A Novel Red Mud Treatment Process : Process design and preliminary results

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Abstract

A novel energy and exergy efficient 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. Economically, besides solving the red mud disposal problem, the single step co-production of two highly valuable by-products (pig iron and mineral wool) has the potential to significantly increase the versatility and profit margin of the alumina producing industry. In this paper a thermodynamic model of the process is developed and verified both by small scale lab experiments as well as exploratory EAF test results.

Keywords : Red Mud treatment; Bauxite Residue Reuse

1. Introduction

Today primary aluminium 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 aluminium, which is performed according to the Hall-Héroult process. The Bayer process [1], patented in 1888 by Karl Joseph Bayer, is essentially a cyclic chemical process, characterized by a very low exergy efficiency (3%) [2] 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. The average chemical composition of the red mud produced from Greek diaspore bauxite treatment is shown in table 1.

Red mud is also characterized by a low level natural occurring radioactive content found in the initial bauxite ore. The gamma-phasmatoscopy using a high purity Germanium sensor for

Table 1 : Average Chemical Analysis of red mud on a dry basis

Chemical Species	%wt
Al_2O_3	16.22%
Fe_2O_3	47.74%
CaO	10.73%
SiO_2	6.08%
TiO_2	5.93%
Na_2O	2.51%
V_2O_5	0.21%
$-SO_3$	0.60%
$-CO_2$	1.63%
H_2O(cry)	8.19%
Total	100.00%

a red mud sample showed that it is characterized by an activity concentration index (I) of 3.65, which according to EC's legislation on Radiological Protection Principles concerning the Natural Radioactivity of Building Materials [3] makes this material suitable for use as a superficial building material with restricted usage (like for tiles, boards, etc), as through such a use it will emit gamma radiation in annual doses of less than 1 mSv.

Therefore, red mud is classified by EC as a non hazardous waste [4], however its small particle size (dust-like, mean particle size 0.49μm), high alkalinity and large amounts (30 to 35 million tonnes per year on a dry basis worldwide [5]) 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) [5,6]. 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. The novel Red Mud Treatment process

2.1 General description

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 aluminium production industry (ENEXAL)” collaborative research project [7].

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[8]. These 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 [9]. 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[10]), then one can expect that the proposed red mud treatment process will be economically viable.

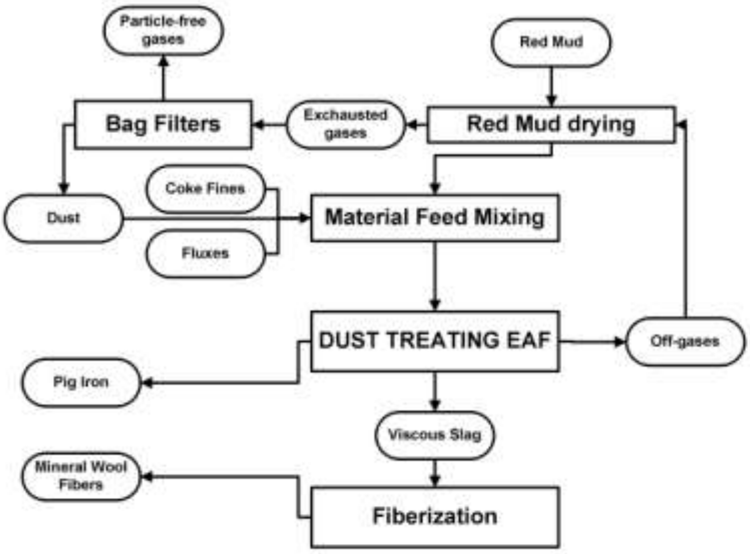

Fig 1 : The novel red mud treatment

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 realising 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.

