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ENEXAL: NOVEL TECHNOLOGIES FOR ENHANCED ENERGY AND EXERGY EFFICIENCIES IN PRIMARY ALUMINIUM PRODUCTION INDUSTRY

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Abstract

Primary aluminium production industry is the world's larger industrial consumer of energy and 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 economic and social point of view, not only for EU 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. The Project ENEXAL concept was developed under EC's FP7 Cooperation ENERGY.2009.8.1.1 Work programme and it demonstrates 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.

Key words: primary aluminium production, alumina, sustainable industrial production, red mud, carbothermic reduction, energy and exergy efficiency

Overview

Aluminium represents 8% of the earth's crust, being the third (following oxygen and silicon) most abundant element in our planet [0]; however its commercial production is relatively recent, dating a little more than a century. Despite this, the world's aluminium production exceeds today the production of all the other non-ferrous metals combined. Due to a unique combination of properties, aluminium is a prevalent

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material for numerous applications. Aluminium is a light-weight, durable, flexible, corrosion-resistant metal with high electrical and thermal conductivity, which is used in a vast array of products in all areas of modern life including transport, construction, food, medicine, packaging, electronics and electricity transmission. As a result, aluminium is the world's second most-used metal after steel and the aluminium production industry is the largest, in volume of metal produced, in non-ferrous metal industry. In 2006, the world's primary aluminium production was approximately 34 million tonnes, while aluminium recycling produced another 16 million tonnes. This total of about 50 million tonnes in aluminium greatly exceeds the 17 million tonnes of copper, 8 million tonnes of lead and 0.4 million tonnes of tin produced worldwide.

Primary aluminium production is associated with serious environmental problems including high energy demand, substantial GHG emissions and solid waste generation. Primary aluminium industry is the world's largest industrial consumer of energy. It consumes about 1% of the globally produced electric energy and about 7% of the total energy consumed by industry worldwide [[2]] and it is responsible for the 2.5% of the world's anthropogenetic CO_2-equivalent emissions [[3]] as well as for the generation of 30 to 35 million tonnes per year of the red mud solid waste (on a dry basis) worldwide [[4],[5]].

Currently, about 25% of the world's aluminium production takes place in Europe (including Russia) and more than 10% in EU Member States. Aluminium industry is ranked among the most important and vital sectors of EU from both, social and economic point of view. It represents directly a workforce of about 200 000 people and has an annual turnover in the order of 25 billion €. More than 60% of the EU aluminium production corresponds to primary aluminium. In 1997, the primary aluminium production in Europe (excluding Russia) amounted to 3.9 million tonnes, whereas in 2006 it peaked at 5.1 million tonnes, representing a growth of about 30% [[6]]. The major European primary aluminium producers are located in Norway, Germany, France, Spain, United Kingdom, Netherlands, Iceland, Italy, Greece, Montenegro, Romania, Hungary, Slovakia, Sweden and Switzerland. Although European aluminium industry is flourishing and profitable with anticipated strong growth for the next decade and beyond, Europe remains an important net importer of primary aluminium, with imports of 2.9 million tonnes in 2006.

Considering the key policies of the EU Action Plan for Energy Efficiency and the priorities of the EU revised strategy for Sustainable Development, it is clear that the sustainability and viability of the European primary aluminium industry depend strongly on the improvement of its energy and exergy efficiencies, the substantial reduction of its GHG emissions and the elimination of its wastes. Particularly, the European primary aluminium industry has to operate in a smarter way, be more energy efficient and make efforts to meet the requirements laid down for the environmental protection. It must maintain its competitive position and fasten its viability in the world's markets with well established industries attempting to regain ground by enhancing business opportunities. This can be achieved only through an evolution that will provide the industry with radical new technologies and novel business strategies.

Current production process

Primary aluminium is produced from bauxite ore that is converted into aluminium oxide (alumina), which in turn is reduced to aluminium. The common industrial production practice consists 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 aluminium, which is performed according to the Hall-Héroult process. Both processes were developed at the end of the 19th century and since then both have been extensively investigated and optimized through many technological improvements; however their basic scientific principles and environmental issues remain unchanged [[7]].

I. The Bayer Process

In the Bayer process [[8]], alumina is extracted from bauxite with sodium hydroxide solution, under pressure (3.5 MPa) and elevated temperature (140-300°C), in digesters. The produced slurry contains dissolved sodium aluminate and a solid residue called “red mud”, which is removed in thickeners. The aluminate solution is then seeded with gibbsite at 60°C to accelerate the precipitation of trihydrate alumina (gibbsite), which in turn is calcined at 1100°C to produce powdered, high grade metallurgical alumina.

