Novel Technologies For Enhanced Energy And Exergy Efficiencies In Primary Aluminium Production Industry

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Abstract: The EC funded research project "ENEXAL" develops and demonstrates novel technologies for increasing the energy and exergy efficiency of the primary aluminium industry, which is currently amongst the most energy intensive industries in the world. In this paper a presentation of novel technologies for the red mud treatment and the carbothermic reduction of alumina are presented. Accordingly, the red mud by-product of the Bayer process is transformed into valuable products such pig-iron and mineral wool fibers through reductive smelting in a dust treating EAF. Aluminium and aluminium-silicon alloy are being produced through carbothermic reduction in EAF.

Keywords: Red Mud, Bauxite residues, Carborthermic reduction of alumina, Al-Si alloy.

1. 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. It also generates enormous quantities of wastes that further decrease the exergy efficiency of its production process. However, this industry is one of the most vital sectors from an economic and a social point of view, not only for Europe but also for the entire world. In order to remain viable and competitive, primary aluminium industry has to operate in a smarter way, be more energy efficient and meet the environmental requirements of our times. This can be achieved only through radical new technologies and novel business strategies, which will enable the industry to maintain its competitiveness and fasten its viability in the world's markets, and explore new business opportunities.

The main goal of the EC funded ENEXAL project is to provide primary aluminium industry with "green" innovative technological and economical solutions, focusing on the (i) *significant improvement of energy and exergy efficiencies of the production process, (ii) substantial reduction of GHG emissions and (iii) complete elimination of its solid wastes*.

In this paper three technologies developed in the above framework are presented.

2. The red mud treatment

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 mass 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.

Utilizing modern Electric Arc Furnace reduction smelting technology today it is feasible to process dry fine 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 amount of the red mud is transformed into a viscous slag. The latter, through slag engineering, can be transformed into inorganic fibers suitable for the production of a variety of marketable products commonly known as mineral (or slag, rock) wool products

To establish the process, batch scale tests were conducted in NTUA's semi-industrial scale 400 kVA dust treating EAF. The red mud used was supplied by ALUMINIUM SA, the Greek aluminum producer plant, and it was dried in a stationary electric dryer before feeding to the EAF. The optimal feed recipe used in the experiments, consisted of mixing dry red mud with coke fines and appropriate silica and lime bearing fluxes, so that the C to Fe atomic ratio was set at 2.4 and the basicity ratio of the feed (CaO + MgO/SiO_2) was set at 0.94.

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. The temperature at the surface of the melt produced was measured with an optical pyrometer at 1540^{o}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 1.

Table 1: EAF Experimental Results

Pig iron %wt	**Fe**	**C**	**S**	**P**	**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_2O_3**	**SiO_2**	**CaO**	**TiO_2**	**MgO**	**Fe_2O_3**	**Na_2O**	**Cr_2O_3**	**-SO_3**
	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	

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 magnesium chromite furnace refractory lining which was partially dissolved during the carbothermic reduction.

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). The chemical composition of the slag is within the empirical limits set by the mineral wool industry, as reported in [1]. 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 1, 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.

