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ALUMINA AND BAUXITE

Waste Recovery

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THE ENEXAL BAUXITE RESIDUE TREATMENT PROCESS: INDUSTRIAL SCALE PILOT PLANT RESULTS

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Abstract

The main by-product of the Bayer process is the bauxite residues (BR), a red slurry consisting of the un-dissolved portion of the bauxite ore. On a dry basis BR are produced at an almost 1:1 mass ratio with alumina, amassing to a total of 100 to 120 million tones per year globally. Due the lack of an economically viable processing method all BR are disposed in artificial ponds or landfills. A novel process for treating BR has been developed; Through EAF carbothermic smelting the BR are fully converted into two marketable products: pig iron and mineral wool fibers. No solid or liquid by-products are produced. This novel process has been applied for more than a year in an industrial scale pilot plant housing a 1MVA EAF and a melt fiberizing line. The mass and energy balance of the process, along with a preliminary scale up calculations are presented in this paper.

Introduction

The primary aluminium production industry is the world's larger industrial consumer of energy and is ranked among the most CO_2 intensive industries. The industry is separated into two types of plants: alumina refiniries where bauxite ore is refined to metallurgical alumina (Al_2O_3) according to the Bayer process and aluminum smelters where metallurgical alumina is electrolytically reduced into metallic aluminum according to the Hall-Heroult process.

While the electrolytic Hall-Herloult process has the largest energy consumption and carbon intensity, the hydrometallurgical Bayer process leaves also a heavy environmental footprint.

The Bayer process is essentially a cyclic process designed to extract the alumina from the bauxite ore through high temperature caustic leaching and controlled precipitation, according to the simplified reaction scheme:

$$Al_2O_3{*}3H_2O_{[bauxite]} + 2NaOH_{[aq]} \rightarrow 2NaAlO_{2[aq]} + 4H_2O_{[l]} \qquad (1)$$

$$2NaAlO_{2[aq]} + 4H_2O_{[l]} \rightarrow Al_2O_3{*}3H_2O_{[s]} + 2NaOH_{[aq]} \qquad (2)$$

The hydrated alumina from the Bayer process is subsequently calcined at 1100°C to produce metallurgical alumina.

$$Al_2O_3{*}3H_2O_{[s]} + Q \rightarrow Al_2O_{3[s]} + 3H_2O_{[g]} \qquad (3)$$

Significant process heat is required during alumina calcination and bauxite while the precipitation stage requires long retention times and continuous recirculation of large liquor volumes and seed. The overall resource utilization or exergy efficiency of the Bayer process (including alumina calcination) is 3% [1], meaning that for every 100 J of exergy spent in the process as raw materials and utilities 97 J are lost as by-products and waste heat (exergy destruction) and only 3 J are embodied in the final dehydrated alumina product (although these 3 J do not reflect the "exergetic gain" from crystallizing alumina at such slow and controlled rates in order to achieve a product with very narrow and strict physical specifications).

While a major part of this exergetic inefficiency is inherent with the cyclic nature of the process, another part is due solely to the generation of un-exploitable by-products. On average the Bayer process for the production of metallurgical alumina requires 2.65 kg of bauxite ore to produce 1 kg of alumina, while the remaining amount of the ore is removed from the process as slurry, following the liquor clarification stage. This by-product, called Bauxite Residue (BR), also known as "red mud", on a dry basis is produced in almost a 1 to 1 mass ratio to alumina and consists from various metal oxides of Fe, Al, Ti, Si, Na, V (depending on the initial chemical composition of the bauxite ore) along with inclusions of unwashed sodium aluminate solution. On average iron oxides in the BR produced in the combined refiner - smelter plant of ALUMINION S.A. in Greece (AoG) account for 43 to 45% the total dry weight.

BR are generally classified as a non hazardous waste, however their small particle size (dust-like, mean particle size 0.49μm), high alkalinity and large amounts (100 to 120 million tons per year on a dry basis worldwide) makes their disposal a significant problem. Today, the residues are disposed into sealed or unsealed artificial impoundments, leading to important environmental issues (e.g. groundwater pH change, leakage, overflow, air pollution by dust) and substantial land use. The catastrophic BR spill in Hungary in October 2010 is indicative of the magnitude of the residue disposal problem. Despite significant RTD efforts, due mainly to high costs and low yields, no extensive industrial application of bauxite residues is in effect. China recently reported [2] that 3.0 to 3.6 million tons from the 40 million tons of BR produced there annually are being utilized for various applications like iron ore substitute, mineral filler for plastics and rubber, raw material for building materials and others.