2.2 Process Design

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. Additionally the chemical composition of this slag phase should be such that will allow its usage in the construction industry, especially in regards to the presence of natural occurring radioactive contents. Typical chemical standards for steelmaking pig iron are C ~4% wt, Si 0.4-0.8% wt, Mn 0.4% wt , P ~0.05%wt and S 0.02%wt while the the desired slag phase according to EC legislation on radioactivity limits for construction materials should have an activity concentration index between 2 and 6, and physicochemical properties similar to those of melts used in typical fiberization process for the production of mineral wool fibers (e.g. viscosity ~10 Poise and surface tension of 0.45 N/m at 1450 °C [11]). Based on the chemical analysis of the red mud and the above mentioned criteria a theoretical model of the process is developed in order to define and optimize the following key operational conditions: (i) EAF operational temperature (temperature of reductive smelting), (ii) required amount of carbon and (iii) required amount and composition of fluxes.

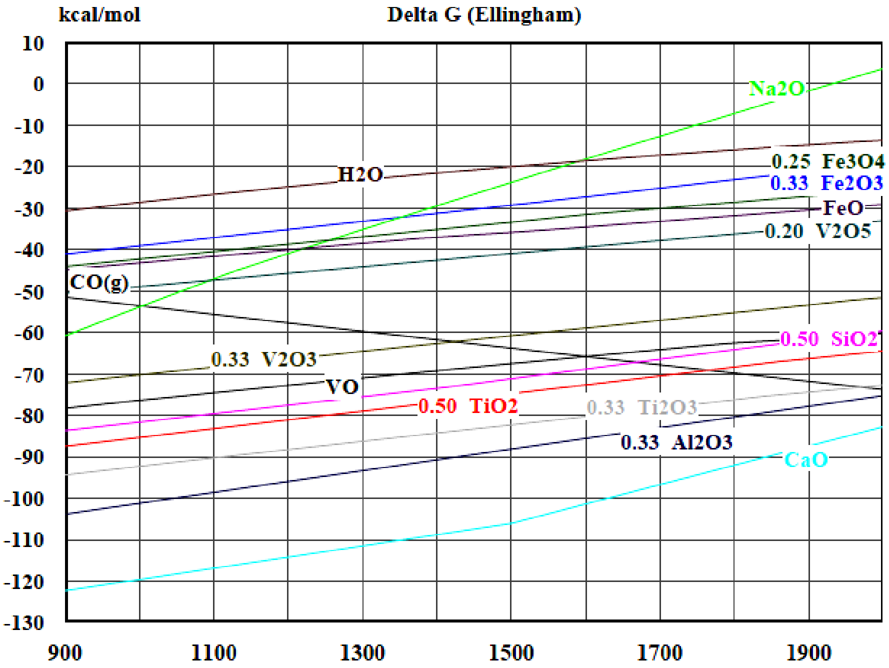

Fig 2 : Ellingham Diagram calculated from HSC Chemistry 6 software (temperatures in degrees Celsius)

2.3 Red Mud Reductive Smelting thermodynamic model

According to the chemical analysis of the red mud and the Ellingham diagram presented in Figure 2, the oxidation of carbon to CO can reduce H_2O, Fe_2O_3, Na_2O and V_2O_5 at temperatures higher than 900^0C, it can reduce SiO_2 and TiO_2 at temperatures higher than 1700^0C while Al_2O_3 and CaO cannot be reduced at temperatures lower than 2000^0C. As the melting point of pure iron is 1537^0C the furnace operational temperature should be in the range of $1500^0C < T < 1700^0C$ in order to effectively reduce the iron in the red mud while avoiding silicon and titanium reductions. The furnace operational temperature for this study is therefore set at 1600^0C.

To account for side reactions consuming carbon the reductive smelting was studied at four different initial carbon concentrations: Stoichiometric carbon (e.g. carbon needed stoihiometrically to fully reduce all iron and hydrogen content of 1 kg of red mud according to reactions (1) and (2)), carbon in 5% excess from stoichiometric carbon, carbon in 7.5% excess and carbon in 10% excess. The final composition of the system in each case was calculated using the Equilibrium module of the FactSage 6.2 software and the results are presented in tables 2 and 3 respectively.