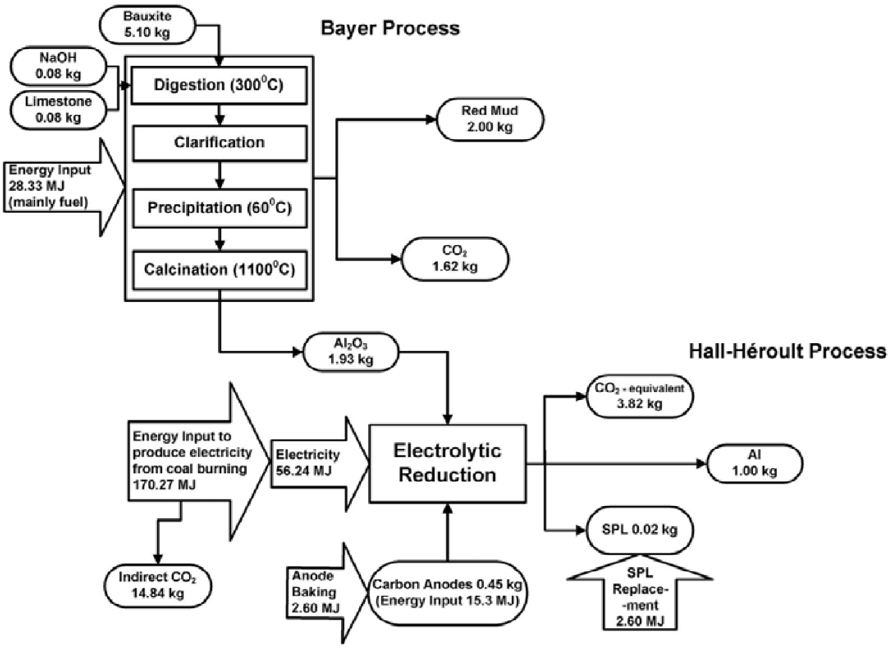

Fig. 1 Mass & energy balances in current industrial process of primary aluminium production

According to the energy and mass balance diagram of the primary aluminium production presented in Fig. 1, the Bayer process requires significant amounts of heat (28.33 MJ/kg Al) [[6],[7]], which are supplied through fuel burning. Moreover, it is related to the generation of a solid residue known as red mud, which consists from metal oxides of Fe, Al, Ti, Si, K, Na, V, Ga, according to the chemical composition of the initial bauxite ore. Although red mud is classified by EC as a non hazardous waste [[9]], its small particle size (dust-like), high alkalinity and large amounts (approximately 1 kg of red mud is produced for each kg of Alumina [[10],[6]]) 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) [[4],[5],[11]].

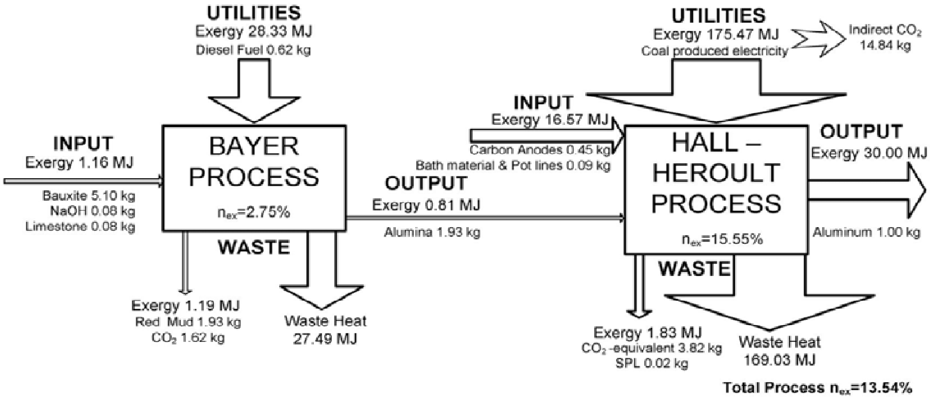

Fig. 2 Exergy analysis of the current industrial process for primary aluminium production, with coal based electricity (all input and output flows are calculated at 25^{o}C and atmospheric pressure)