In the framework of the EC funded ENEXAL project [3] a novel process for the treatment of the bauxite residues and its transformation into valuable products has been developed in NTUA and is being demonstrated in industrial scale at AoG. The process revisits the idea of carbothermically producing pig-iron from BR but in order to safeguard its environmental and economical sustainability introduces modern day dust treating EAF technology and slag engineering to co-produce mineral (slag) wool insulating products. First results from the year long industrial campaign at AoG are presented in this paper.

Process design

With an annual alumina production of 800,000 tonnes the AoG plant generates approximately 650,000 tons of BR. In order to safely dispose this inland, the AoG plant was among the first plants in Western Europe to install filter-presses. These presses dewater the BR producing a filter cake, shown in Figure 1, with 25 – to 28% wt water content.

The novel process developed aims at transforming 100% of this filter cake into valuable products. Utilizing modern Electric Arc Furnace (AMRT-EAF) technology today it is feasible to process dry dusty BR directly without the need for a costly agglomeration pre-treatment step. The pig-iron produced in such a way would amount to approximately to 28- 32% of the initial BR weight, while 55-60% of the BR would remain as an aluminosilicate slag. To make an environmentally and financially sustainable process the slag of the process will be transformed into inorganic fibers suitable for the production of a variety of marketable products commonly known as mineral (or slag, rock) wool products.

Figure 1. Dewatered BR exiting the filter presses in AoG

Mineral wool products due to their light weight, low thermal coefficient, incombustibility and high temperature melting points (>1000^oC) are widely used as refractory, thermal and acoustic insulation or even light weight construction materials [4]. In 2003 mineral and glass wool products accounted for 60% of the thermoinsulation market in Europe [5]. Taking into consideration that the EAF slag can be fiberized in situ, therefore avoiding the expensive melting phase of conventional mineral wool production (which accounts for up to 70% of the total mineral wool production energy [6]), then one can expect that the proposed Bauxite Residues treatment process will both economically viable and environmentally sustainable.

The goal of the novel process described above is to achieve: (a) High reduction of red mud iron content and the production of a metal phase (pig-iron) suitable for usage in the secondary steel industry and (b) the production of a slag phase with such physicochemical properties that will allow both a good separation from the metal phase as well as an effective fiberazation process. From the end-user perspective, for a pig iron to substitute 20-30%wt of steel scrap in secondary EAF steel mills, it must have less than 0.1 %wt in S,P and less than 1.0 %wt in Si, Cr, Mn; while for a melt to be used in conventional melt spinning equipment it should have primarily a viscosity of 10-15 poise at temperatures of 1450^oC [6]. Additional empirical industrial indexes to characterize the "fiberise-ability" of a melt are presented in [8], while some empirical compositional restrictions for the melt include sodium oxide content less than 5%wt and iron oxide content above 5%wt. Given the last restriction the process has to aim for less than full iron reduction in order to produce high quality fiber products.

The process design and preliminary experiments have been reported in [9] and results of semi-industrial EAF (400 kVA) experiments have been reported in [8]. Accordingly at least a C to Fe atomic ratio of 2 (with 1.5 being the stoicheometric ratio of hematite carbothermic reduction) and an addition of 350 kg /ton of red mud of fluxes (lime and silica sand) is needed to achieve the objectives of the process. The overall weight ratio of CaO to SiO_2 (basicity ratio) in the feed can vary between 0.8 to1.1. The conceptual flowsheet of the novel process is presented in Figure 2.

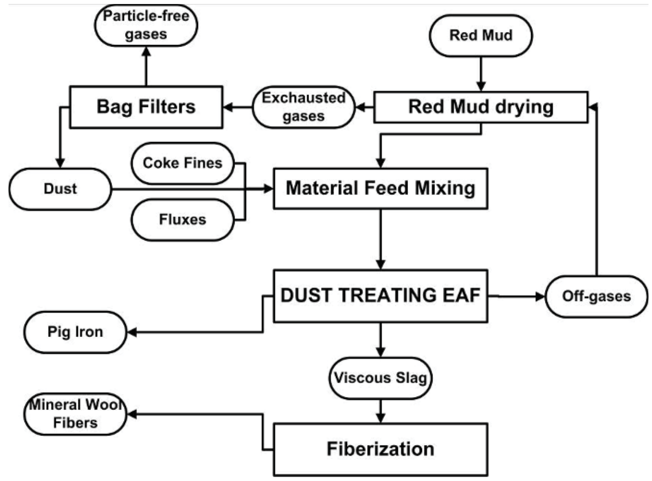

Figure 2. Conceptual design of the ENEXAL BR treatment process

Pilot Plant – Experimental Campaign

For the purposes of testing the process in industrial scale a pilot plant was erected in AoG, housing a 1 MVA EAF capable of directly treating dusty feed material (AMRT technology) and 2-disk melt spinner fiberization line (Gamma Meccanica).

