EXERGETIC ANALYSIS OF THE ENEXAL BAUXITE RESIDUE TREATMENT ON THE OVERALL RESOURCE EFFICIENCY OF THE PRIMARY ALUMINA REFINING PROCESS

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Abstract

In the framework of the ENEXAL FP7 project, a novel process for treating bauxite residues has been developed and demonstrated in industrial scale. The novel process developed, fully converts the bauxite residues in to marketable products such as pig iron and mineral wool fibers. In this work a detailed exergy analysis of the new process is presented and coupled with the flow-sheet of the primary alumina refining process (Bayer), in order to deduce its effect on the overall resource efficiency and exergy utilization. A methodology for evaluating the chemical exergy of mineral phases and solid solutions is also discussed.

Keywords: Exergy Analysis; Red Mud; Bauxite residues; Alumina refinery; Bayer process

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. 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. A mass and energy flow sheet of both processes is presented in figure 1, based on the operations of the vertical refiner - smelter plant of ALOUMINION S.A. in Greece (ALSA).

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 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 (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.

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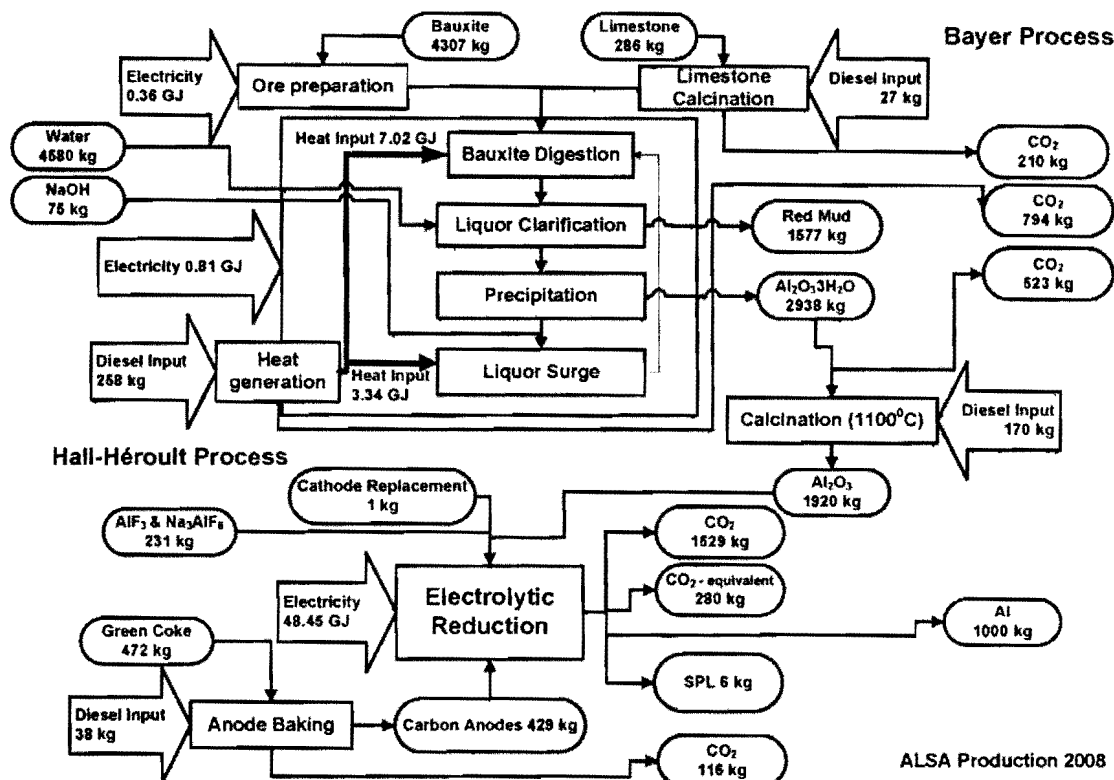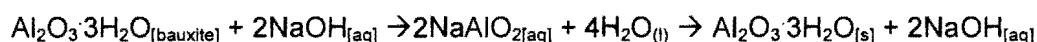

Fig. 1: *The mass and energy flow sheet of ALOUMINION S.A. plant*

In the framework of the EC funded ENEXAL project [1] a novel process for the treatment of the bauxite residues and its transformation into valuable products has been developed and demonstrated in industrial scale at ALSA. In this work the exergy analysis of the novel process is presented and compared with the established industrial practice.