As shown in Fig. 2, where the exergy analysis of the primary aluminium production is presented, although the Bayer process is highly optimized in terms of energy consumption, it is still characterized by a very low exergy efficiency (n_{ex} = 2.75%), as it consumes significant amounts of petrol fuel for process heat without producing significant increases in the exergy of the material output (sum of chemical exergy of products and wastes). Additionally, the alumina produced embodies approximately 40% of the total chemical exergy output of the Bayer process, as a significant portion of the process chemical exergy is embodied in the red mud waste. One kg of dry red mud carries approximately 0.23MJ of chemical exergy, a quantity similar to that of an average bauxite ore (0.20MJ/kg). This relatively high exergy embodied in the red mud is mainly due to its high content of Fe_2O_3 (43% per weight), which could characterize red mud as an industrial feedstock rather than an industrial waste. To this end, many attempts have been made to produce pig iron from red mud, but so far no economically viable solution has been found. The extremely fine particles of red mud require agglomeration prior to feeding in conventional reactors; their high alkaline nature is unsuitable for blast furnace reductive smelting and the low, when compared to iron ores, content in iron oxides makes the production of pig iron a cost ineffective process [[12],[13]]. Valuable metals like Ti, Ga and V contained in the red mud can be extracted [[14],[15]], but again with no economical benefits [[12]]. Other proposed uses for red mud include the production of construction or ceramic materials [[4]], as well as utilizing red mud in waste waters or polluted soils treatments [[4],[16],[17]]. Till this day, due mainly to high costs and low yields, no industrial application of red mud reuse is in effect.

II. The Hall-Héroult process.

In the Hall-Héroult process, aluminium is produced by the electrolytic reduction of high grade alumina, which is dissolved in a molten bath consisting mainly of cryolite (Na_3AlF_6), at a temperature of about 960°C. Consumable carbon anodes (0.45 kg for each kg of Al [[7]]) and a potential of 4.6 V [[7]] are employed in the electrolytic cell to produce molten aluminium, which is periodically withdrawn from the cathodes by vacuum siphon. The electrolytic cells used in the process need to be periodically replaced, producing a carbon based solid waste (0.02 kg/kg Al) known as Spent Pot Lining (SPLs), which is classified as a hazardous waste [[9]], due to its chemical content (12 % F^- and 0.15 % CN^-).

Based on the data given in Figures 1 and 2, it can be concluded that the Hall-Héroult process is very energy and CO_2 intensive. Approximately 56 MJ of electrical energy are consumed directly in the electrolytic reduction of alumina for each kg of aluminium produced, assuming hydroelectric energy utilization that constitutes the best practise according to the relevant Best Available Technique (BAT) [[6]]. Additionally, another 5.20 MJ/kg Al are spent on carbon anode baking and SPL replacement. In the same production process, 3.82 kg of CO_2 equivalent GHG [[7]] are directly released for each kg of aluminium produced; 1.65 kg of CO_2 are released from anode consumption and approximately 2.20 kg of CO_2 equivalent [[7]] of hazardous perfluorocarbons [[9]], CF_4 and C_2F_6, are resulted from the process upset known as anode effect. Both CF_4 and C_2F_6 are powerful climate gases with 100 years Global Warming Potential (GWP) of 6500 and 9200, respectively.

In the worst case scenario, assuming coal-based electricity generation which is the case used by most primary aluminium plants worldwide, approximately 170 MJ [[7],[8]] of energy are consumed for the electrolytic reduction and an additional 14.84 kg of CO_2 are indirectly released though coal burning for each kg of aluminium produced in this way. The Hall-Héroult process is therefore - by design - the most energy intensive stage in the primary production of aluminium, consuming up to 191 MJ/kg Al, while its total (direct and indirect) CO_2 and CO_2 equivalent emissions are up to 18.66 kg per kg of Al produced. The exergy efficiency of the Hall-Héroult process is low (Fig. 2, n_{ex} = 15.5%), given that large sums of high-exergy content electricity are lost in cells overpotentials as non-recoverable waste heat.

Alumina point-feeders, minimization of the anode-cathode distance and advance process control are some of the key technological advancements that have been used to reduce energy consumption of the Hall-Héroult process [[7],[18]]. Research today is focused on designing cells with inert anodes and wetted cathodes, which could theoretically reduce energy consumption and avoid PFC emissions. However, the Hall-Héroult process will always suffer from its basic volumetric inefficiency, since the reduction takes places practically in a two dimensional plane between the electrodes and thus, results in significant thermal losses.

