IRON RECOVERY AND PRODUCTION OF HIGH ADDED VALUE PRODUCTS FROM THE METALLURGICAL BY-PRODUCTS OF PRIMARY ALUMINIUM AND FERRO-NICKEL INDUSTRIES

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Abstract

This work reviews a single methodology for converting metallurgical by-products into novel high added value products, through what is essentially a zero waste process. Thermodynamic modelling and semi-industrial scale experimental results are presented along with preliminary financial data.

Introduction

The Greek primary metallurgical production is dominated by two large industries, being the alumina refinery and aluminium production plant of Aluminium of Greece (ALSA) and the Ferro-Nickel plant of LARCO. The plants rely on unique Greek bauxite and laterite deposits, respectively, and both are owned exclusively by the Greek private (ALSA) or state owned (LARCO) sector. Today, both industries face significant challenges in respect to the handling and disposal of their by-products. The bauxite residue slurry, also known as red mud, produced during alumina refining and the Fe-Ni slag produced during reductive EAF smelting, represent key by-products produced in large amounts: 0.8 tonnes of bauxite residue on a dry basis per tonne of metallurgical alumina and 14 tonnes of Fe-Ni slag per tonne of Fe-Ni alloy produced. On a yearly basis these by-products accumulate to 650000 tonnes of bauxite residue on a dry basis and 2 million tonnes of Fe-Ni slag. NTUA's laboratory of Metallurgy sets as a key priority to research and develop technologies that will allow the sustainable valorisation of both by-products.

Thermodynamic considerations

The chemical similarity between the red mud by-product and the Fe-Ni slag is illustrated in Table 1, which presents their average chemical analysis. In both cases iron oxides represent 40 wt% or more of the by-product. A basic thermodynamic
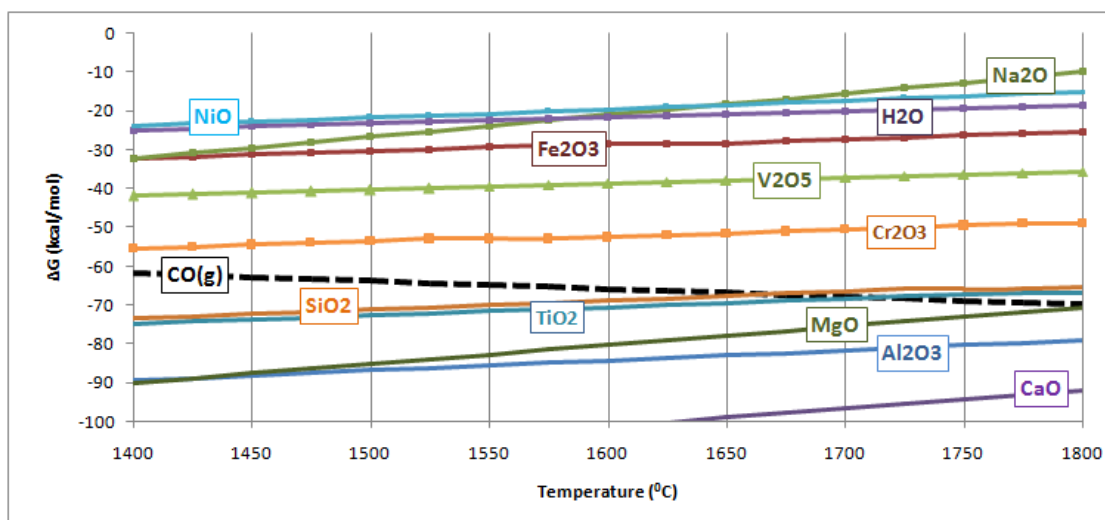
Figure 1: Ellingham diagram for the reduction of various oxides between 1400 and 1800°C at standard pressures. All reactions have been normalised to 0.5 oxygen mole production. Metal oxides above the CO(g) line are thermodynamically fully reduced by carbon at the given temperature. (Calculated by HSC Chemistry 6 software)

analysis of the Ellingham diagram for both systems (Figure 1) reveals that a carbon reductive smelting of either material at temperatures between 1400 to 1600°C would reduce the Fe, Cr, Ni, V and Na oxides to their metallic states, according to the general reaction:
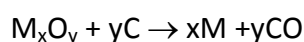
$$M_xO_y + yC \rightarrow xM + yCO$$