2. The Bayer Process

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:

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

A detailed energy and exergy analysis of the process has been presented by the authors in [2] based on an average industrial flow sheet. As discussed, the Bayer process in total is characterized by very low exergy efficiency as large amounts of exergy are spent solely to achieve the chemical separation of alumina from the bauxite "solid- solution". Based on the data given in Fig 1, the mass and exergy analysis of the plant is given in table 1 and Fig 2 (details on the chemical exergy calculations of the species are presented in the appendix).
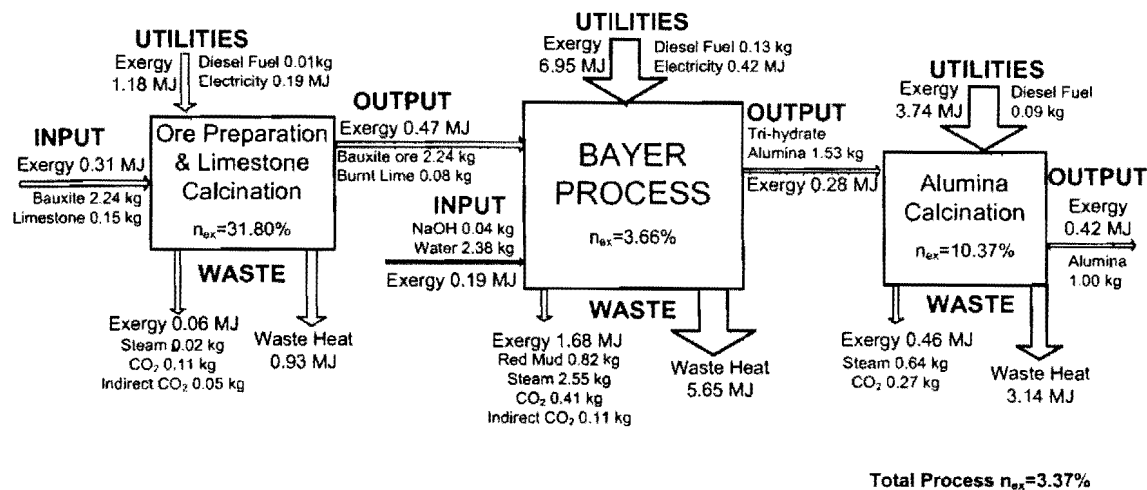
Fig. 2: *The exergy analysis of the ALSA alumina refinery*

Table 1: Alumina Refinery Plant (exergy of all species calculated at 25°C, 1 atm)

		Mass	**Exergy**
INPUT	Diaspore ore	1.644 kg	0.205 MJ
	Tropic ore	0.600 kg	0.073 MJ
	Limestone	0.149 kg	0.029 MJ
	Caustic Soda (NaOH)	0.039 kg	0.076 MJ
	Water (H_2O)	2.385 kg	0.112 MJ
	TOTAL INPUT	**4.817 kg**	**0.494 MJ**
UTILITIES	Electricity		0.613 MJ
	Coal based electricity	0.056 kg	1.856 MJ
	Heat demand		5.400 MJ
	Diesel (Heat production)	0.237 kg	10.010 MJ
	TOTAL UTILITIES	**0.293 kg**	**11.866 MJ**
PRODUCT	Alumina	1.000 kg	0.417 MJ
	TOTAL PRODUCT	**1.000 kg**	**0.417 MJ**
WASTE	Bauxite Residues	0.821 kg	0.160 MJ
	CO_2 from process	0.066 kg	0.030 MJ
	H_2O from process	2.916 kg	1.521 MJ
	CO_2 from Diesel	0.729 kg	0.328 MJ
	H_2O from Diesel	0.291 kg	0.152 MJ
	CO_2 from Electricity	0.162 kg	0.073 MJ
	TOTAL WASTE	**4.984 kg**	**2.263 MJ**
WASTE HEAT (EXERGY LOSSES)			**9.680 MJ**
Exergy Efficiency of process (without electricity production)		3.75%	
Exergy Efficiency of process (coal based electricity production)		3.37%	
Total CO_2 emissions (direct and indirect)		0.96 kg	

