A NOVEL RED MUD TREATMENT PROCESS

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SUMMARY: A novel "zero-waste" process is being developed under the EC-funded ENEXAL project, for the direct transformation of 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.

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 (Al_2O_3) 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. The Bayer process (Jürgen Buschow K.H. et al., 2001), patented in 1888 by Karl Joseph Bayer, is essentially a cyclic chemical process, characterized by a very low exergy efficiency (3%) (Balomenos E. et al, 2011) as it requires large amounts of heat (12.77 MJ/kg of Al_2O_3), usually generated through heavy fuel burning (leading to 0.83 kg of CO_2/kg Al_2O_3 including limestone calcination). 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, Ga (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 (30 to 35 million tons per year on a dry basis worldwide (Mason L.G., 2007)) 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 (and thus substantial costs for the alumina producing industry) (Gleich A, 2006). 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.

2. PROCESS DESIGN

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 (Balomenos E. et al., 2009).

The process is based on the reinvestigation of the idea to treat the red mud through carbothermic reductive smelting and produce pig-iron and slag. Utilizing modern Electric Arc Furnace (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 would amount to approximately to 35% of the initial red mud charge, therefore pig-iron production alone would not solve the industry's waste disposal, as 65% of the red mud would still have to be disposed as EAF slag, while the expected turnover from selling such amounts of pig-iron would not suffice to make for an economically viable process.

The novel red mud treatment process however aims at turning all of the red mud waste into valuable products and this includes transforming the EAF slag into inorganic fibers suitable for the production of a variety of products commonly known as mineral (or slag, rock) wool products. Mineral wool products due to their light weight, low thermal coefficient, incombustibility and high temperature melting points (>1000^{o}C) are widely used as refractory, thermal and acoustic insulation or even light weight construction materials (Fitzer E., 2009). This broad range of applications guarantees a large market for the red mud treatment EAF slag. Indicatively, in 2003 mineral and glass wool products accounted for 60% of the thermoinsulation market in Europe (Karamanos A.K., 2005). 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 (IPPC, 2001), then one can expect that the proposed red mud treatment process will be economically viable.

Thus the proposed red mud treatment comprises of four stages as shown schematically in Figure 1. The first stage is the red mud drying stage, as even red mud dewatered in filter presses contains significant amounts of moisture (up 25% w/w). This stage can take place in a double skin rotary kiln, utilizing the heat content of the hot off-gases from the EAF. In the next stage of the process the material feed of the EAF is prepared by mixing the dry red mud, coke fines and appropriate fluxes to adjust the properties of the produced slag. This mixture is feed into the EAF where the raw materials undergo reductive smelting and are transformed in three distinct fluid phases: liquid slag, liquid pig-iron and off-gases. The off-gases after heat exchange in the red mud dryer are sent in a bag-house unit to remove dust particles prior to releasing them to the atmosphere. The dust collected is recycled in the feed material. The liquid pig-iron and slag phases are separated by sequential pouring (or by tapping in a continuous process) and the slag is driven directly to the final stage of the process, where the liquid slag is fiberized to produce inorganic fibers and mineral wool products.