Table 2: Model prediction of pig iron produced from the smelting of 1 kg of red mud with the different amounts of carbon

Pig Iron elements	**Stoich. Carbon**	**5% excess**	**7.5 % excess**	**10 % excess**
	(% wt)			
Fe	98.982	98.931	98.718	98.153
C	0.079	0.253	0.583	1.080
Si	0.000	0.006	0.047	0.236
S	0.550	0.451	0.299	0.155
Ti	0.000	0.000	0.003	0.028
V	0.356	0.347	0.344	0.342
Al	0.000	0.000	0.001	0.002
TOTAL	**99.97**	**99.99**	**99.99**	**100.00**
Fe Recovery (%)	96.46	99.02	99.61	99.83

From this theoretical study, it was concluded that an excess of at least 7.5% carbon is needed to sufficiently cover all side/secondary reactions occurring in the system and thus, achieve high recovery of iron from the red mud. The gas phase produced is dominated by CO and H_2; while the absence of SO_2 from the gas phase indicates that all sulfur remains in the slag and metal phases. In addition, small amounts of Na vapours are predicted, although 58% of Na remains as oxide in the slag phase.

However, the slag produced under these conditions is highly alkaline (basicity ratio > 1.8), comprising a significant drawback for the process implementation, due to the potential loss of the furnace refractory. Besides, this slag is characterized by rather high liquidus temperature (>1450 ^oC) and low viscosity, rendering unsuitable for an effective fiberization process.

Table 3 : Theoretical characteristics of slag produced from the smelting of 1 kg of red mud with the different amounts of carbon.

Slag oxides	Stoich. Carbon	5% excess	7.5 % excess	10 % excess
	(% wt)			
CaO	25.45	26.27	26.61	26.94
SiO_2	14.23	14.67	14.79	14.62
Al_2O_3	37.92	39.13	39.63	40.13
TiO_2	12.49	11.85	10.69	9.35
Ti_2O_3	1.24	2.22	3.43	4.76
Na_2O	5.02	4.67	4.15	3.57
FeO	3.56	1.01	0.41	0.18
S	0.09	0.16	0.30	0.44
TOTAL	100.00	100.00	100.00	100.00
Liquidus Temperature (^oC)	1545	1485	1540	1455
Basicity Ratio	1.79	1.79	1.80	1.84

Table 4 : Theoretical Red Mud treatment mass balance

INITIAL CHARGE – CONDITIONS

Dry Red Mud	1000 kg
C	178 kg
CaO	133 kg
SiO_2	217 kg
TOTAL	1528 kg

PREDICTED OUTPUT

341 kg of Pig Iron	
Wt% Fe	97.510%
Wt% C	0.966%
Wt% Si	0.989%
Wt% S	0.158%
Wt% Ti	0.032%
Wt% V	0.340%
Wt% Al	0.001%
Fe Recovery: 99.73%	

431 kg of Gases	
Wt% CO	97.11%
Wt% H_2	2.12%
Wt% CO_2	0.13%
Wt% H_2O	0.07%
Wt% Na	0.47%

754 kg of Molten Slag	
Wt% CaO	31.97%
Wt% SiO_2	35.63%
Wt% Al_2O_3	21.47%
Wt%TiO_2	5.45%
Wt% Ti_2O_3	2.14%
Wt% Na_2O	2.95%
Wt% FeO	0.15%
Wt% S	0.23%
Slag Properties	
Liquidus Temp (^oC): 1320	
Activity Conc. Index (I) :4.84	
Basicity Ratio: 0.90	
At 1450 ^0C	
Viscocity (Poise): 7.97	
Surface Tension (N/m): 0.4614	

Even more importantly, if radioactive elements contained within red mud are assumed to be transferred completely to the slag phase, then the produced slag will contain sufficiently higher radioactive content (activity concentration index I = 9), which makes it unsuitable to be used as typical superficial construction material (e.g. insulating mineral wool).