Table 1: Average Chemical composition of the Red Mud from the Aluminium of Greece plant and Fe-Ni slag from the LARCO plant Fe-Ni Plant

Red Mud	Al_2O_3	CaO	SiO_2	TiO_2	**Fe_2O_3**	Na_2O	V_2O_5	LOI
(wt%)	16.22	10.73	6.08	5.93	**47.74**	2.51	0.21	10.42
Fe-Ni slag	Al_2O_3	CaO	SiO_2	MgO	**Fe_2O_3**	Cr_2O_3	NiO	LOI
(wt%)	9.69	3.47	38.27	5.13	**39.78**	2.47	0.10	0.95

Metallic iron is liquid at 1538°C but in the presence of carbon, a binary eutectic system is formed (pig iron) which is liquid from as low as 1154°C (ledeburite eutectic point). Therefore, at thermodynamic equilibrium, a carbothermic reductive smelting of either by-product above 1400°C would produce a pig iron metal phase in which V, Ni and Cr would also be dissolved[1]. At temperatures around 1600°C, Si and Ti may

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[1] Metallic Na above 883°C is gaseous and therefore would not be found in the pig iron. More so, it must be stressed that in the cases where the sodium oxide is part of sodium-aluminosilicate phases (as in red mud) the carbon reduction reaction is thermodynamically impossible at these temperatures.

also be reduced to a small extent, as the respective metals dissolved in the pig iron phase may have lower activities than the pure ones. The pig iron produced in this way could be sold directly to the secondary steel industry as a "scrap" substitute[2].

The oxides which thermodynamically cannot be reduced from carbon at these temperature will form a slag phase, which in both cases will amount to at least 50% of the initial by-product weight and 90% of which will consist of Al_2O_3-SiO_2-CaO oxides. To provide a true sustainable solution for the management of these industrial products, environmentally, economically and socially acceptable, it is imperative that this slag phase is fully transformed into marketable products. Such products could include mineral wool insulation products, cement additives, geopolymer products and others.

Therefore, the key goal of the envisioned by-product treatment is to achieve in a single step the production of both high quality pig iron and slag product, by regulation and optimisation of the process conditions, *e.g.* smelting temperature, amount of carbon used and flux additions. Temperature and carbon directly affect the extent of the reduction reactions and, therefore, control the distribution of elements between slag and pig iron. Fluxes such as silica sand and burnt lime regulate the composition primarily of the slag phase, affecting directly its physicochemical attributes such as liquidus/solidus temperatures, viscosity, surface tension, *etc*. Traditional pyrometallurgy uses fluxes in order to enhance metal production and operational conditions, through achieving low temperature melts, good phase separation, pig iron desulphurisation, protecting furnace refractories *etc*. In the by-product treatment discussed here, the fluxes are used both to optimise operational conditions as well as to achieve the production of a specifically designed slag phase.

The Red Mud Treatment

Process design

The proposed bauxite residue treatment comprises of four stages as shown schematically in Figure 2. 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