Electricity used in the process is considered to be produced through coal burning and is evaluated in the process as the worst case scenario (including indirect CO_2 emissions). The overall efficiency of the alumina refining plant in ALSA is 3.37% and in terms of chemical exergy, the bauxite residue embodies 58% of the total chemical exergy of the initial bauxite ore and is therefore clear that these residues should be treated as a resource rather than as a waste.

3. The novel bauxite residue treatment

The novel bauxite residue treatment comprises of four stages as shown schematically in Figure 3. The first stage is the residue drying stage, as even red mud dewatered in filter presses (current Best Available Technology for bauxite residue handling) contains significant amounts of moisture (up 25% w/w). This stage can take place in a double skin rotary kiln, utilising 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 fed 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 fiberised to produce inorganic fibers and mineral wool products.
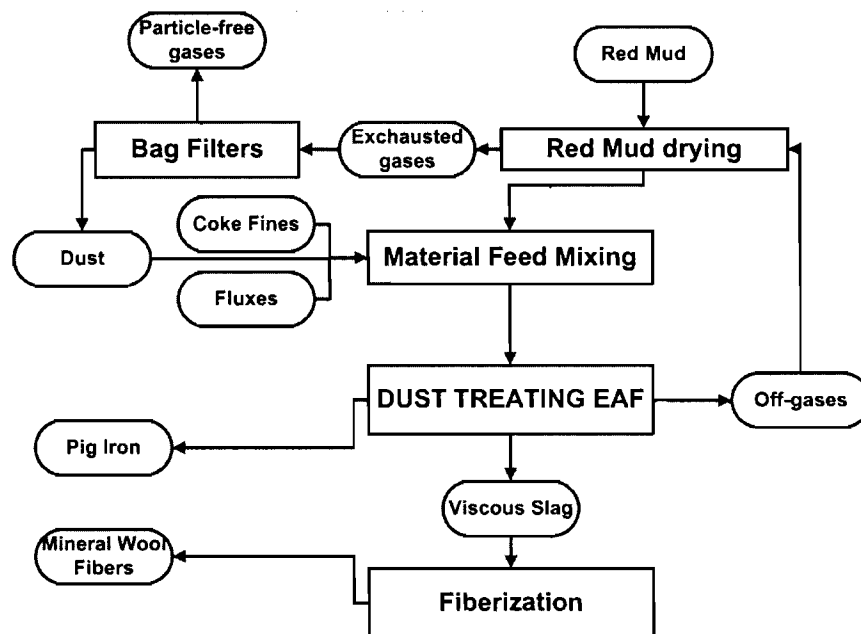

Fig. 3: *The envisioned process*

In the framework of the ENEXAL project, a 1MW Dust treating EAF was set up in the ALSA plant and treated in batch mode 1 ton of dried bauxite residues along with 200 kg of coke

fines, 180 kg of silica sand and 150 kg burnt lime The furnace operated at 1600°C, and produced 230 kg of pig iron and 784 kg of glassy slag. On average the power consumption of the pilot plant was 2000 kWh per ton of bauxite residue treated (including energy consumption for plant utilities such as cooling water circulation and off-gasses suction pumps); the chemical analysis of the products is presented in Table 2. Additionally Table 2 presents empirical chemical composition indexes used in the mineral wool production industry to evaluate the "fiberise-ability" of a melt [3]. As seen from these indexes the produced melt is within most of the empirical limits.[9]