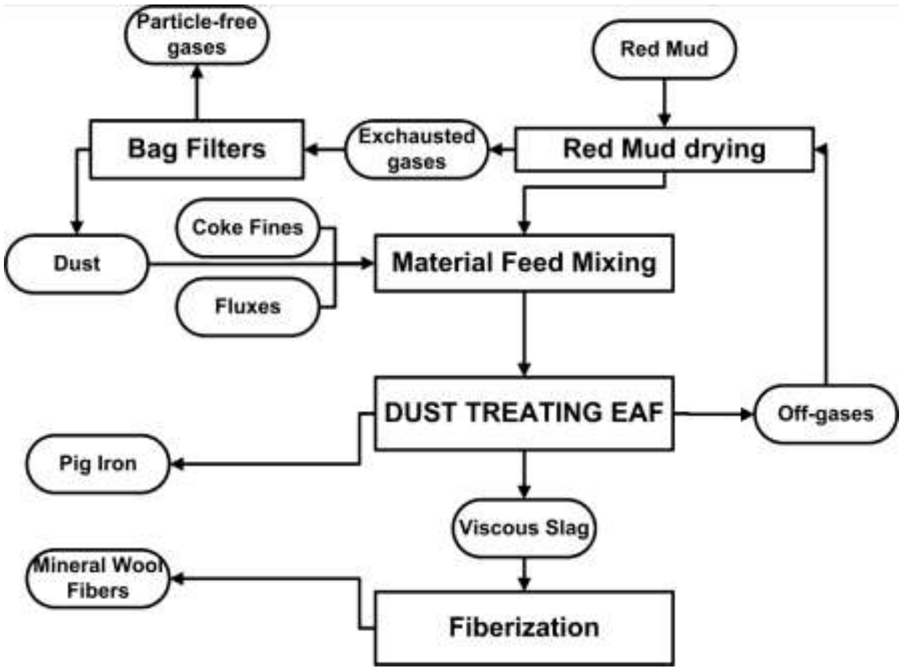

Figure 1: The envisioned novel red mud treatment

3. PRELIMINARY EAF EXPERIMENTS

To establish the process, and following previous thermodynamic modeling and lab scale experiments (Balomenos et al., 2011b), batch scale tests were conducted in semi-industrial scale. A 400 kVA dust treating EAF was operated in batch feed manner. 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.

Table 1 – Dry red mud sample analysis and batch feed “recipe”

Chemical Species	%wt	Mineralogical Phases	Batch Charge in EAF Furnace	
Al_2O_3	17.35%	Hematite [Fe_2O_3]	Dry Red Mud	350 kg
Fe_2O_3	45.72%	Goethite [FeOOH]	Coke Fines	77 kg
CaO	7.10%	Gibbsite [Al_2O_3*3H_2O]	Burnt Lime	53 kg
SiO_2	8.22%	Diaspore [Al_2O_3*H_2O]	Silica Sand	70 kg
TiO_2	8.13%	Boehmite [Al_2O_3*H_2O],	**TOTAL**	**550 kg**
Na_2O	1.02%	Cancrinite		
V_2O_5	0.11%	[$Na_6Ca_2(Al_6Si_6O_{24})(CO_3)_2$]		
-SO_3	0.67%	Katoite		
-CO_2	2.42%	[$Ca_3Al_2(SiO_4)(OH)_8$]		
H_2O(cry)	9.25%	Calcilte [$CaCO_3$]		
Total	**100.00%**			

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 3kg/min rate, through a feeder tube at the top of the furnace (Figure 2). The temperature of the melt produced was measured at 1540^{o}C. 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.

Table 2 - EAF Experimental Results

Weight of phases			
	Pig Iron	**Slag**	**Total**
(Kg)	120	280	400 kg
Chemical analysis			
Pig Iron Element	**(% wt)**	**Slag Oxides**	**(%wt)**
Fe	87.093	**Al2O3**	24.226
C	4.047	**SiO2**	32.624
S	0.050	**CaO**	29.650
P	0.202	**TiO2**	6.786
Si	1.705	**MgO**	4.646
Ti	0.455	**Fe2O3**	1.106
V	0.281	**Na2O**	1.890
Cr	4.427	**Cr2O3**	0.409
Mn	0.115	**- SO3**	1.090
Fe Recovery	97.31%	**Basicity Ratio**	1.05