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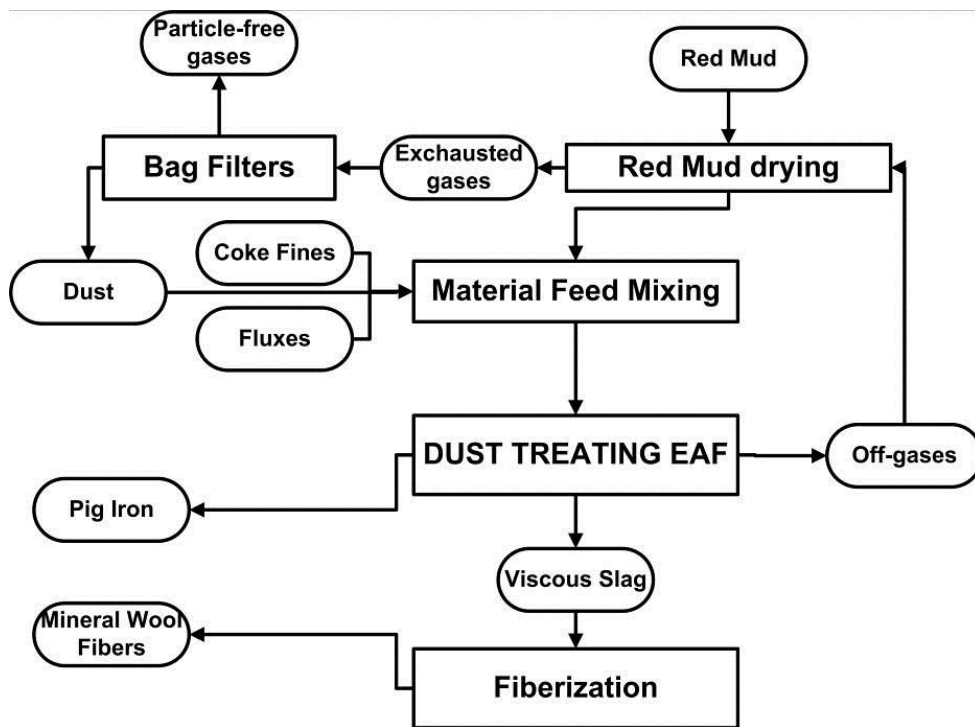[2] Pig iron scrap is valued currently at 400 €/tonne.

Figure 2: The envisioned novel red mud treatment

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.

Thermodynamic modelling

To design the processing parameters of this process the products' specifications must be taken into account. Typical chemical standards for steelmaking pig iron are C ~3-4 wt%, Si 0.4-0.8 wt%, Mn ~0.4 wt%, P ~0.05 wt% and S < 0.02wt%. The melts used in typical mineral wool fiberisation process are liquid at 1450°C with viscosities of 10-15 Poise[1]. The chemical composition of such melts depends strongly on the raw material used (mineral, slag, glass) and the intended use of the wool product[2]. Slag wool may have SiO_2 40-50 wt%, Al_2O_3 10-20 wt%, CaO 10-40 wt%, Fe_2O_3 1–6 wt%, while sodium, titanium, and magnesium oxides may also be present.