Table 2: Experimental Results

Pig iron %wt	Fe	C	S	P	Si	Ti	V	Cr
	95.47	3.36	0.26	0.08	0.03	0.00	0.18	0.82

Pig iron phase weight		230 kg		Fe recovery in pig iron			70%

Slag %wt	Al_2O_3	SiO_2	CaO	TiO_2	MgO	Fe_2O_3	Na_2O	V_2O_5
	20.90	27.60	31.19	5.63	8.89	5.01	2.45	0.20

Slag phase weight		784 kg		Slag Basicity Ratio			1.24

Empirical indexes	A [<1.8]	P [<15]	k2 [0.8-1]	SHG [1.3 - 1.4]	KNB [30-40]	N [<5%]	F [>5%]	
	1.58	9.34	1.06	1.07	36.64	2.45	5.01	

Empirical Indexes (oxides in wt%) A = $(SiO_2 +Al_2O_3 + TiO_2)/(CaO+MgO)$; N = $4.9/[(MgO+CaO+Fe_2O_3 +Na_2O + TiO_2)/(SiO_2 +Al_2O_3)]$ -0.45; k2 = $[100 - (SiO_2 +Al_2O_3)]/(SiO_2 +Al_2O_3)$; SHG = $(SiO_2 +Al_2O_3)/(1.4 MgO+ 0.4 Fe_2O_3 + CaO + TiO_2$; KNB = $Na_2O + MgO + CaO$; N = Na_2O; F = Fe_2O_3.

Based on the chemical analysis of the feed and the thermodynamic model of the process the off-gases of the process at 25°C (at thermodynamic equilibrium with the atmosphere) are 689 kg of CO_2 and 151kg of H_2O. Table 3 presents the mass and exergy analysis of the new process, based on the above data.

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[9] The actual fiberization of the slag is not examined here, due to lack of experimental data. Yet this has little effect on the conclusions of the study as the process for melt fiberization is hardly energy or resource intensive.

Table 3: Bauxite Residue treatment (exergy of all species calculated at 25°C, 1 atm)

		Mass	Exergy
INPUT	Bauxite Residues	1.000 kg	0.194 MJ
	Coke fines	0.200 kg	6.640 MJ
	Silica Sand	0.180 kg	0.004 MJ
	Burnt lime	0.150 kg	0.348 MJ
	TOTAL INPUT	**1.530 kg**	**7.187 MJ**
UTILITIES	Electricity		7.200 MJ
	Coal based electricity	0.655 kg	21.800 MJ
	TOTAL UTILITIES	**0.655 kg**	**21.800 MJ**
PRODUCT	Pig iron	0.230 kg	1.556 MJ
	Mineral wool	0.784 kg	3.033 MJ
	TOTAL PRODUCT	**1.014 kg**	**4.589 MJ**
WASTE	CO_2 from process	0.689 kg	0.310 MJ
	H_2O from process	0.151 kg	0.079 MJ
	CO_2 from Electricity	1.90 kg	0.855 MJ
	TOTAL WASTE	**2.741 kg**	**1.244 MJ**
WASTE HEAT (EXERGY LOSSES)			**23.153 MJ**
Exergy Efficiency of process (without electricity production)			**31.90%**
Exergy Efficiency of process (coal based electricity production)			**15.83%**
Total CO_2 emissions (direct and indirect)			**2.59 kg**