For all these reasons, the optimization of the produced slag by the addition of process fluxes (SiO_2 and CaO) was investigated. In figure 3-right the effect on the activity concentration index of the produced slag in relation to the total mass of fluxes used in the red mud smelting process is examined. As seen to achieve an I lower then 6 at least 220 kg of fluxes per tonne of red mud treated are required.

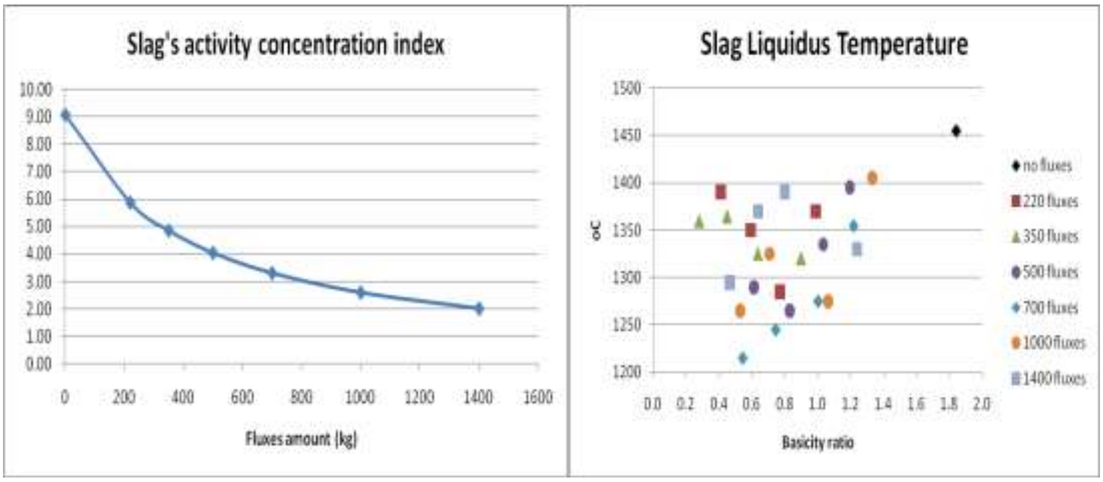

Fig 3 : (right) Activity concentration index (I) of the produced slag phase in relation to the amount of fluxes added in the initial system of 1000 kg of red mud and carbon in 10% excess. (left) Calculated slag phase liquidus temperature under different total amounts of added fluxes and basicity ratios.

The slag phase exact liquidus Temperature as calculated using Factsage calculations for different total amount of fluxes and different CaO to SiO_2 mass ratio (basicity ratio) is presented in figure 3-left, where in all cases examined the liquid slag phase is created below 1400 ^{o}C and therefore is suitable both for the pig-iron production process and the slag fiberization process.

Taking into account the economic viability of the process which could be hindered by the addition of large amount of fluxes or from the production of highly aggressive slag (acid or basic) which would damage furnace refractories and fiberizing equipment, the use of a total of 350 kg of fluxes per ton of red mud is proposed with an overall CaO to SiO_2 mass ratio between 0.8 and 1.0. The final “recipe” for the proposed red mud treatment and the resulting products are shown in table 4 (slag viscosity and surface tension where calculated according to the empirical models found in [11] and [12] respectively).

3. Laboratory Experimental verification of the model

The experimental verification of the model includes a series of experiments in a laboratory-scale 25 KVA inductive furnace using a graphite crucible. All experiments were performed with chemical reagents of analytical grade

3.1 Red mud sample

The chemical analysis of the red mud sample used in all experiments is given in table 1 and was determined in NTUA through wet chemical analysis: fusion of sample with $Li_2B_4O_5$, dissolution with HNO_3 and determination of metal contents by Atomic Absorption Spectroscopy. Carbon and Sulphur content where measured by combustion analysis in LECO CS-200 equipment. Mineralogical phases were determined through X-Ray Diffraction analysis (XRD) shown in table 5.