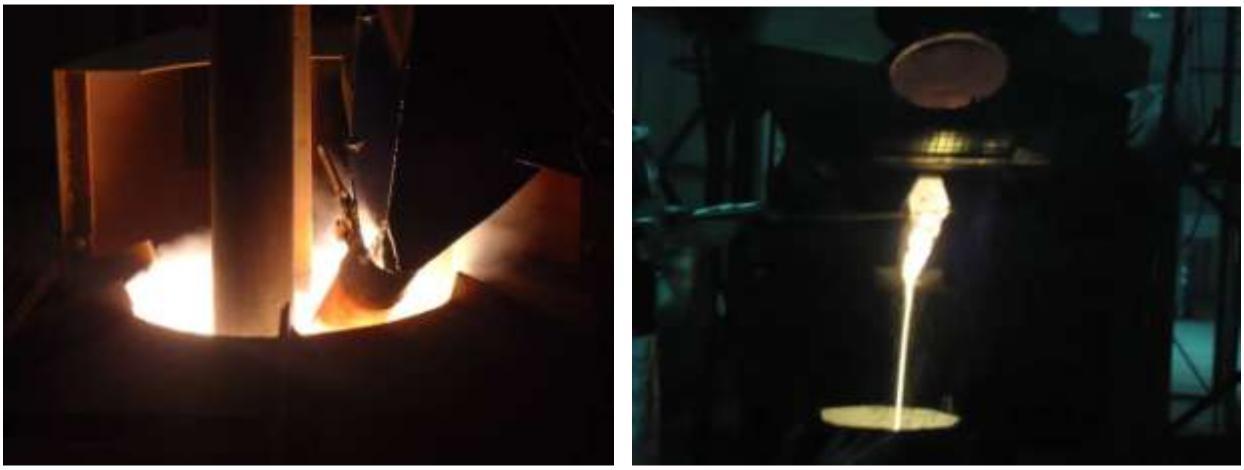

Figure 2: Photos of the EAF during batch feeding (left) and during pouring (right).

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 SiO_2) = 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 results (Balomenos E. et al., 2011b).

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 μm 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.

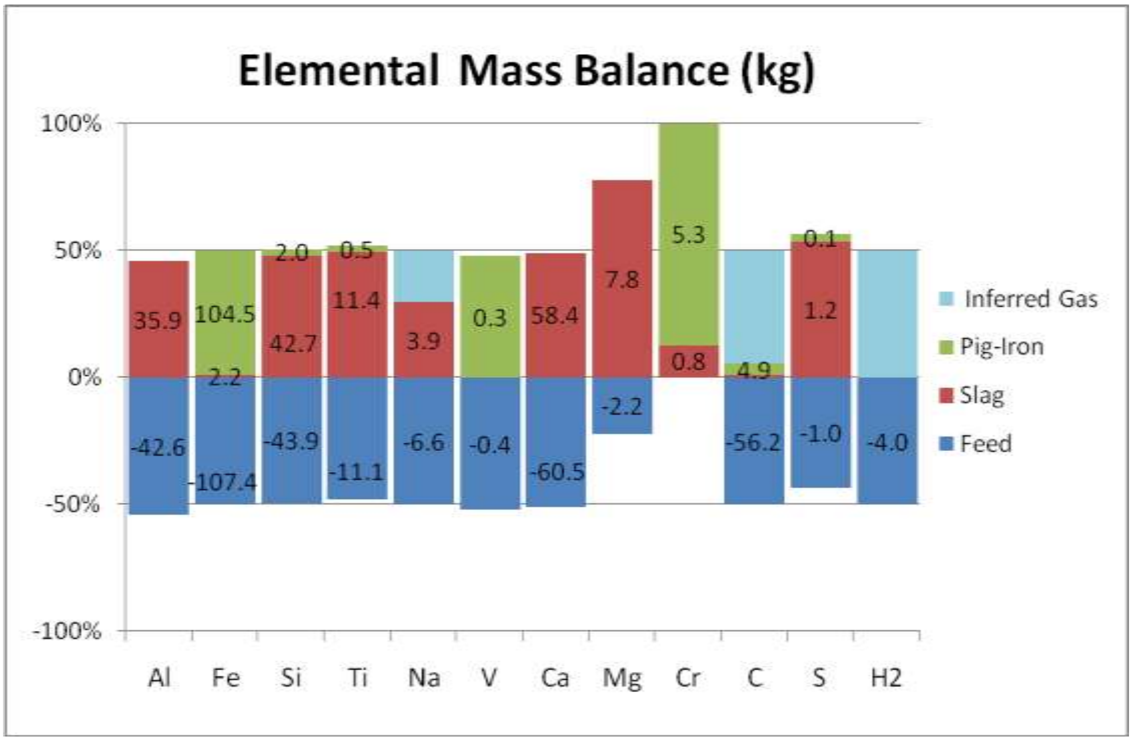

Figure 3: Normalized elemental mass balance of batch feed and EAF smelting phases. Feed is represented in negative values, while pig iron, slag and inferred gas in positive values. Labels represent actual weight of respective elements in kg