To produce a pig iron quality metal from the carbothermic reduction of the red mud, one must define the C to Fe atomic ratio in the feed material. A ratio of 1.5 corresponds to stoichiometric ratio of hematite – carbon reduction. However, since several side reactions occur (see Figure 1) an excess of carbon is needed. The detailed thermodynamic model and preliminary lab scale inductive furnace experiments, reported previously by the authors[3], concludes that at least a ratio of 2 is needed to achieve high iron recovery in the metal phase. Calcium oxide presence in the system is also important to prevent excessive sulphur presence in the pig iron, through the desulphurisation reaction:
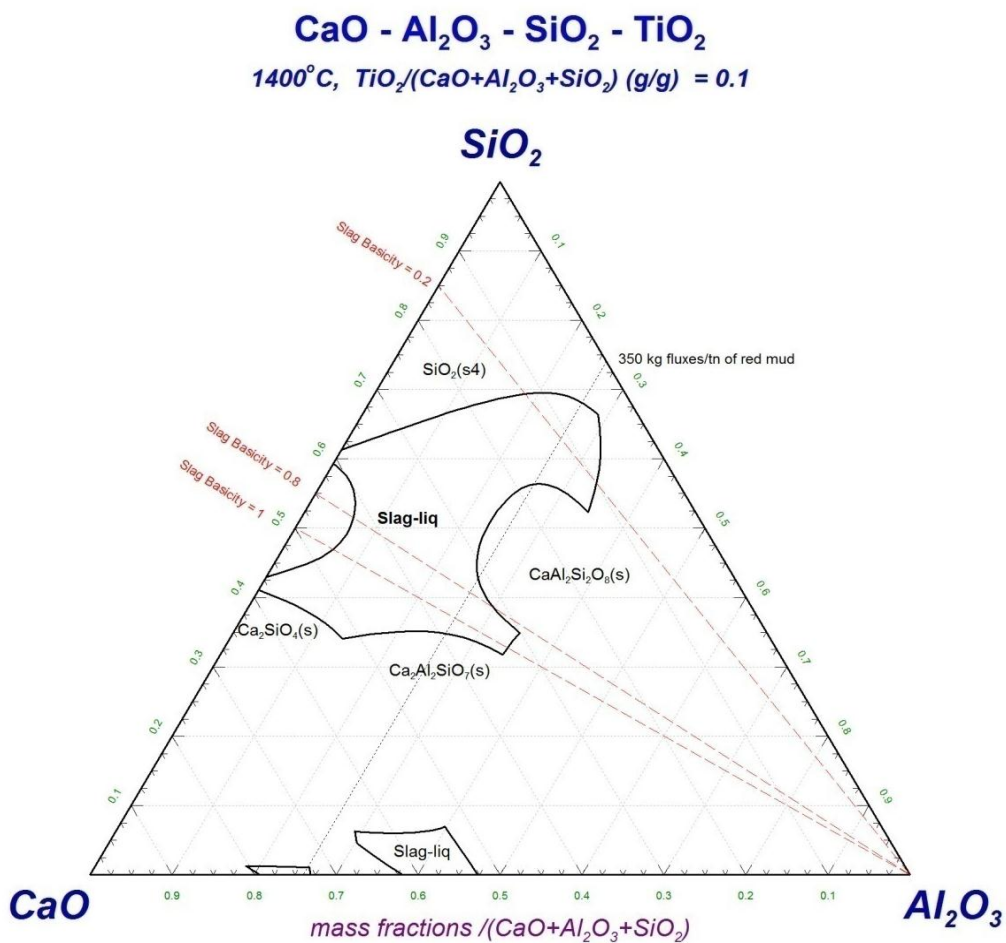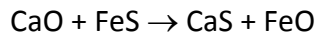
$$CaO + FeS \rightarrow CaS + FeO$$

Figure 3: Predicted triangular phase diagram for the liquid slag phase thermodynamic stability as predicted by FactSage 6.3 software, for a system of varying CaO, Al_2O_3 and SiO_2 composition and constant TiO_2 composition (other red mud slag oxides are omitted from the calculation) at 1400°C

To produce a "fiberisable" slag, the slag phase of the system should be first of all liquid at 1400°C and should contain at least 60 wt% in SiO_2 and CaO. Using FactSage, the phase diagram of the expected slag system was calculated. As seen in Figure 3, by adding a total of 350 kg of fluxes per tonne of red mud processed the resulting slag of the system would have two liquid regions at 1400°C, one in a highly acidic region (slag basicity 0.2) and one in the near neutral region (slag basicity 0.8 – 1.1). In order to protect furnace refractories and avoid excessive sulphur in the pig iron phase, the neutral region is selected.

Semi industrial scale EAF experiments

To establish this, process experiments in a semi-industrial scale (400 kVA) Electric Arc Furnace were conducted. The red mud used was supplied by ALSA and was dried in a stationary electric dryer before feeding to the EAF. The optimal feed recipe used consisted of mixing 350 kg of dry red mud with 77 kg coke fines and 70 kg of silica and 54 kg of burnt lime. The C to Fe atomic ratio in the feed was thus 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 (approximately 1 hour long), followed by the feeding of the material which was done at approximately 3 kg/min rate, through a feeder tube at the top of the furnace (Figure 4). The temperature at the surface of the melt produced was measured with an optical pyrometer at 1540°C (average value). In the end of the batch feeding, two distinct phases were poured from the furnace, i.e. slag and pig iron, their weights and chemical analyses of which, are presented in Table 2, along with thermodynamic model predictions for the same feed. Additionally, Table 2 presents empirical chemical composition indexes used in the mineral wool production industry to evaluate the "fiberise-ability" of a melt[4]. As seen from these indexes the produced melt is within or marginally within the empirical limits.