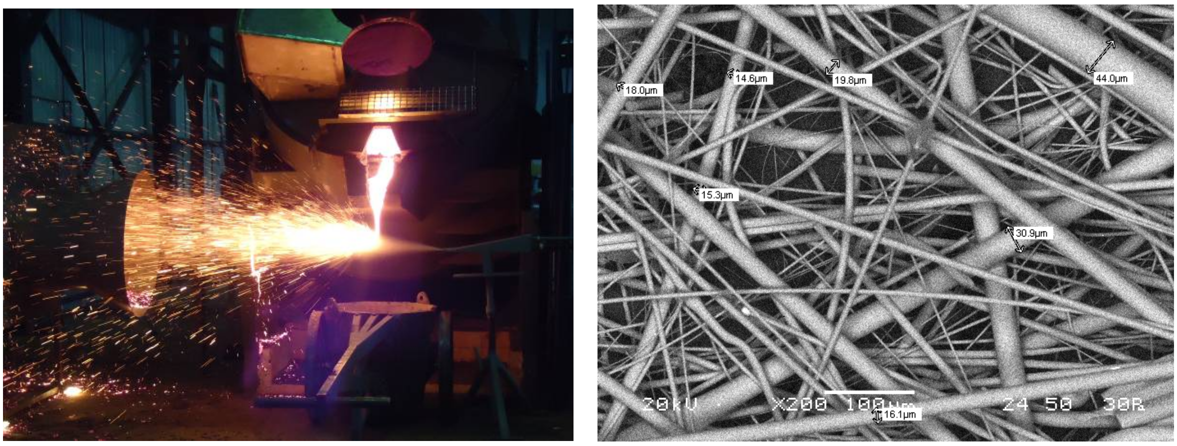

Figure 1: Photos of air/water jet slag fiberization test (left) SEM photograph of inorganic fibers produced (right).

3. Carbothermic production of Aluminium

A recent thermodynamic study of the carbothermic reduction of alumina presented in [2], demonstrated the major thermodynamic role of aluminium volatilization phenomena in reducing liquid aluminum yields at high temperatures. Accordingly, to achieve an efficient one-step reduction process either one has to reduce the liquid aluminum activity or move to conditions favoring complete gaseous aluminum production. Both routes are investigate in the ENEXAL project

3.1 Gaseous Aluminum production

As seen in Figure 2, for the systems Al_2O_3 + 3C at atmospheric pressures temperatures above 2500^{0}C thermodynamically one can achieve aluminum reduction yields above 90%. To test this process a custom hollow electrode DC-EAF, depicted in Figure 3, located at IME, RWTH Aachen was used, capable of achieving temperatures above 2400^{0}C in the arc zone between the tip of the hollow electrode and the bottom electrode. Through the use of the hollow electrode the material feed can be directly fed in the arc zone, allowing thus for fast reactions at high temperatures. The lid of the EAF is water cooled and was fitted with a customized copper condenser, in order to directly solidify gaseous aluminum products.

Following an optimization experimental campaign the optimum feeding rate of alumina carbon pellets (at stoicheiometric ratio), condenser cooling rate, as well as the optimum Ar overpressure in the furnace (in order to avoid back-reactions with oxygen) was established. Accordingly the dusty material retrieved from the condenser, shown in figure 3, contained practically only metallic Al, with minimal amounts of Al_2OC, Al_4C_3, and Al_4O_4C (figure 4).

Quantitatively, the total mass of the material pellets which was fed during the experiment was 30g and at end of the experiment 16 g of dusty material were retrieved from the condenser. In accordance with the chemical composition of the pellets and the XRD analysis presented above, one can deduce that approximately 77% of all Aluminium was retrieved in the condenser in the metallic state.

Therefore the process is proved successful both in quality of produced condensate and in quantity of Aluminium recovery. With an improved condenser design (e.g. by eliminating the lid condensation surface and further improving cooling rates) one should be able to achieve practically full aluminum recovery.