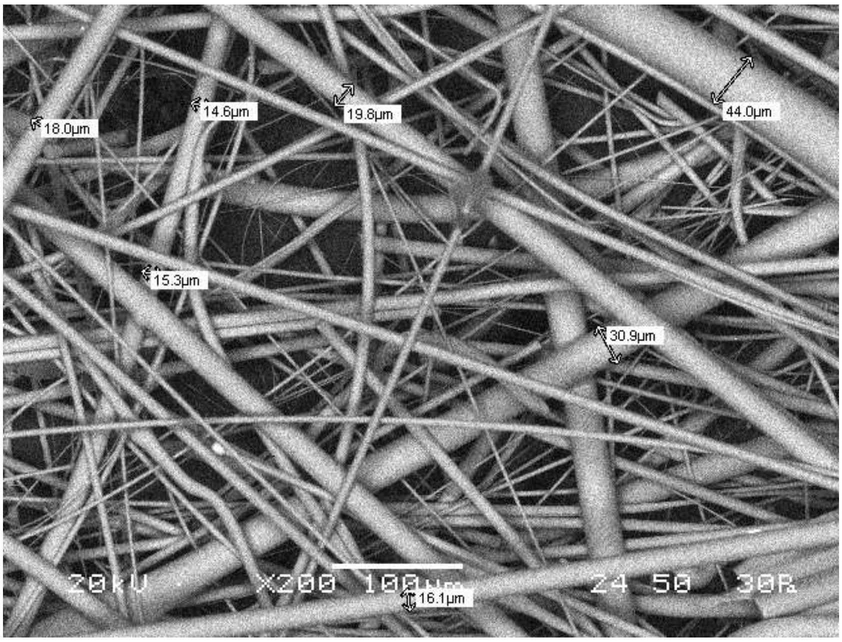

Figure 4: SEM photograph of inorganic fibers produced from the red mud treatment process slag

4. CONCLUSIONS-FUTURE WORK

Previous thermodynamic modeling and laboratory experiments along with the preliminary semi-industrial EAF experiments presented here, prove that the reductive smelting of red mud at 1600^{o}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 versatile 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.

Before however this process can be industrially implemented, further research and more lab and EAF experiments are needed in order to refine the qualities of the produced products, especially more so in respect to the chemical and physical properties of the produced inorganic fibers, which depend greatly on the fluxes used in the reductive smelting. Investigations into more suitable refractories for the process are also needed.

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REFERENCES

Balomenos E. et al., (2011a), "Energy and Exergy Analysis of the Primary Aluminium Production Processes – A Review on Current and Future Sustainability", *Mineral Processing & Extractive Metall. Rev*., 32 1–21.

Balomenos E. et al., (2011b) "A Novel Red Mud Treatment Process : Process design and preliminary results" , TRAVAUX Vol. 36 (2011) No. 40 - ISCOBA Conference 2011 India

Balomenos E. et al., (2009) "ENEXAL: Novel technologies for enhanced energy and exergy efficiencies in primary aluminium production industry", *MJoM* Vol 15, 203-217

Fitzer E., ed. (2009), *Ullmann's Encyclopedia of Industrial Chemistry,* Fibres, 5. Synthetic Inorganic (John Wiley & Sons, Inc)

Gleich A., ed., (2006), *Sustainable Metals Management,* Chapter 4: Prospects for a sustainable Aluminium Industry, (Springer) pp 97-111,

IPPC, (2001) *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Glass Manufacturing Industry* (European Commission, 2001)

Jürgen Buschow K.H. ed (2001), *Encyclopedia of Materials: Science and Technology*, Chapter: Aluminum Production and Refining, (Elsevier Science Ltd., 2001) pp 132-140

Karamanos A.K. et al. (2005), "Comparative evaluation of stone wool and extruded polystyrene", *Heleco '05* 1-11 (in greek).

Mason L.G., ed. (2007), *Focus on Hazardous Materials Research,* Chapter 3: Red Mud and Paper Mill Sludge Treatment and Reuse for the Recovery of Contaminated Soils, Sediments and Waters: A focus on latest trends, (Nova Science Publishers, Inc.) pp. 77-142.