compounds, mineral fibre products and specialty cements with more limited markets in term of product volumes but significantly higher product values, enhances the economy of the flow sheet.

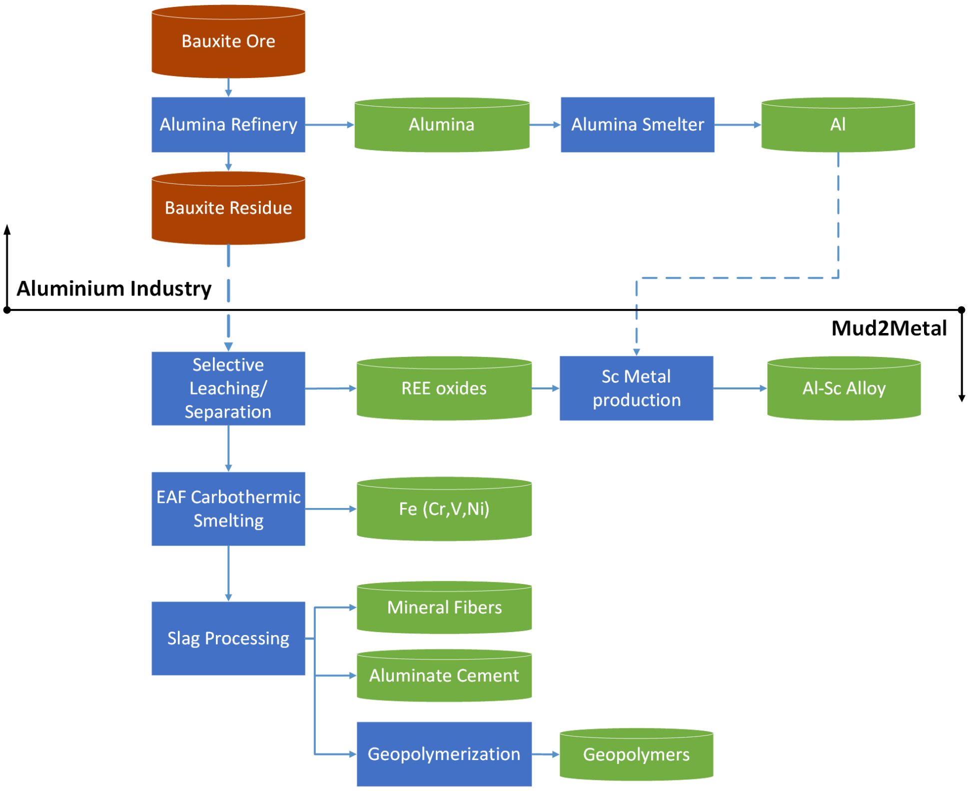

Figure 1: Mud2Metal flow sheet: from BR "waste" to various high added value products

Pyrometallurgical Treatment for Iron Recovery

Iron recovery from BR has been thoroughly investigated and the developed technologies have been reviewed in several publications.[2] Iron recovery from BR has been studied with several hydro- as well as pyrometallurgical methods. The pyrometallurgical recovery of iron from the BR valorises approximately half of the BR stream and at the same time alters the properties of the remaining material (slag) in such a way that it can be further processed, resulting in a zero solid/liquid waste process. Through EAF (Electric Arc Furnace) carbothermic reduction smelting the iron content of BR can be extracted as pig-iron and sold as steel scrap substitute (current price 300 EUR/t) to the secondary steel industry. BR trace elements like V, Cr, and Ni, which are of great value to the iron/steel industry, are collected in the produced iron. The EAF carbothermic smelting technology was developed in the ENEXAL project[1] and resulted in metal product with composition presented in Table 1. The pig iron produced was suitable for the secondary steel industry as a 15 wt% scrap substitute in EAF processing. Larger BR pig iron utilisation 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. Still given the size of the iron and steel market, the secondary steel industry could absorb all the BR pig iron even at low scrap substitute rates (i.e. the European steel industry's iron ore imports in 2011 where 132 Mt).

With further optimisation and technological innovation of the iron production process, one could control the presence of secondary elements in the alloy and produce directly cast iron alloys (i.e. grey cast iron) which are sold at significantly higher prices (i.e. 1,000-1,300 EUR/t).