Figure 4: Photos of the EAF during batch feeding (left) and during pouring (right)

Table 2: Thermodynamic model (FactSage) and experimental results from processing 350 kg of red mud in a semi industrial scale 400 kVA EAF

Pig Iron (wt%)	Model Prediction	EAF Exp		Slag (wt%)	Model Prediction	EAF Exp	Empirical indexes for mineral wool production	
%Fe	86.57	87.09		CaO	31.19	29.65	A [<1.8]	1.85
%C	4.67	4.05		SiO_2	32.71	32.64	P [<15]	15.06
%S	0.16	0.05		Al_2O_3	29.68	24.23	k2 [0.8-1]	0.76
%P	-	0.20		TiO_2	1.97	6.78	SHG [1.3 - 1.4]	1.26
%Si	1.89	1.71		MgO	1.40	4.65	KNB [30-40]	36.19
%Ti	6.38	0.46		Na_2O	2.69	1.89	N [<5%]	1.89
%V	0.29	0.28		Fe_2O_3	0.05	1.11	F [>5%]	1.11
%Cr	-	4.43		-SO_3	0.57	1.09		
Total weight	124 kg	120 kg		Total weight	271 kg	280 kg		
Fe Recovery	100%	97%		Slag Basicity	0.99	1.05		

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.

The pig iron chemical analysis shows that, as expected, the metal produced has concentrated practically all the iron and the vanadium content of the red mud. Small amounts of silicon and titanium metal have also been reduced. Sulphur, originating from the red mud and the coke, and phosphorus 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 4wt%. The chromium metal presence in the pig iron is not attributed to the feed material, but rather to magnesia-chromite refractory furnace lining, which was partially dissolved during the carbothermic reduction. The slag phase chemical analysis shows that as expected aluminium, silicon, calcium, magnesium and titanium remained as oxides in the slag phase, in an overall neutral melt (basicity ratio = (mass of CaO + MgO)/(mass of SiO_2) = 1.05). The overall elemental distribution is shown in Figure 5, where both the partial dissolution of the furnace lining and the partial evaporation (app 41 wt%) of sodium content is apparent. The latter result is in line with previous experimental observations[3].
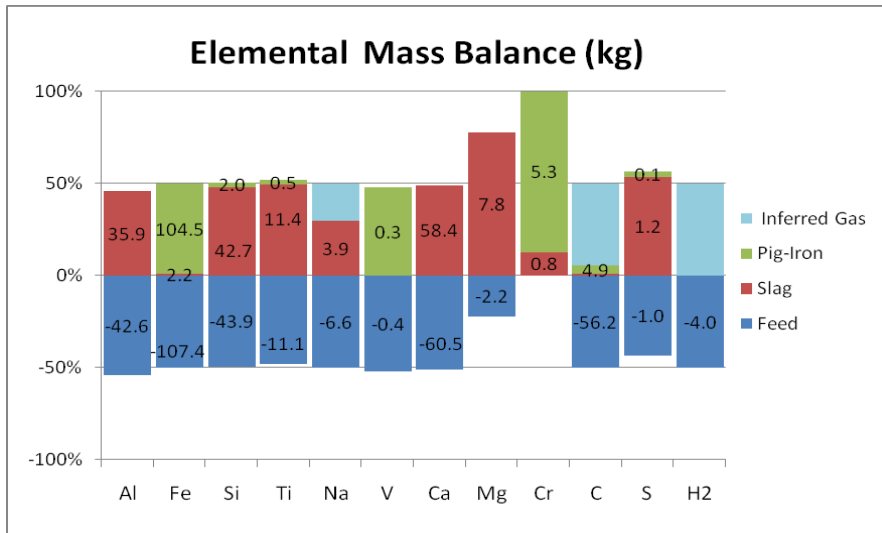
Figure 5: Normalised elemental mass balance of batch feed and EAF smelting phases. Feed is represented in negative values, while pig iron, slag and inferred gas in positive values. Labels represent actual weight of respective elements in kg