ENEXAL: Novel technologies for a new primary aluminium industry

The analysis presented here clearly indicates that the primary aluminium industry operates with great energy and CO_2 intensity and low exergy efficiency. The energy cost in primary aluminium production accounts for approximately 30% of the total production cost and it is connected mainly with the electricity demand in the Hall-Héroult process. When this electricity is produced from fossil fuel burning (as is the case in Europe) the resource cost (exergy consumption) is tripled and CO_2 emissions quadruple, while exergy efficiency is halved. When this industry is compared to the primary production process of four other basic metals, namely Fe, Cu, Zn and Pb, aluminium production is related to the largest non-embodied exergy losses per unit output [[10]]. Of the total utilities exergy inputs in electricity and fuel, only 14% is embedded in products or wastes; the rest 86% is discarded as waste heat. Bearing in mind that both, Bayer and Hall-Héroult, have been continuously optimized for more than a century, it is logical to conclude that significant energy and exergy improvements cannot be achieved through further optimizations of these technologies. Therefore radical changes in the primary aluminium production industry are needed, in order to achieve major breakthroughs in the energy and exergy efficiency of the industry. Such changes should focus on reducing energy consumption in the alumina reduction and improving exergy efficiency in the Bayer process by utilizing the red mud waste.

Towards this direction and under EC’s FP7 Cooperation ENERGY.2009.8.1.1 Work programme, a consortium of European Universities, Research Institutes and Industrial Partners has been formed to provide the primary aluminium industry with “green” innovative technological and economical solutions, for the significant improvement of energy and exergy efficiencies of its production process, the substantial reduction of its GHG emissions, the complete elimination of its solid wastes and the increase of its economical competitiveness. The project ENEXAL (Novel technologies for enhanced energy and exergy efficiencies in primary aluminium production industry) will demonstrate novel technologies for the reduction of alumina and the utilization of red mud that will play a key role for the sustainability, competitiveness and viability of primary aluminium production industry, so as to render it a leader industry for energy-efficient technologies and products in Europe and worldwide. A pilot-scale demonstration of the proposed technologies in actual industrial conditions (long term continuous demonstrations in the Aluminum S.A. plant located in Greece) will ensure feasibility for the immediate industrial application of the proposed novel technologies.

The technological innovations that will be demonstrated in the course of the ENEXAL project are presented in the following paragraphs.

A. High temperature carbothermic reduction of alumina

The only alternative to the electrolytic reduction of alumina is its direct chemical reduction. From the reducing agents considered suitable for industrial production like C, CO, CH_4, H_2, Si only carbon has the thermodynamic capacity to reduce alumina, as aluminium is one of the most reactive metals and one of the most efficient reducing agent itself. Thus, the basic alternative to the Hall-Héroult process is the carbothermic reduction of alumina, that has been proposed by various researchers in the last 50 years [[8],[7]]. This process is theoretically described by the following chemical reaction occurring at temperatures higher than 1900 °C :

$$Al_2O_3 + 3C = 2Al + 3CO \qquad (1)$$

The industrial application of this process has not yet been achieved, as the occurrence of side-reactions, resulting in the formation of undesired products, such as the aluminium carbide Al_4C_3 and the Al-oxycarbides Al_2OC and Al_4O_4C, as well as of aluminium and aluminium sub-oxide Al_2O vapours [[8],[19]], which substantially reduce the aluminium yield as seen in Fig. 3.

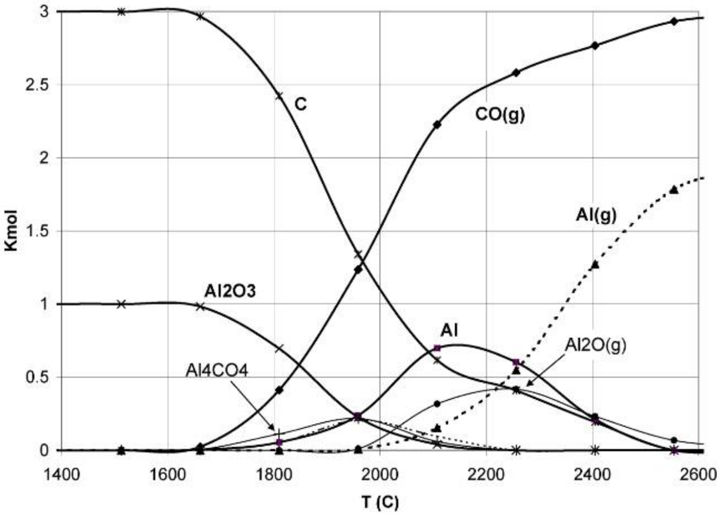

Fig. 3. Equilibrium composition in the Al_2O_3/C system as a function of temperature (using the HSC Chemistry 6.12 software)

Aluminium yields as high as 67 % have been obtained by staging the reactions to produce aluminium carbides at 1930–2030°C and then in a second step reducing the carbides with alumina to produce aluminium and carbon monoxide at 2030–2130 °C [[20],[7]]. Scientific research is focused on increasing this yield through either, alternative chemical routes or the development of specific reactors with better thermal efficiency and advance vapour management [[7],[19],[20],[21]].