4. The Novel alumina refinery

The integration of the bauxite residue treatment in the alumina refinery would produce a new plant with complete bauxite ore exploitation and zero solid/liquid wastes. The mass exergy analysis of the new plant is presented in table 4 and Fig 4. Burnt lime (CaO) used in the process is consider to be produced from limestone burning within the plant.
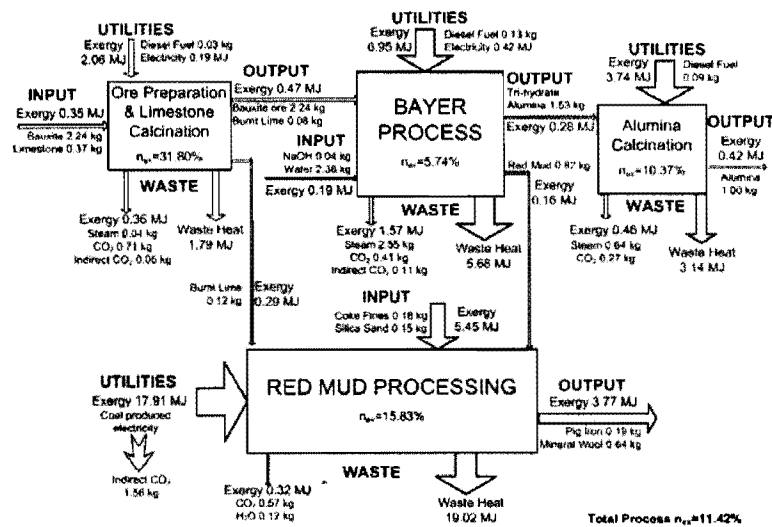

Fig. 4: *The exergy analysis of the new alumina refinery*

Table 4: New Alumina Plant (exergy of all species calculated at 25°C, 1 atm)

		Mass	Exergy
INPUT	Diaspore ore	1.644 kg	0.205 MJ
	Tropic ore	0.600 kg	0.073 MJ
	Limestone	0.369 kg	0.073 MJ
	Caustic Soda (NaOH)	0.039 kg	0.076 MJ
	Water (H_2O)	2.385 kg	0.112 MJ
	Coke fines	0.164 kg	5.454 MJ
	Silica Sand	0.148 kg	0.003 MJ
	TOTAL INPUT	**5.349 kg**	**5.995 MJ**
UTILITIES	Electricity		6.528 MJ
	Coal based electricity	0.594 kg	19.764 MJ
	Heat demand		0.000 MJ
	Diesel	0.258 kg	10.901 MJ
	TOTAL UTILITIES	**0.852 kg**	**30.665 MJ**
PRODUCT	Alumina	1.000 kg	0.417 MJ
	Pig iron	0.189 kg	1.278 MJ
	Mineral wool	0.644 kg	2.492 MJ
	TOTAL PRODUCT	**1.833 kg**	**4.187 MJ**
WASTE	CO_2 from process	1.229 kg	0.553 MJ
	H_2O from process	3.039 kg	1.586 MJ
	CO_2 from Diesel	0.729 kg	0.328 MJ
	H_2O from Diesel	0.317 kg	0.166 MJ
	CO_2 from Electricity	1.723 kg	0.775 MJ
	TOTAL WASTE	**7.037 kg**	**3.408 MJ**
WASTE HEAT (EXERGY LOSSES)			**29.065 MJ**
Exergy Efficiency of process (without electricity production)		17.87%	
Exergy Efficiency of process (coal based electricity production)		11.42%	
Total CO_2 emissions (direct and indirect)		3.68 kg	

5. Conclusions

This work presented a detailed mass and exergy analysis of an actual alumina refinery along with results from industrial demonstrations of a novel process to treat bauxite residues. When this novel process is intergrated in the alumina refinery plant the overall increase in the exergy efficiency of the alumina refinery plant is greater than 8 percentile points, marking a significant improvement in the resource efficiency of the plant, as the bauxite ore is exploited in full and three marketable products are produced instead of one.

Acknowledgements

APPENDIX – Chemical Exergy of complex metallurgical products

In general the chemical exergy (e_x) of matter defines the maximum work obtainable by the chemical interaction (reaction) of matter with its environment.

In cases of fuel, chemical exergy is measured by the heating value of the fuel [4]. For diesel used in this study the HHV was 42.20 MJ/kg; its emissions were 2.96 kg CO_2 and 1.23 kg H_2O per kg of diesel burned. To produce 1MJ of electrical exergy through coal burning, 3.03 MJ of coal exergy was assumed to be consumed (the higher heating value, HHV, of coal used was 34.1 MJ/kg of coal [5]).