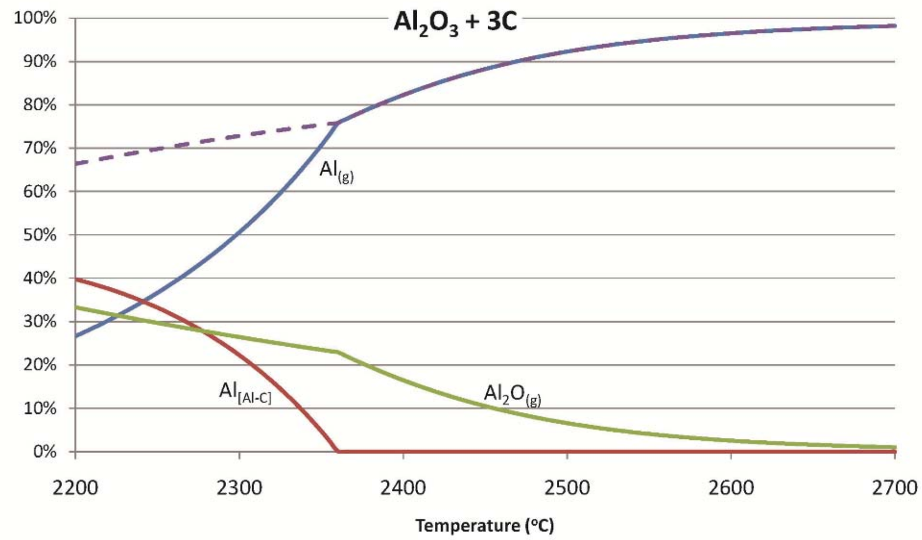

Figure 2: Factsage calculated distribution of aluminum species at thermodynamic equilibrium for various temperatures at atmospheric pressure in a system with initial molar composition of 1 Al_2O_3 + 3 C. The dashed line signifies the total alumina to metallic aluminum reduction yield (Al-C alloy and $Al_{(g)}$). The [Al-C] subscript denotes the liquid aluminum alloy metal phase.

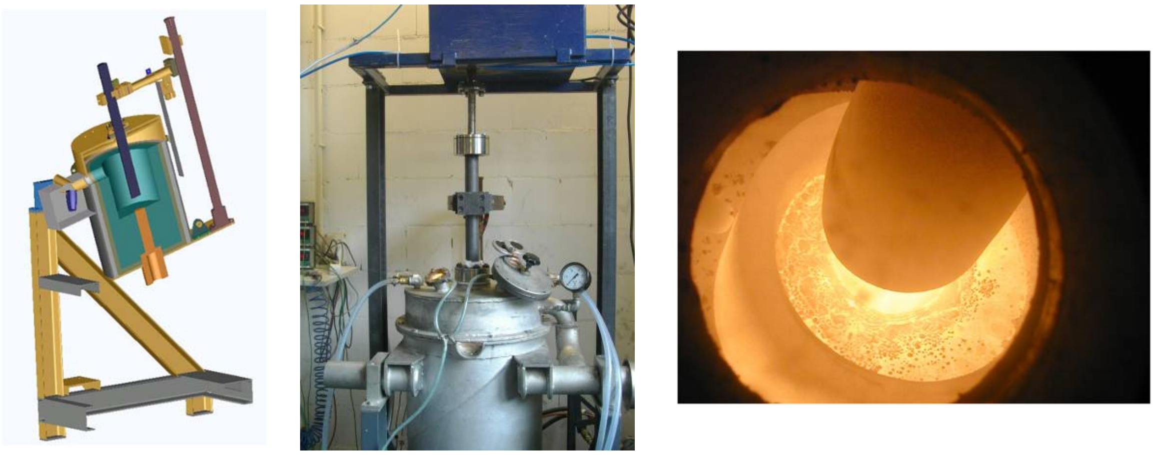

Figure 3: Schematic drawing and photograph of the EAF used. On the right picture of the reaction zone during operation (the graphite crucible is seen in the bottom while the hollow electrode tip is directly above it). No liquid melt formation is observed.