Recent studies [[22]], prove that thermodynamically it is possible to reduce alumina to aluminium with carbon, achieving high yields without the formation of carbides, if high enough temperatures (>2400°C) are applied. At these temperatures however, the problem of aluminium vaporization becomes significant resulting in large amounts of aluminium vapours in off-gases, as seen in Fig. 3.

In order to suppress the aluminum vaporization, the use of carbon in excess is proposed, thereby suppressing vaporization, due the reduction of the produced Al_2O oxide. In this way the process can become very efficient at substantially lower temperatures (93% Al yield at 2100°C), as is seen in Fig. 4. Preliminary laboratory tests support this theory and indicate that the process is suitable for industrial scale production.

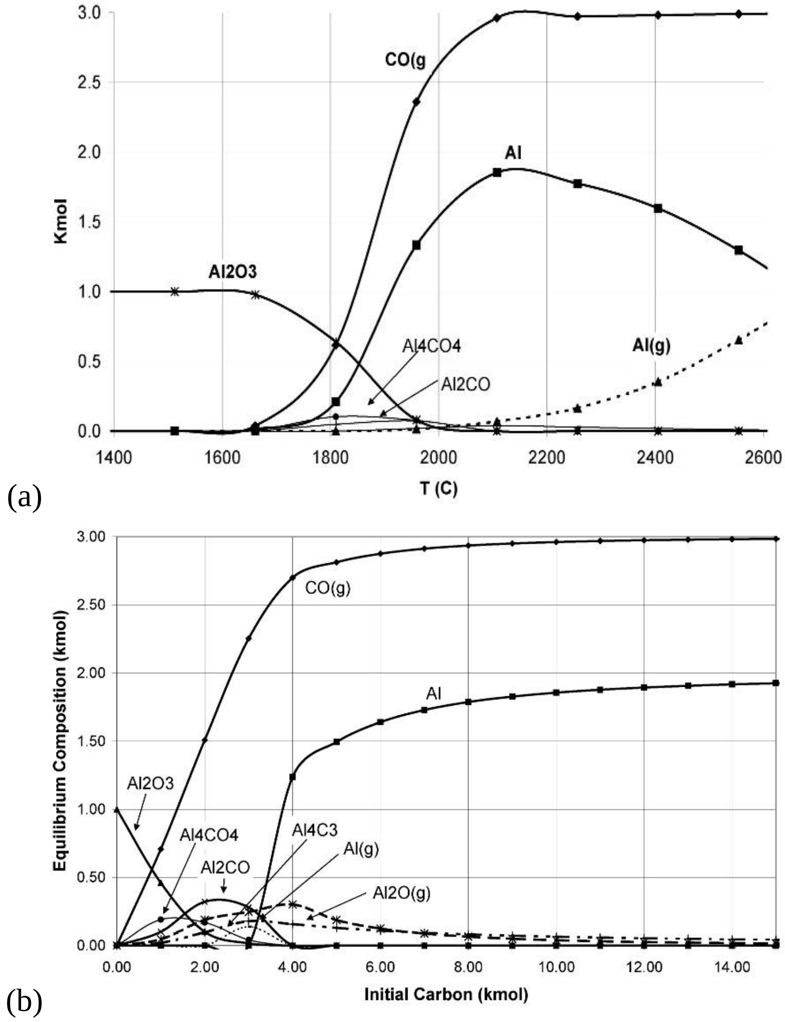

Fig. 4 Equilibrium composition in the Al_2O_3/C system (a) as a function of temperature with initial composition 1 kmol of Al_2O_3 and 10 kmol C and (b) as a function of initial C amount at 2100 ^{0}C (using the HSC Chemistry 6.12 software)

To produce the process heat needed to achieve this high temperature at a rate that will hinder back and side reactions, an electric arc furnace (EAF) or a plasma reactor must be used. An EAF is preferred, as arc technology is mature and has been successfully applied to various metallurgical processes. The proposed technology will be a slag free process taking place in an EAF reactor operating in open bath mode, with a potential for direct application in the industrial production of primary aluminium.

Additionally, the reduction of alumina in the EAF will take place in a three dimensional reaction space instead of the practically two dimensional space between the anodes and the cathodes in the Hall-Héroult process. This will lead to a significant increase of volumetric efficiency [[7]] and an overall reduction to the industrial space needed.