Slag fiberisation tests

During the slag phase pouring, part of the slag was fiberised 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 6, 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 temperature differences of the poured slag stream as it cools from the furnace mouth to the level of the air/water jet. The CFD model of this flow[5] is shown in Figure 7. From this experiment, it is evident that the slag melt can be fiberised and with an automated industrial system (*e.g.* melt spinners) uniform fibers could be produced.
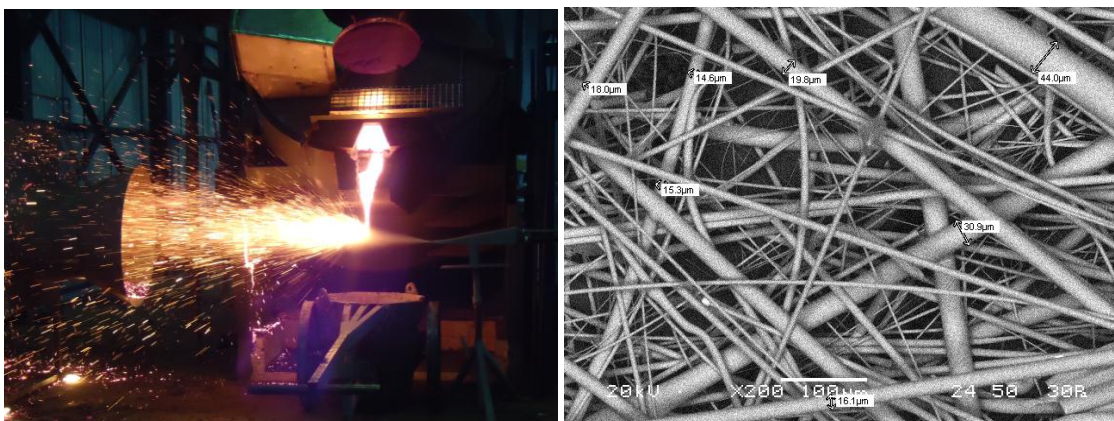

Figure 6: Photos of air/water jet slag fiberisation process (left) SEM photograph of inorganic fibers produced (right)
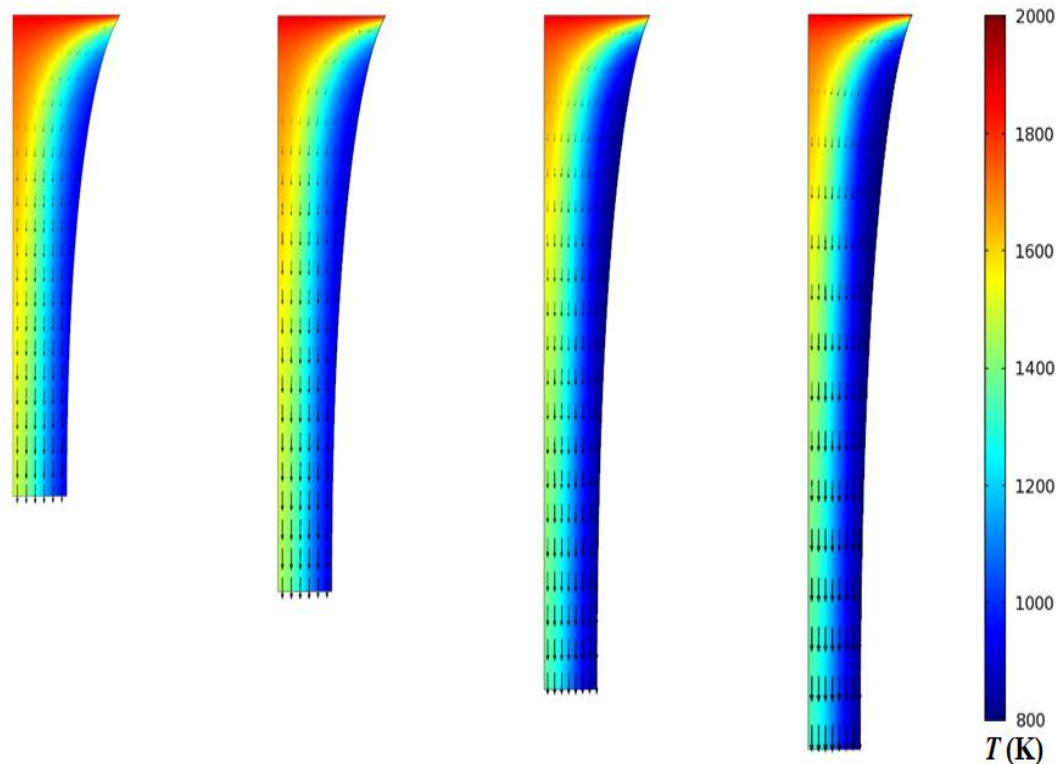
Figure 7: CFD model of vertical slag stream temperature and flow field as a function of impingement point (L = 0.6, 0.8, 1.0, 1.2 m) with the air/water jet[5]