Raw materials used in the plant were BR from the AoG plant along with commercial silica sand, burnt lime and Coke fines, the chemical analysis of which is given in Table 1.

Table I - Chemical analysis of raw materials used

Species	%wt			
	BR	Silica	Lime	Coke
Fe_2O_3	43.02	0.42	0.15	0.83
SiO_2	5.73	98.90		3.42
CaO	9.90		93.60	1.26
MgO	0.23		2.61	0.14
Al_2O_3	21.22	0.38		1.91
TiO_2	5.23			0.10
V_2O_5	0.18			
Na_2O	2.11	0.03		0.16
"-CO_2	2.39		2.29	
"-SO_3	0.39			
H_2O - crystalic	6.09			
H_2O - moisture	3.32			3.30
Fixed C				80.21
P in Coke				0.03
S in Coke				0.77
Volatiles				7.38
Total	**99.81**	**99.73**	**98.65**	**99.61**

The BR received from the AoG alumina plant's filter presses were dried at 150^oC in a static bed electric drier with 500 kg capacity in order to achieve moisture contents below 2%.

The reductive smelting tests done in the EAF were batches of 750 to 1200 kg of feed material, were weight ratios of Coke : BR were varied between 13 to 20%, Fluxes (silica and lime) : BR between 33 to 35% and CaO+MgO:SiO_2 between 0.9 -1.1. After preheating the EAF for 20 -30 min with 70 kg of slag and 20 kg of lumpy coke, the mixed dusty material feed was charged continuously from the top of the furnace at rates between 4 to 7 kg/min (see Figure 3).

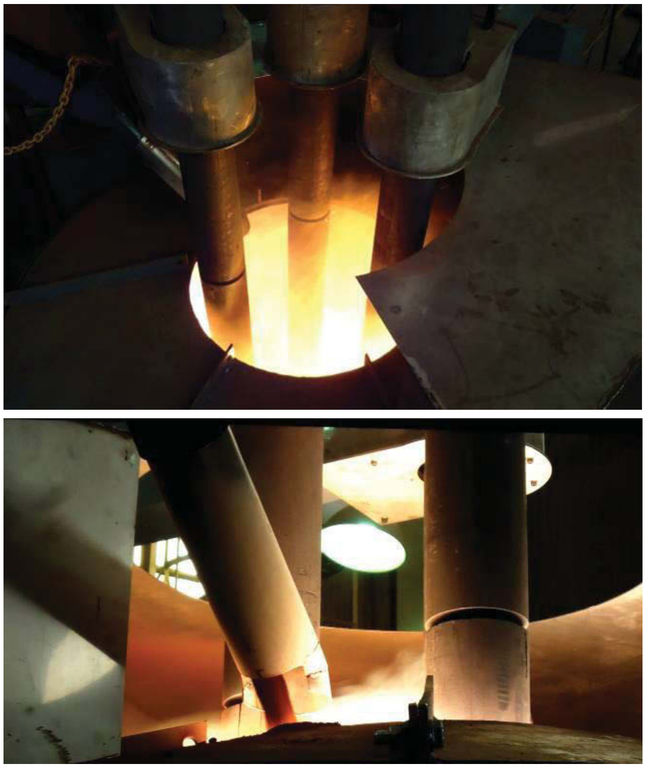

Figure 3. Photographs of the continuous feeding of the EAF with the dusty material mix, through a top lance feeder in the AoG pilot plant.

After the end of the feeding process the slag and metal phases were poured out of the furnace sequentially (see Figure 4) and sampled for chemical analysis with XRF and Mass Spectrometry respectively. The dust collected in the bag filters and the energy consumed in each run were measured and recorded.
Finally part of the slag produced in some experiments was transferred with a ladle to the fiberizing line to test the production of mineral wool.

Figure 4. Pouring of slag (left) and metal phase (right) in the AoG pilot plant

Indicative Results

In the first year of the pilot plant operation 25 tons of dry BR was treated producing approximately 5 tons of pig iron and 16 tons of slag. The optimum feed recipe and respective operational parameters are presented in Table 2. Chemical analysis of produced phases is presented in Table 3.