Table 5 : Red mud sample

Chemical Species	%wt	Mineralogical Phases
Al_2O_3	17.35%	Hematite [Fe_2O_3] Goethite [FeOOH] Gibbsite [Al_2O_3*$3H_2O$] Diaspore [Al_2O_3*H_2O] Boehmite [Al_2O_3*H_2O], Cancrinite [$Na_6Ca_2(Al_6Si_6O_{24})(CO_3)_2$] Katoite [$Ca_3Al_2(SiO_4)(OH)_8$] Calcilte [$CaCO_3$]
Fe_2O_3	45.72%	
CaO	7.10%	
SiO_2	8.22%	
TiO_2	8.13%	
Na_2O	1.02%	
V_2O_5	0.11%	
$-SO_3$	0.67%	
$-CO_2$	2.42%	
H_2O(cry)	9.25%	
Total	100.00%	

3.2 Inductive furnace experiments

During the initial experiments in the inductive furnace it was observed that at the selected slag region (0.9 basicity) the melt produced exhibited high viscosity leading to significant problems in phase separation. Additionally the furnace EMF effected the metallic iron produced further hindering the phase separation. Thus a more acidic slag region was selected (0.7 basicity) as it was observed that in this area better phase separation was achievable. The new charge composition based on the chemical analysis of table 5 and the desirable slag region is presented in table 6. The model described in the previous section was applied for the new initial conditions and its results are presented in table 7,8 and 9.

During the reductive smelting experiments a white powder was deposited on the furnace wall. Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM –EDS) and X-Ray Diffraction analysis (XRD), revealed the powder to be Na_2CO_3 deposits. This sodium carbonate was formed due to the exothermic reaction between sodium and CO vapours on the colder furnace walls , which takes places under 1100 ^{o}C, according to $2Na(g) + 3CO(g) = Na_2CO_3(s)$

Table 6: Initial Charge In Inductive Furnace

Dry Red Mud	68.35 g
C	7.75 g
CaO	9.36 g
SiO_2	14.56 g
TOTAL	100 g

Table 7 : Model predictions and experimental results - weight of phases

(g)	MODEL	EXPERIMENT	Deviation
Metal phase	21.44	21.48	0.31%
Slag phase	53.27	51.57	3.19%

The reductive smelting took place under a N_2 atmosphere and with a gradual increase of furnace power, the crucible reached 1600^0C within 1 hour (app. 26 deg/min). The crucible remained at 1600^0C $\pm 50^0$C for one hour and thereafter was rapidly cooled from 1600 ^{0}C to 400 ^{0}C in 15 minutes (app 80 deg/min).

Fig 4 : Top and section view of graphite crucible with glassy slag and pig iron produced from red mud reductive smelting

Photographs of the produced glassy slag and metal phase are shown in figure 4 . The weight distribution of these two phases coincided with model prediction as shown in table 7 (deviation in slag phase weight should be attributed to material losses during weighting).

The metal phase was chemically analyzed after appropriate grinding and sampling through wet chemical analysis. Iron content was analyzed through dissolution in HNO_3 + HCl acids and determination by Atomic Absorption Spectroscopy (AAS), Silicon content was analyzed according to the Gravimetric method described in ASTM E350-95/46-52, Titanium content by the Spectrophotometric method ASTM E350-95/258-268, Vanadium content by the AAS method ASTM E350-95/239-248 and Carbon and Sulphur content where measured by combustion analysis in LECO CS-200 equipment. The slag phase was analyzed using the same AAS method used for the chemical analysis of the red mud sample.