Economic viability

The most vital aspect of the novel process, however, is its ability to be profitable to the industry. By extrapolating the 400 kVA EAF results to a 5 MVA EAF processing 1300 tonnes of dry red mud per month, one calculates a production of 440 tonnes of pig iron and 980 tonnes of slag to be fiberised. Taking into account the current cost of raw materials, electrical energy and labour in Greece, the overall operation cost of such a unit is predicted at 766217 € per month. Based on the current prices for pig iron scrap, selling the pig iron alone would only cover 25% of the unit's operational cost. By adding the slag fiberisation, the overall operation would become viable if the mineral wool product was sold at minimum of 626 €/tonne (break-even price). Currently, commercial mineral wool products values range in between 600 to 1000 €/tonne.

To further evaluate the financial viability of the process, larger scale experiments are needed; namely continuous operation in industrial scale EAF, in order to deduce exact power and material consumption. Furthermore, it is evident that a different furnace refractory lining should be used. Under the FP7 ENEXAL project, a 1 MVA EAF

pilot plant has already been set up in ALSA in order to perform long term and continuous testing of the process.

Fe-Ni Slag Treatment

Using a similar methodology as described in section 3, a process to treat Fe-Ni slag for the production of pig iron and a high added value slag product can be envisioned. The chemistry of the system is more simple and, due to the high silicon oxide content, only the addition of lime is needed as a flux to regulate the basicity of the final slag melt. The FactSage phase diagram calculation for the system (Figure 8), shows that a liquid slag can be produced at 1400°C for practically any slag basicity ratio. Again, for the reasons mentioned in the red mud treatment, the neutral slag
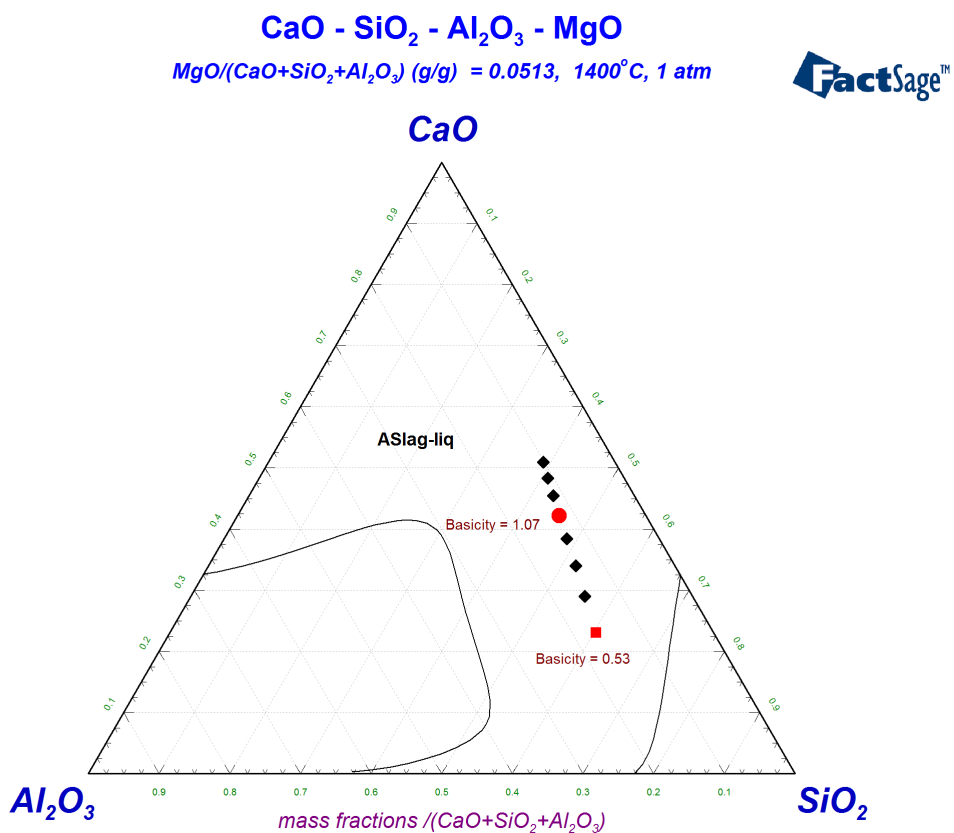