The toxic carbon monoxide evolved, as required by Equation (1), obviously must not be released to the atmosphere. Rather, it is a valuable resource, as it embodies significant chemical exergy which along with its heat content (2100^{o}C) can be retrieved in effective heat exchanges within the industry. Below 800^{o}C and in the presence of oxygen the monoxide is oxidized in an exothermic reaction, delivering the CO_2 which will be the final off-gas of the process.

The diagram of energy and mass balances and the exergy analysis of the proposed technology are shown in Figures 5 and 6. In Table 1, the carbothermic reduction of alumina in an EAF powered with electricity from a hydroelectric plant (scenario A) or from a coal burning plant (scenario B) is compared with the correspondingly powered Hall-Héroult process. The new process requires, in both scenarios, less energy and has higher exergy efficiency, as high-exergy content electricity is no longer used to electrolytic reduce alumina. Instead, low-exergy content carbon is used to directly reduce alumina resulting in a more efficient energy and resource utilization (exergy efficiency). The GHG emissions are also reduced, as in both scenarios PFCs are no longer produced and in scenario B the reduction in electrical power needed leads also to less indirect CO_2 emissions. Finally the new process avoids completely the generation of SPL solid wastes.

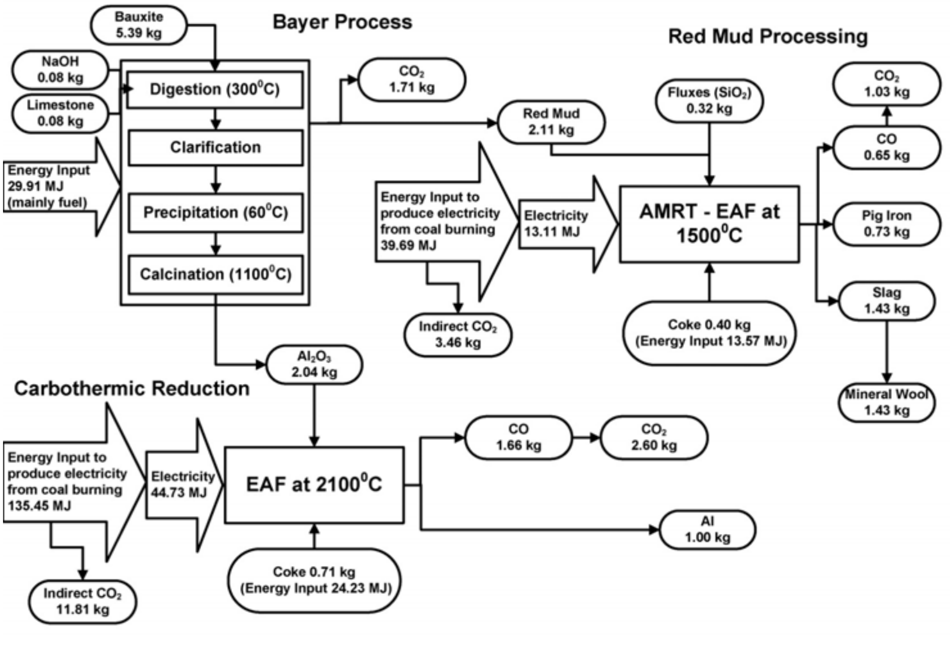

Fig. 5 Mass & energy balances of the proposed carbothermic alumina reduction and red mud treatment co-production scheme