Table 8 : Model predictions and experimental results for pig iron chemical analysis

Element (% wt)	MODEL	EXPERIMENT	Metal Recovery % (Experiment)
Fe	98.723	93.206	97.95
C	0.386	4.802	7.98
Si	0.144	0.737	1.70
S	0.547	0.066	8.16
Ti	0.002	0.566	3.90
V	0.19	0.174	98.28
TOTAL	99.99	99.55	

The results of these chemical analysis are presented in the tables 8 and 9, along with the relative model predictions. As seen iron recovery in the metal phase was very high and in-line with model predictions. Vanadium was likewise fully recovered. Model predictions and experimental results differ however in the cases of C, Si, Ti and S. These differences should be attributed to the carbon crucible used in the experiment which created locally an excess of carbon not predictable by the model. This would explain the substantially higher carbon content in the pig iron as well as the increased levels of Ti and Si as the excess of carbon lead to local higher reducing conditions. As seen in table 9 similar high deviation are observed in TiO_2 and SiO_2 slag oxides. The decrease in expected of amount of silica oxide in the slag, produced a more basic slag (basicity 0.76 instead of 0.70) which explains the desulphurization of the metal phase.

Table 9 : Model predictions and experimental results for slag phase chemical analysis

Oxides (%wt)	MODEL	EXPERIMENT	Difference
CaO	26.64	26.91	-0.2 pc. p.
SiO_2	37.67	35.43	2.2 pc. p.
Al_2O_3	22.24	22.19	0.1 pc. p.
TiO_2	10.40	8.02	2.4 pc. p.
Na_2O	1.29	1.56	-0.3 pc. p.
FeO	1.64	1.19	0.5 pc. p.
S	0.12	0.24	-0.1 pc. p.
TOTAL	100.00	95.54	
Basicity Ratio	0.7072	0.7597	

4. Preliminary Field Experiments

In order to establish further a proof-of-concept a preliminary batch experiment of the red mud treatment process was conducted in an 750 KVA dust treating EAF located in South Africa. The melt temperature during operation was measured at 1608 ^{0}C and at the end of the experiment two distinct liquid phases were formed and poured sequentially. During the slag

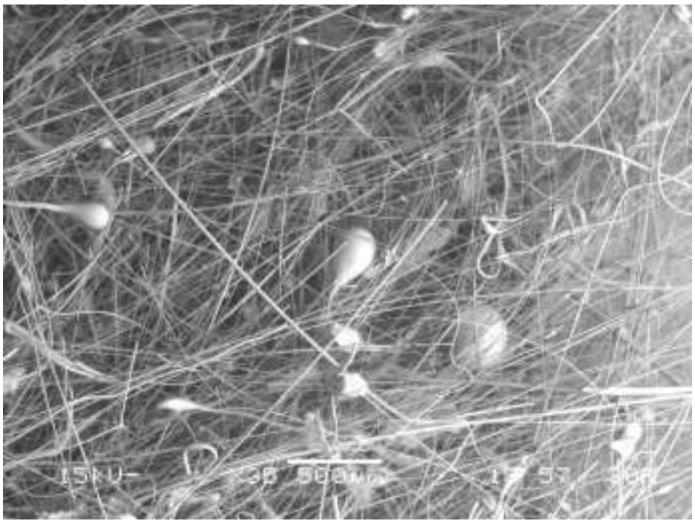

Figure 5 : SEM photograph of inorganic fibers produced from the red mud treatment process slag

phase pouring part of the slag phase was fiberized using a high speed air/water jet. The inroganic 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 5, fibers with diameters less than 20 μm were mostly formed, along with some substantially thicker fibers ending in oval shaped slag inclusions. 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 this preliminary experiment. In general, it is apparent that the slag from the red mud treatment process can be fiberized.

5. Conclusions-Future work

Thermodynamic modelling and laboratory and preliminary field experiments have proven 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 fibres suitable for mineral wool production.

For the primary aluminium industry the proposed Bauxite residue treatment is expected to be highly profitable as it will replace the costly disposal of the red mud waste with two valuable products. Key economical aspect of the process is the production of the mineral wool, which is a versatile product with multiple applications and though this novel process is produced at a 70% lower energy, thereby providing the industry with a significant commercial advantage.

Before however this process can be industrially implemented, further research and more lab and field 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.

6. Acknowledgements

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