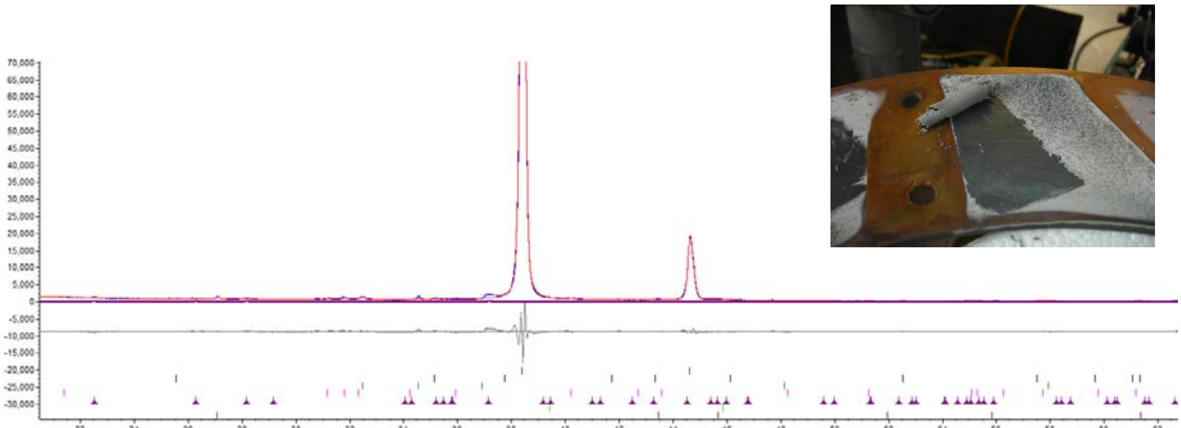

Figure 4: XRD analysis of the dust collected from the condenser. Both major picks correspond to metallic aluminium (2theta 38,10 and 44.37). Rietveld-method analysis shows at least 76.91% metallic Al, followed by cubic Alumina 9.37%, 4% or less in Al_2OC, Al_4C_3 and Al_4O_4C. Cubic alumina is the result of metallic aluminum re-oxidation after the end of the experiment. **Inlet Picture:** Dust collected from copper condenser surface.

3.2 Direct Al-Si master alloy production

An alternative process developed in ENEXAL is the carbothermic co-reduction of alumina and silica in EAF in order to produce directly an Al-Si master alloy. Al-Si alloys are used in casting application which approximately account for 30% of all Aluminium utilization.

Small addition of silicon in the aluminum melt reduces the activity of the melt thereby hindering volatilization phenomena and increasing liquid aluminum metal yields as shown in figure 5 calculated using FactSage.

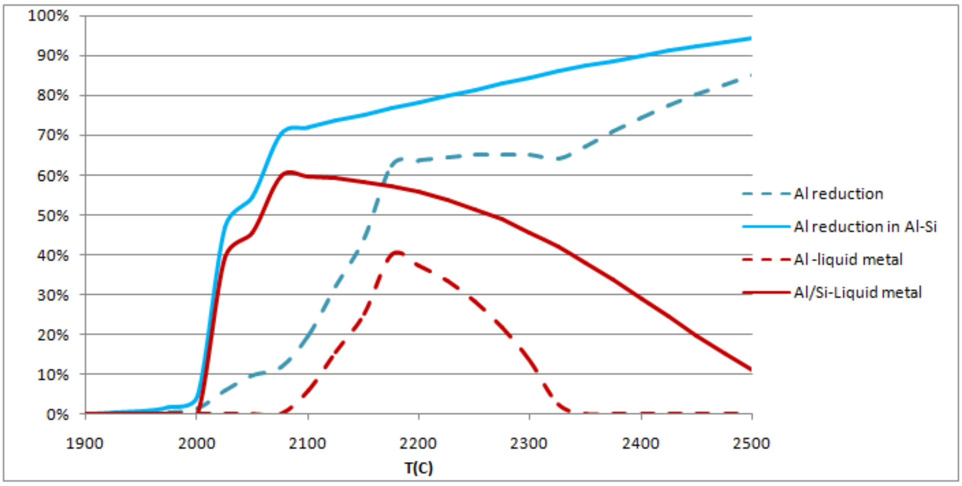

Figure 5: Prediction of aluminium overall reduction rate and aluminium liquid metal recovery rates for the system 2 Al_2O_3 + 1 SiO_2 + 8 C (solid lines) and the system Al_2O_3 + 3 C (dashed lines).

