EAF Treatment for the Efficient and Complete Exploitation of the Bauxite Residue (Red Mud) Produced in the Bayer Process

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Abstract

A novel "zero-waste" process is being developed under the EC-funded ENEXAL project, for the direct transformation of bauxite residues (red mud) into valuable products, such as pig –iron and mineral wool. The novel process utilizes a dust treating electric arc furnace (EAF) to achieve the carbothermic reduction of the red mud waste towards the production of pig iron and viscous slag suitable for direct mineral wool production. Thus the environmental footprint of the Bayer process is reduced substantially, as the initial bauxite ore is exploited in full and no new solid wastes are produced. In this paper experimental results from pilot tests in 400 kVA EAF are presented.

1 Introduction

Today primary aluminum is produced exclusively from bauxite ore through a common industrial production practice consisting of two distinct stages:

- (i) the production of high grade metallurgical alumina (Al₂O₃) from bauxite that is performed according to the Bayer process and
- (ii) the electrolytic reduction of alumina to aluminum, which is performed according to the Hall-Héroult process.

On average the Bayer process requires 2.65 kg of bauxite ore to produce 1 kg of alumina, while the slurry containing the remaining bauxite ore, which is removed from the thickeners during the liquor clarification stage, is by far its greatest environmental problem. This by-product, called bauxite residue or "red mud", on a dry basis is produced in almost a 1 to 1 kg ratio to alumina and consists



from various metal oxides of Fe, Al, Ti, Si, K, Na, V (depending on the initial chemical composition of the bauxite ore) along with inclusions of unwashed sodium aluminate solution.

Red mud is classified by EC as a non hazardous waste (Commission Decision 2000/532/EC), however its 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 its disposal a significant problem. Today, red mud is 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 red mud spill in Hungary in October 2010 is indicative of the magnitude of the red mud waste disposal problem. Till this day, due mainly to high costs and low yields, no industrial application of red mud reuse is in effect.

A novel process is been developed for the direct transformation of red mud into valuable products and is currently being optimized under the EC-funded "Novel technologies for enhanced energy and exergy efficiencies in primary aluminum production industry (ENEXAL)" collaborative research project [1, 2]. Utilizing modern Electric Arc Furnace (AMRT-EAF) technology today it is feasible to process dry dusty red mud directly without the need for a costly agglomeration pre-treatment step. The pig-iron produced in such a way amounts to approximately to 35 % of the initial red mud charge, while the remaining as 65 % of the red mud is transformed into a viscous slag. The latter is transformed into inorganic fibers suitable for the production of a variety of marketable products commonly known as mineral (or slag, rock) wool products.

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 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.

The process design and preliminary experiments have been reported in [2] while the thermodynamic analysis and calculation of the optimum operational conditions have been reported in [3]. 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 for the process. The overall weight ratio of CaO to SiO₂ (basicity ratio) in the feed can vary between 0.8 to1.1 as shown in Figure 1.



Figure 1: Predicted triangular phase diagram for the liquid slag phase thermodynamic stability as predicted by Factsage 6.2 software, for a system of varying CaO, Al₂O₃ and SiO₂ composition and constant TiO₂ composition (other red mud slag oxides are omitted from the calculation at 1400 °C

2 Semi-industrial scale EAF experiments

To establish the process, batch scale tests were conducted at semi-industrial scale in 400 kVA dust treating EAF. The red mud used was supplied by Alouminion AE, the Greek aluminum producer plant, and its chemical and mineralogical analysis is presented in Table 1. The red mud was dried in a stationary electric dryer before feeding to the EAF. The optimal feed recipe used in the experiments is presented in Table 1, consisting of mixing dry red mud with coke fines and appropriate silica and lime bearing fluxes. The C to Fe atomic ratio was set at 2.4 and the basicity ratio of the feed (CaO + MgO/SiO₂) was set at 0.94.

Chemical Species	%wt	Mineralogical Phases	Batch Charge in EAF Fur- nace		
Al ₂ O ₃	17.35 %	Hematite [Fe ₂ O ₃]	Dry Red Mud	350 kg	
Fe ₂ O ₃	45.72 %	Goethite [FeOOH]	Coke Fines	77 kg	
CaO	7.10 %		Burnt Lime	53 kg	
SiO ₂	8.22 %	Gibbsite $[Al_2O_3*3H_2O]$	Silica Sand	70 kg	
TiO ₂	8.13 %	Diaspore [Al ₂ O ₃ *H ₂ O]	TOTAL	550 kg	
Na ₂ O	1.02 %	Boehmite [Al ₂ O ₃ *H ₂ O],			
V ₂ O ₅	0.11 %	Cancrinite			
-SO3	0.67 %	$[Na_6Ca_2(Al_6Si_6O_{24})(CO_3)_2]$			
-CO ₂	2.42 %	Katoite [Ca ₃ Al ₂ (SiO ₄)(OH) ₈]			
H ₂ O(cry)	9.25 %	Calcilte [CaCO ₃]			
Total	100.00 %				

Table 1: Dry red mud sample analysis and batch feed "recipe"

Each batch experiment consisted of a furnace pre heating stage (app 1 hour long), followed by the feeding of the material which was done at approximately 3 kg/min rate, through a feeder tube at the top of the furnace (Figure 2). The temperature at the surface of the melt produced was measured with an optical pyrometer at 1540 °C (average value). In the end of the batch feeding, two distinct phases were poured from the furnace, slag and pig iron, their weights and chemical analyses of which, are presented in Table 2.