Table 1: Iron alloy compositions

Element (wt%)	Fe	C	Mn	Si	P	S	Ni	Cr	V	Cu
ENEXAL BR Pig iron (300 kg/t of BR)	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
Grey cast iron alloy	92.78	3.40	0.5	1.80	0.20	0.07	-	0.35	0.15	-

Slag Engineering for Building Products

The carbothermic smelting of BR can reduce up to 60 % the total weight of the BR, leaving behind an alumina rich slag phase, an indicative chemical composition of which is presented in Table 2. The valorisation of this phase is essential in creating a both economically and environmentally viable BR treatment process. Based on its composition and especially its high alumina content, with appropriate hot or cold engineering, this slag phase could be used not only as raw material in cement (as additive in the clinker or directly as slag cement) production but also as a raw material for higher added value products like mineral wool and aluminate cements products. Yet in contrast with iron products and cement such high added value products have much more limited markets, which could not absorb the high amounts of BR slag potentially produced. Therefore the Mud2Metal process aims at the production of multitude of slag products, ranging from low cost bulk applications like slag cement to niche applications like mineral wool and aluminate cements.

In the ENEXAL project the possibility to produce mineral wool products from the slag of the BR EAF processing was demonstrated. The wool produced had a thermal conductivity coefficient of λ = 0,034 W/mK [UNI EN 12667], similar to market insulation product and superior mechanical resistance due to its unique chemical composition (high Al_2O_3 and TiO_2 context in comparison to typical products). Given that 85 % of the energy in mineral wool production is associated with the melting of the mineral, co-production of mineral wool with the carbothermic production of BR, results in both a significant environmental and economic advantage for the industry.

Table 2: Slag products compositions

wt%	Al_2O_3	CaO	MgO	SiO_2	TiO_2	FeO	Na_2O
Expected/ENEXAL BR Slag (400 kg/t of BR)	37.0	29.0	0.7	25.0	8.0	1.0	-
Typical Blast Furnace Slag	7-16	32-45	5-15	32-42	-	0.1 - 1.5	-
Calcium Aluminate Cement	36-42	36-42	0.1	3-8	< 2	12-20	0.1
Typical slag wool products	5-16	20-43	4-14	38-52	0.3-1	0-5	0-1
Refractory ceramic fibers	35-51	< 1	< 1	47-54	0-20	0-1	< 1

Apart from the cement industry, BR has been used directly in geopolymer development. Geopolymerisation is a rapidly developing and innovative technology, which utilises solid aluminosilicate materials to produce a wide range of revolutionary materials, i.e. “geopolymers”, which can further add to the range of added value BR slag products.

There is a lot of research concerning the use of BR as an aluminosilicate source for developing geopolymers;[3] BR, however, is not a good aluminosilicate source for geopolymerisation because in sodium hydroxide solutions only small portion of its aluminosilicate phases can be dissolved. Therefore, in all cases BR was used mainly as filler in geopolymers produced from other aluminosilicate sources such as fly ash, rice husk ash, several types of metakaolin and slag. In contrast, the produced BR slag from the Mud2Metal flow sheet would be more easily dissolved in sodium hydroxide solutions as it is an amorphous aluminosilicate matrix, the composition of which can be regulated through appropriate flux additions, to produce optimum geopolymer precursors.

Hydrometallurgical Pre-Treatment for REE Recovery

REEs, in particular the heavy REEs, are classified as the most critical raw materials for Europe in terms of economic importance and supply risk. Investigations by NTUA[4,5] have shown that AoG BR contains ~1 kg REEs/ton (incl. Sc) and that this concentration is fairly constant, with a variation of only 8 % over a period of 15 years.[6] The enrichment factor of the rare earths in BR compared to bauxite is about a factor of two. The economic impact of extracting Sc and REE from the Greek BR can be very significant as (a) the REE content in the annual Greek BR production amounts to 10% of the annual European REE imports (8000 tpa) and (b) Sc content in BR (135 ppm) is considered a financially exploitable concentration. Furthermore Scandium is an element of high technical and economic importance mainly because of its applications in high performance Al-Sc alloys and in emerging Solid Oxide Fuel Cell technology. Scandia-stabilised-Zirconia (ScSZ) is found to be an excellent solid electrolyte while Al-Sc alloys represent a new generation of high performance alloys with superior properties over all other Al alloys. [7]