For matter that is not fuel, the standard chemical exergy $\left(e_x^0\right)$ can be calculated from its theoretical reaction of formation at the environmental standard state (T_0, P_0)

$$aA + xX + yY \rightleftharpoons A_a X_x Y_y \tag{I-1}$$

according to the relationship

$$e_{x, A_a X_x Y_y}^0 = \Delta G_{f, A_a X_x Y_y}^0 \left(T_0\right) + \sum_i v_i e_i^0 \tag{I-2}$$

where $\Delta G_{f, A_a X_x Y_y}^0 \left(T_0\right)$ is chemical free energy of formation of the substance, v_i is the stoichiometric coefficient and e_i^0 is the standard chemical energies of element i. The standard chemical exergy of elements is related to reference substances found more commonly in the environment and are given in literature ([4], [6], [7]). In the present study the standard chemical exergy values of De Meester [7] were used.

The chemical exergy of solution containing n chemical species at the environmental state (T_0, P_0) is

$$e_x = \sum_i n_i e_{x,i} = \sum_i n_i e_{x,i}^0 + RT_0 \sum_i n_i \ln \gamma_i x_i \tag{I-3}$$

Equation (I-3) can be applied with approximation for solid solutions where all mineral phases can be considered in thermodynamic equilibrium and the activity coefficient of all species is considered to be unitary. However in more complex phases resulting from metallurgical processing the above calculation is not as easily performed. Phases formed under non-equilibrium conditions or phases with complicated mineralogical compositions, for which thermodynamic data may not be available, represent a problem for the metallurgical exergy process analysis.

In this study the use of thermodynamic calculation software is proposed. To define the mineralogical phases of bauxite residues, the equilibrium module of FACTSAGE was used, in order to conclude the most probable distribution of the elements in various chemical/mineralogical species. In this way the red mud with the chemical analysis shown in table I1, was reduced to a list of mineralogical species with known thermodynamic data. Through use of equation (I-3) the chemical exergy of red mud was then calculated at 0.19 MJ/kg.

Table I1: Red Mud predicted mineralogical species

Chemical analysis	%wt	Mineralogical Species	%wt
Al_2O_3	16.22%	Fe_2O_3 hematite	47.74%
Fe_2O_3	47.74%	$Al_2O_3*3H_2O$ gibbsite	17.83%
SiO_2	6.09%	$CaTiO_3$ perovskite-a	10.10%
TiO_2	5.93%	$NaAlSiO_4$ nepheline	9.36%
Na_2O	2.51%	$Ca_3Al_2Si_3O_{12}$ grossularite	5.31%
V_2O_5	0.21%	$CaCO_3$ aragonite	3.70%
CaO	8.39%	$Ca(OH)_2$	3.27%
$CaSO_4$	1.02%	$Na_2SO_4(H_2O)_{10}$	2.18%
$CaCO_3$	3.70%	$(CaO)_3(V_2O_5)$	0.40%
H2O(cry)	8.19%	Na_2SO_4	0.10%
TOTAL	**100%**	**TOTAL**	**100%**

Taking this approach one step further, the slag produced from the red mud smelting process, which due to rapid cooling, is an amorphous (glassy) solution of Al, Si, Ca, Ti and other oxides, was modeled using FACTSAGE's "FT-oxid SLAG" liquid solution phase. The later represents an oxidic solution model capable of predicting the thermodynamic properties of slag melts. Based on the slag chemical analysis presented in table 2, FACTSAGE's excess Gibbs energy prediction for this phase extrapolated at 25°C was used directly as the excess mixing term in (I-3), thus allowing the calculation of the chemical exergy of the glassy slag at 3.87 MJ/kg. This higher value compared to red mud, is justified as the slag represents a "frozen" non-equilibrium phase with highly "reactive" components like CaO (2.32 MJ/kg) and Na_2O (4.82 MJ/kg).

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