Table 2 - Optimum BR treatment batch production

Feed	Batch	Per 1 ton BR
Dry BR (kg)	700	1000
Silica (kg)	126	180
Lime (kg)	105	150
Coke (kg)	140	200
Total Feed (kg)	**1071**	**1530**
EAF Energy Consumption (excluding furnace pre-heat)	1056 kWh	1508 kWh
Feeding rate	6.65 kg/min	
Maximum measured melt temperature	1580^{o}C	
Produced phases	**Weight (kg)**	**%wt of feed**
Pig Iron	154	14%
Slag	622	58%
Dust in Bag Filters	44	4%
Total non-gaseous phases	**890**	**77%**

Table 3 - Chemical analysis of products

Pig Iron	%wt	Slag	%wt
Fe	95.47	Fe_2O_3	5.01
C	3.36	SiO_2	27.6
S	0.26	CaO	25.3
P	0.08	Al_2O_3	20.9
Si	0.01	Cr_2O_3	2.98
Cr	0.82	MgO	8.89
Total	**99.99**	TiO_2	5.63
		V_2O_5	0.20
		Na_2O	2.45
		$-SO_3$	0.42
		Total	**99.38**
Fe Recovery	**70%**	**Slag Basicity**	**1.24**

Dust in the bag filters comprises almost entirely of fine-sized BR which is sucked by the off-gas pumps before reaching the melt, and as such can be recycled in the process.
The iron recovery in the metal phase is low, as 14% of the total iron is missing from the mass of the products (metal, slag and bag filter dust). This mass balance deficit is attributed mainly to partial metal and slag mixing during the tilting of the furnace for melt pouring (Figure 4). A different furnace design that would allow melt tapping instead would resolve this problem. The presence of Cr in the pig iron and the high MgO wt% in the slag are attributed to partial dissolution of the Cr/Mg refractory mass used in the furnace bowl. This problem is currently being remediated by substituting the refractory mass with alumina-carbon refractory bricks, which in laboratory tests proved to be more resilient to the aggressive slag melt produced in the process.
Due to its high Cr, the pig iron produced from this first campaign has been used as a steel scrap substitute in white iron production. Namely 2 tonnes of the BR-Pig iron were used to substitute up to 21% of steel scrap used for producing wet-mill grinding balls (see Figure 5).

Figure 5. Produce Pig-iron ingots (left) and respective white iron grinding balls from Guca foundry in Serbia (right), produced with up to 21%wt steel scrap substitution from BR-pig iron (ball diameter: 70 mm, ball composition: Fe 92.7% wt, Cr 2.81%wt, Si 0.51% wt, S 0.05%/ wt, P 0.07%wt).

The slag produced is within most of the empirical indexes ranges reported in [8]. Furthermore the fiberize-ability of the melt has been proven by tests performed in the melt spinner line, as shown in Figure 6. The evaluation of the fibers from appropriate end-user to determine their potential market value is currently under way.

Figure 6. Production of mineral wool fibers from BR-slag in the AoG pilot plant

Discussion

Energy and Exergy efficiency

The experimental campaign in the AoG pilot plant has so far proven the feasibility of the process to efficiently treat BR and transform them to marketable products.

A Factsage [10] thermodynamic equilibrium calculation for the 1000 kg BR system described in Table II at 1600^{o}C and with all feed components at an initial temperature 25^{0}C, predicts the overall enthalpy change of the system to be 1316 kWh. In comparison to the experimental 1508 kWh EAF energy consumption, the furnace operates with only 14.5% energy losses.

The total energy consumption of the pilot plant is calculated to around 2000 -2200 kWh/ton of BR, taking into account utilities like the static BR dryer (160-280 kWh/t BR) the water pumps for the cooling water (60 kWh/t BR) and the bag filter air compressors (110 kWh/t Br).

Still even with a 2000 kWh/t BR electrical energy consumption the novel process could significantly improve the resource utilization efficiency of the alumina refining plant as discussed by the authors in [11]. Accordingly, the exergy efficiency of the BR treatment is 32% and when integrated in the alumina refinery flowsheet it increases the overall exergy efficiency of the plant from 3% to 12%.

Figure 7. The ENEXAL BR treatment process in AoG; dewatered BR is transformed 100% to pig-iron ingots and mineral wool

Process Scale-up

By extrapolating the results presented here to a 5 MVA continuous operation EAF, with a capacity for processing 1300 tonnes of dry BR per month (or 2 tons BR/h) at 2000 kWh/ton BR total energy consumption (including all plant utilities), one calculates a production of 300 tonnes of pig iron and 865 tonnes of slag to be fiberized. The above 5MVA EAF scale up is still a "pilot scale scenario" as its capacity could treat less than 3% of the BR produced in the AoG plant. To scale up to an appropriate industrial level (i.e. 40 - 60 MVA) would require different process design, yet one can argue that the overall energy consumption per ton of treated BR, should remain the same or be reduced, as larger scale brings higher processing efficiency and greater automation. However, the economy of the proposed process would be undermined in such scale. If all the 700,000 ton BR produced annually in AoG were treated in this process approximately 500,000 ton of mineral wool products would be produced, effectively saturating the local markets and driving mineral wool prices down. Thus this novel process can be considered an economically viable solution for treating the BR of the primary alumina production only when it is seen as a starting point for transforming BR and BR-slag into a series of other commercial by-products, such as cement additives [12], geo-polymers [13], catalysts [14] and others [15,2].

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