Experiments were conducted in laboratory EAF in IME at RWTH Aachen utilizing as feed material pellets from technical grade alumina and silica combined with ca. 7 % corn starch as binder and lignite coke or wood charcoal as reducing agent. The experiments took place in carbon crucible which was filled with feed pellets and heated for approximately 1 hour to achieve the full melting of the charge. Optimum results where achieve for a feed molar ratio of Si to Al of 0.26, as shown from the chemical analysis of the metal products received through different experiments (table 2). In all cases shown the crucible was removed from the furnace below a temperature of 1000 °C and cast in a mould, resulting in Al-Si block shown in Figure 7.

Table 2: Chemical analysis of obtained Al-Si samples from co-reduction EAF trials in Aachen, measured by Optical Emission Spectrometry and C and O_2 Analysis

Identification Number	Al wt.-%	Si wt.-%	Fe wt.-%	Mn wt.-%	Ti wt.-%	O_2 wt.-%	C wt.-%
Si/Al 0.26 A	72.53	25.58	1.62	0.028	0.032	0.03	0.06
Si/Al 0.26 B	71.37	25.95	2.32	0.034	0.032	0.06	0.34
Si/Al 0.35 A	68.85	30.79	0.11	0.017	0.042	0.43	0.11
Si/Al 0.35 B	61.79	>33.60	0.21	0.029	0.051	0.07	0.57
Si/Al 0.35 C	59.87	>33.60	0.26	0.030	0.050	0.03	0.27

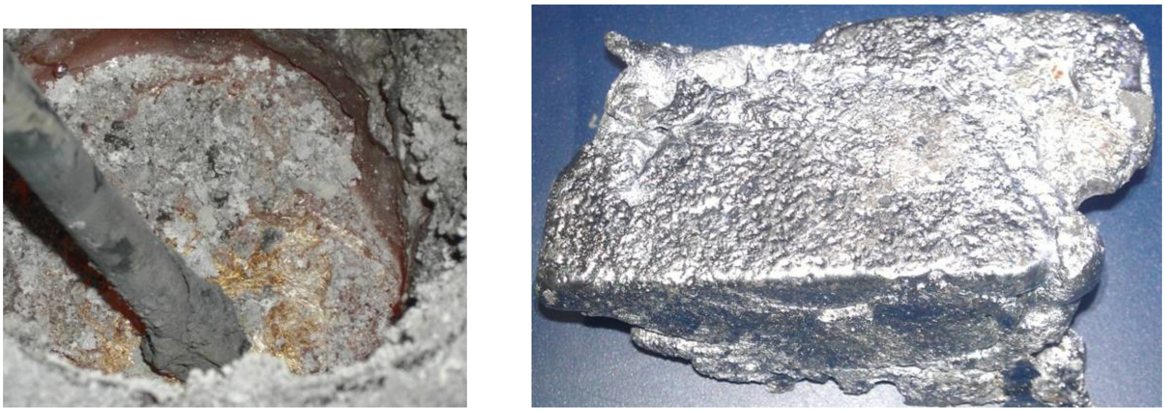

Figure 6 - Left: Visible aluminium melting "skin" during solidification process of the melt, **Right:** Picture of the casted carbothermically produced Al-Si alloy.

4 Conclusions

The ENEXAL project has researched and developed three new technologies which have a direct potential for application in the primary aluminum production industry, greatly improving its sustainability.

The red mud process can remove completely the bauxite residues of the Bayer process for alumina production in a zero waste process which yields commercially valuable products. The process is ready for pilot scale industrial application, which will take place in the ALUMINIUM SA, plant in Greece.

The gaseous aluminum production is an innovative approach in producing a one-stage process for replacing the energy intensive Hall-Herlout electrolytic process. However the process requires further development until it can be considered for pilot scale industrial application.

Finally the Al-Si direct production represents an interesting alternative, for producing directly a commercial master alloy with an industrially mature technology (EAF), which is expected to have a significantly lower energy and carbon footprint than the currently established process for producing separately metallic Al and Si.

Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Programme ([FP7/2007-2013]) under grant agreement n° ENER/FP7/249710/ENEXAL (www.labmet.ntua.gr/ENEXAL)

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