Figure 8: Predicted triangular phase diagram for the liquid slag phase thermodynamic stability as predicted by Factsage 6.3 software, for a system of varying CaO, Al_2O_3 and SiO_2 composition and constant MgO composition (other Fe-Ni slag oxides are omitted from the calculation) at 1400°C. The corresponding slag from the treatment for different lime additions is shown with bullets. The square corresponds to the addition of 10 kg of CaO per 100 kg of Fe-Ni slag and the circle to the addition of 30 kg of CaO per 100 kg of Fe-Ni slag

region is selected. The FactSage model predictions along with empirical melt composition indexes are presented in Table 3.

Using the same financial scenario as in the case of the red mud treatment, the process in a 5 MVA EAF would produce 403 tonne of pig iron and 1100 tonnes of fiberisable slag with an operational cost of 724581 €/month. This would mean that the break-even price for the mineral wool product could be as low as 533 €/tonne. Moreover, if the processing unit is set up within the FeNi industry, then the slag could be processed before cooling, therefore tremendously reducing the energy and time needed in the 5 MVA EAF. Hypothetically, 7 times more slag could be processed this way within the same time and with the same energy consumption, leading to a break-even price of 429 €/tonne of mineral wool.

In contrast to the red mud treatment process, the FeNi slag process has not yet been tested in semi-industrial or industrial scale. Therefore, it is presented here only as a theoretical concept.

Table 3: Predicted thermodynamic equilibrium composition of the phases produced during the processing of a 100 kg of Fe-Ni Slag with 30 kg of lime and 11 kg of Carbon at 1600°C (FactSage 6.3)

Pig Iron (wt%)	Model		Slag (wt%)	Model	Empirical indexes for mineral wool production	
%Fe	89.49		Al_2O_3	29.65	A [<1.8]	1.19
%C	1.98		CaO	32.64	P [<15]	12.45
%Cr	5.11		SiO_2	24.23	k2 [0.8-1]	0.85
%Ni	0.25		MgO	6.78	SHG [1.3 - 1.4]	1.13
%Si	3.17		FeO	4.65	KNB [30-40]	45.60
			CrO	1.89	N [<5%]	0.00
					F [>5%]	0.08
Total weight	31.03 kg		Total weight	84.63		
Fe Recovey	99.79%		Slag basicity	1.07		

Conclusions

A methodology for carbothermically treating iron bearing slags and by-products (with $Fe_2O_3 \geq 40$ wt%) has been developed and tested in semi-industrial scale. Key aspect of the process design is the full exploitation of the slag produced, for the production of added value materials, through appropriate flux regulation. In this work, the case of mineral wool fibers has been presented for both bauxite residues and Fe-Ni slag treatment.

Numerous other slag products could also be produced with the use of appropriate fluxes. Calcium and magnesium bearing slags from blast furnaces have been successfully used for producing geopolymers[6]. The latter can be used as cement additives or as insulation materials[7] or even as fire-proofing materials[8]. The development of numerous slag products is vital for the industrial application of the process, as the preliminary economic analysis clearly shows that the overall profitability is directly linked with the exploitation of the produced slags.

Testing in industrial pilot scale is the logical and required next step, before the process is applied in industry.

Acknowledgements

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