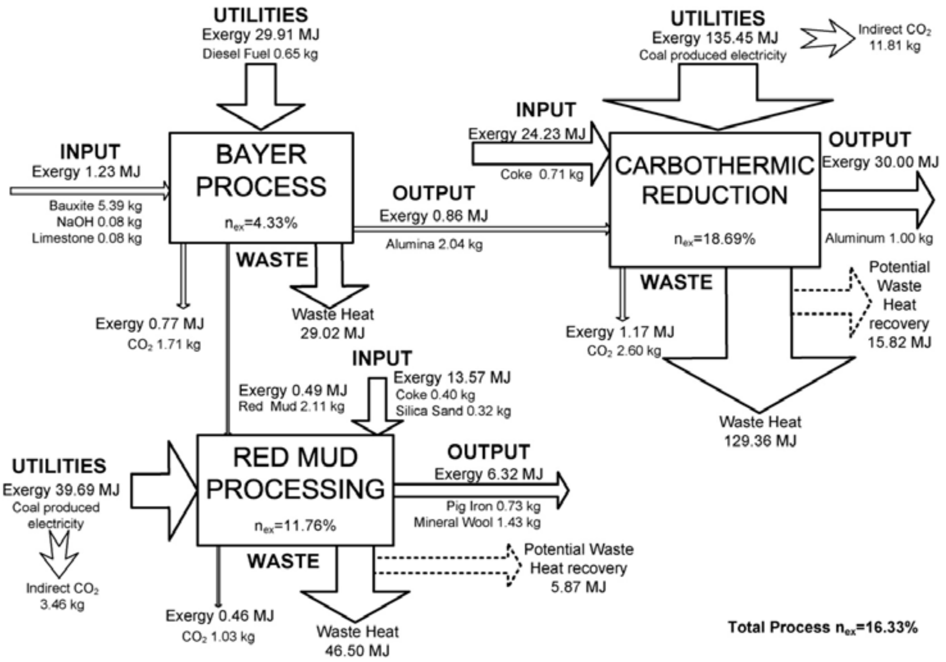

Fig. 6 Exergy analysis of the proposed carbothermic alumina reduction and red mud treatment co-production scheme, powered with coal produced electricity (all are calculated at 25°C and atmospheric pressure).

Table 1: Comparison between the carbothermic reduction at high temperature (A and B) or at moderate temperature (C) and the Hall-Héroult process with different power sources

Energy Source for alumina reduction	Energy Savings	Reduction in GHG Emissions	Exergy Efficiency Percentage Point Increase
A. Electricity from Hydroelectric dams	10%	32%	5
B. Electricity from Coal Burning	16%	23%	3
C. Concentrated Solar Power (compared to hydroelectric powered Hall-Héroult process)	68%	32%	82

Under the ENEXAL project the EAF carbothermic reduction will be optimized and demonstrated in actual industrial conditions.

To further improve the sustainability of the primary aluminium production the carbothermic reduction of alumina in a prototype solar furnace will also be researched under the ENEXAL project. Utilizing concentrated solar power, the heat required for the carbothermic reduction can be provided directly from the sun [[22],[23]] thus eliminating electricity consumption and the associated GHG emissions. Additionally if wood charcoal (a carbon neutral source) is used as the reducing agent then the reduction of alumina will become a truly sustainable industrial process. As expected and seen on Table 1, when the carbothermic reduction in a solar furnace is compared to the best scenario (scenario A) of the Hall-Héroult electrolytic process it can achieve up to 68% energy savings, up to 65% reduction of GHG emissions and 81% increase in exergy efficiency.

B. Red mud treatment

In order to improve significantly the exergy efficiency of the Bayer process and reduce substantially its environmental footprint, an innovative technology for the transformation of red mud into valuable products, is needed. The proposed treatment utilizes a novel Electric Arc Furnace (EAF) technology in order to achieve the reductive smelting of red mud without any pre-treatment, producing pig iron and viscous slag suitable for mineral wool production (see Figures 5 and 6).

This novel EAF is the Advanced Mineral Recovery Technology (AMRT) melt reduction furnace, which has the capability of processing finely sized materials, notably below 1 mm in particle size (dust like), without any dusty material loss in the off-gas stream. An innovative feeder technology can deliver the dusty raw materials directly into the “arc zones” of each of its three electrodes, where flash smelting takes place. This feeder is below the off-gas suction tube thereby preventing loss of material, and it feeds the reactor with small batches at appropriate time intervals in order to allow enough time for ventilation of the off-gases produced from the previous batch (Figure 7). Additionally, a patented digitally-based PLC control system can minimize electrical energy losses by continuous measurement of bath impedance and power supply regulation [[24]]. Therefore this innovative EAF technology is ideal for processing the dust-like red mud (mean particle size less than 500nm) without any pre-treatmentand or substantial energy losses, thus providing the proposed process with a significant industrial advantage.

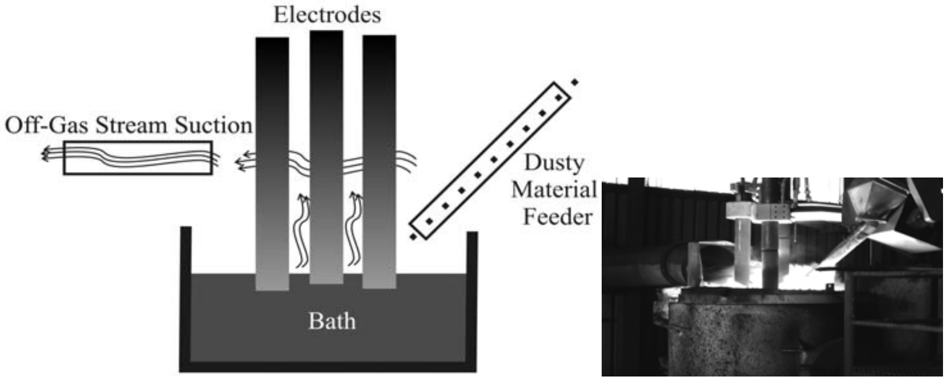

Fig. 7 Schematic diagram and photograph of the innovative AMRT-EAF melt reduction furnace in operation