REEs have to be extracted from the BR stream prior to pyrometallurgical processing as, once dispersed in the oxidic matrix of the slag, they become practically non-leachable. To extract the REE prior to the carbothermic smelting of the BR requires a selective leaching process which will allow the dissolution of the REE content with minimum iron dissolution. Such processes have been studied and developed in NTUA using dilute mineral acids[4] or task specific ionic liquids[5]. In both cases dilute REEs solutions are produced with less than 3 % - 5 % BR iron dissolution. Extraction of REE content and especially of Sc from such dilute solutions is the key processing step which defines the economics of the process. Conventional S-X methods would require far too many processing steps and therefore several groups have investigated selective methods and extractants to be applied in such a process.[8]

The Economic Aspect

The most crucial and defining aspect for the application of an integrated processing flowsheet like the one described in this work is its financial viability. Table 3 presents the prices of the various products that can be produced through the proposed flowsheet along with a first estimation of the relative processing costs (OPEX) based on the results and experience from the ENEXAL project and the work on BR selective leaching by NTUA. The amount produced for each product is based on the processing of the entire annual AoG BR production and on a relative distribution of slag products based on reasonable market size assumptions. Market prices are given as a range, as they will depend greatly on the quality of each product, which in turn is determined by both technological innovation (i.e. efficient Sc extraction from leach solutions or impurity control during iron metal production) and capital investment (i.e. deploying a full S-X plant for REE production or a converter for steel production). The ranges presented in Table 1, vary between a low value which reflects for the most part products already attained and a higher value for products which could be attained through further development/deployment. Figure 2 shows the expected revenues under the two extreme scenarios and a projected OPEX, which for the purpose of this exercise is considered to be invariant in both cases.

Table 3: Economics of the process

Product	Amount produced [t]	Market Price [EUR/t]	OPEX [million EUR]
Iron product (209,000 t per annum)			
Iron Product	209,000	300 -1000	210
Slag Products (300,000 t per annum)			
BR Mineral Wool	60,000	600-800	14
BR Aluminate Cements	50,000	300-600	
BR Geopolymers	80,000	100-200	
BR Slag Cement / raw material for industry	110,000	0-20	
REE products (1038 t per annum)			
Sc_2O_3 99 %	136	500-1000	140
Mixed REO concentrate	902	6-8	

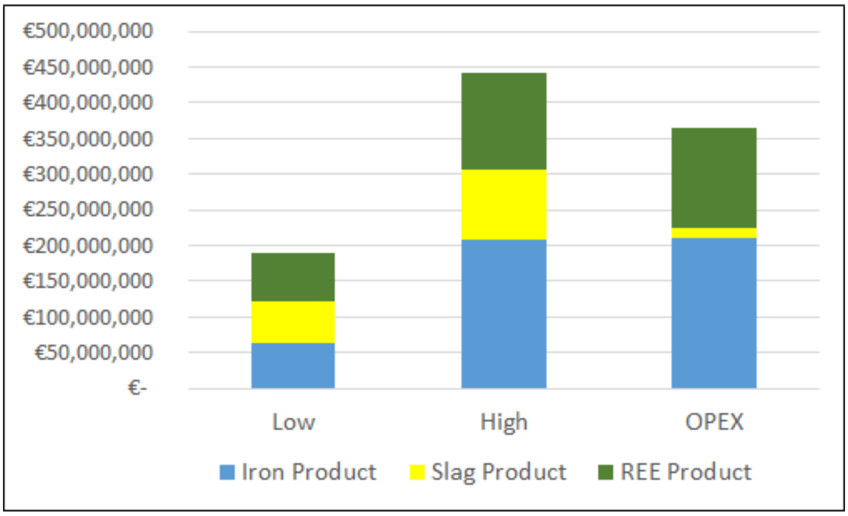

Figure 2: Estimation of revenues and operational costs (OPEX) for the Mud2Metal flowsheet for low and high value products

As seen from Figure 2 the Mud2Metal flowsheet could become profitable given further technological or capital investment deployment, providing a zero waste valorisation solution for the BR.

Furthermore should Sc_2O_3 be upgraded to Sc metal than the latter could be combined with the aluminium metal product of the industry and produce the highest added value product possible from BR, Al-Sc master alloy. In such a case the 136 t of Sc_2O_3, contained within the annual BR production of AoG, would produce 4,450 t of Al-Sc master alloy (2 wt% Sc) the market price of which in 2013 was 150 EUR/kg .

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