The pig iron chemical analysis shows that the metal produced has concentrated practically all the iron and the vanadium content of the red mud, while also small amounts of silicon and titanium metal have also been reduced. Sulfur, originating from the red mud and the coke, and phosphorous originating only from the coke, where kept at minimum values, thus producing a metal which can be easily used in secondary steel production. Carbon content has the typical pig iron value of 4 %wt. The chromium metal presence in the pig iron is not attributed to the feed material, but rather to chromo-magnesium furnace lining which was partially dissolved during the carbothermic reduction.

Pig iron %wt	Fe	С	S	Р	Si	Ti	V	Cr	Mn
	87.093	4.047	0.050	0.202	1.705	0.455	0.281	4.427	0.115
Pig iron phase weight			120 kg		Fe recovery in pig iron			97.31%	
Slag %wt	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	MgO	Fe ₂ O ₃	Na ₂ O	Cr ₂ O ₃	-SO3
	24.226	32.624	29.650	6.786	4.646	1.106	1.890	0.409	1.090
Slag phase weight		280 kg		Slag Basicity Ratio		1.05			

Table 2:EAF Experimental Results



Figure 2: Photos of the AMRT-EAF during batch feeding (left) and during pouring (right).

The slag phase contains the remaining metals of the red mud in form of oxides, in an overall neutral melt (basicity ratio = (mass of CaO + MgO) / (mass of SiO₂) = 1.05). In Figure 3 the elemental mass balance is presented, from which one can derive that approximately 41 % of the initial sodium content of the red mud is missing from the final products, indicating its evaporation from the system, as expected from previous thermodynamic studies [3].

During the slag phase pouring part of the slag was fiberized using a high speed air/water jet. The inorganic fibers produced from the slag were examined with scanning electron microscopy, in order to assess the physical qualities of the fibers. As seen in Figure 4, fibers with diameters less than 20 μ m were mostly formed, along with some substantially thicker fibers. Such imperfections, caused by the slag freezing prior to the completion of the fiber formation, can be attributed to the lack of an automated system during these preliminary experiments. In general, it is apparent that the slag from the red mud treatment process can be fiberized.



Figure 3: Elemental mass balance of batch feed and EAF smelting phases. For each element feed is represented in negative mass (kg) values, while pig iron, slag and inferred gas in positive mass (kg) values.



Figure 4: Photos of air/water jet slag fiberization process (left) SEM photograph of inorganic fibers produced (right).



Figure 5: Preliminary cost analysis (left) and profit margin analysis for different mineral wool prices (right) for a process in 5MVA EAF treating 1300 tons of Bauxite Residues per month

3 Prelimanry Economic Analysis

Based on the results presented in the previous section an extrapolation from the 400 kVA EAF to a 5 MVA EAF is made, estimating an average consumption of 1700 kWh per ton of bauxite residue treated. By treating 1300 tonnes of dry red mud per month, one calculates a production of 445 tonnes of pig iron and 1040 tonnes of slag to be fiberised. Taking into account the current cost of raw materials, electrical energy and labour in Greece, the overall operation cost of such a unit is predicted at 766,217 \notin per month. Based on the current prices for pig iron scrap, selling the pig iron alone would only cover 25 % of the unit's operational cost. By adding the slag fiberisation, the overall operation would become viable if the mineral wool product was sold at minimum of 626 \notin /tonne (break-even price). Currently, commercial mineral wool products values range in between 600 to 1000 \notin /tonne. The results of this preliminary economic analysis are shown in Figure 5.

4 Conclusions-Future Work

Previous thermodynamic modeling and laboratory experiments along with the semi-industrial EAF experiments presented here, prove that the reductive smelting of red mud at 1600 °C, using carbon as reducing agent and appropriate fluxes to regulate the composition of the generated slag, can produce pig iron and a viscous slag. The latter can be converted into glassy fibers suitable for mineral wool production.

For the primary aluminum industry the proposed red mud treatment process is expected to increase its sustainability, as it will increase its overall resource utilization (exergy efficiency) by exploiting the bauxite ore in full and eliminate all solid by-products of the Bayer process through a "zero-waste" process.

From an economic perspective a large volume slurry waste with costly disposal, is replaced, in a single step process, by two valuable by-products thereby significantly increasing the versatility and profit margin of the industry. Especially for the case of mineral wool production, which is a versa-tile product with multiple applications, it must be stressed that through this novel process it will be produced at 70 % lower energy consumption compared to conventional mineral wool production. This will provide the aluminum industry with a significant industrial advantage, for entering a new and highly competitive product market.

The work on the novel process will continue with the demonstration of the process in industrial scale at 1 MVA EAF in the industrial plant of Alouminion AE in Greece. It is expected that in that scale the true technical and economical viability of the process will be properly assessed.

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