Preliminary experiments have already proved that the reductive smelting of red mud at 1500 ^{o}C in an AMRT-EAF, using carbon as reducing agent and appropriate fluxes to regulate the composition of the generated slag, can produce pig iron (0.34 kg/kg red mud) and a viscous slag (0.68 kg/kg red mud) that can be converted into glassy fibres suitable for mineral wool production.

The diagram of energy and mass balances and the exergy analysis of the proposed technology are shown in Figures 5 and 6. The technology proposed for the treatment of red mud is characterized by high exergy efficiency (23% in scenario A of hydroelectric electrical energy or 12% in scenario B of coal produced electrical energy) and produces no solid wastes.

In total the new proposed process for the complete bauxite exploitation (for alumina, pig iron and mineral wool production) will increase the exergy efficiency from 3% in the conventional Bayer Process to 13% in scenario A, or to 9% in scenario B, as the solid waste of the Bayer Process (red mud) with chemical exergy of 0.49MJ/kgAl is replaced by pig iron and mineral wool products, with total chemical exergy 6.32MJ/kgAl. From an economic perspective a solid waste with costly disposal, is replaced by two valuable by-product thereby significantly increasing the profit margin of the industry.

Under the ENEXAL project the AMRT- EAF red mud treatment will be investigated and demonstrated in actual industrial conditions.

C. The new, energy and exergy efficient, production scheme of the primary aluminium industry.

ENEXAL proposes the radical transformation of the primary aluminium production industry to a more energy efficient, economically viable and ecologically sustainable industry. The topography of a primary aluminium production plant will change drastically, as the lengthy Hall-Héroult smelters and the red mud disposal sites will be replaced by new vertical reactors for the carbothermic reduction of alumina and the treatment of red mud. Space optimization in the plant will be crucial in order to facilitate the new products (pig-iron and mineral wool) flows.

Energy optimization of the new plant will also be required. Both new reactors operate at elevated temperatures and produce hot CO off-gases thus, from an exergetic point of view there are significant potentials for waste heat and chemical energy retrieval, as seen in Fig. 6. Approximately 22 MJ/kg of produced Al can be saved only from retrieving the heat content of these off-gases (assuming 75% efficiency in the heat exchange), and using it in the Bayer process to substitute fossil fuel consumption and thus, further mitigate CO_2 emissions by 1.5 kg CO_2/kg of produced Al.

By implementing the new technologies proposed along with the above mentioned energy optimization in the current industrial practice, a new production schema for a sustainable primary aluminium industry will be developed. The sustainability of this new production schema, in terms of energy saving, reduction of GHG emissions and exergy efficiency, is presented in Table 2, for three different energy source scenarios. As the new practice involves the production of two new products, the energy and GHG emissions involved in producing equal amounts of pig iron from iron ore in a standard blast furnace and mineral wool from basaltic ores in a standard cupola furnace, have been added to the energy consumption and GHG emissions of the existing primary aluminium production industry. Pig iron production in blast furnace consumes in total approximately 34.81 MJ and emits 2.88 kg CO_2 (directly and indirectly) for every kg of pig iron [[11]], while glassy fibres production, in a cupola furnace consumes in total approximately 14.65 MJ and emits 1.28 kg CO_2 for every kg of glassy fibres produced [[25],[26]] (assuming coal produced electricity in both cases).

Table 2 Comparison between the new and the existing production schema for the primary aluminium industry (including pig iron and mineral wool production)

Energy Source	Energy Savings	Reduction in GHG Emissions	Exergy Efficiency Percentage Point Increase	Total Exergy Efficiency of the new production process
A. Electricity from Hydroelectric dams	22%	44%	8	35%
B. Electricity from Coal Burning	17%	21%	3	16%
C. Concentrated Solar Power for carbothermic reduction and hydroelectric power for the red mud treatment and the Hall-Héroult process	55%	43%	33	59%

A detailed optimization of space, energy and exergy usage is expected to further improve the percentages presented in Table 2 and ensure that the energy and the CO_2 intensity of the new industrial production schema proposed, will be kept at their minimums.

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