Iron recovery and production of high added value products from the metallurgical by-products of primary aluminum and ferronickel industries

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THIRD INTERNATIONAL SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

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The "Greek" Metallurgical problem

- Two major primary metallurgical plant operate in Greece:
  - Aluminium of Greece (ALSA), alumina refinery and aluminium production plant

ALUMINIUM S.A.

- Producing **810,000 tons of alumina** and **165,000 tons of aluminium** annually
- The leading industrial producer of alumina and aluminium in **South East Europe**
- **The only vertically integrated** bauxite, alumina and aluminium production **plant in Europe.**

The "Greek" Metallurgical problem

- Two major primary metallurgical plant operate in Greece:
  - General Mining and Metallurgical company (LARCO), primary ferro-nickel plant

LARCO

- ❑ Producing **100,000 tons of Fe-21Ni** annually
- ❑ The largest ferronickel producer (mining and smelting) in Europe and one the 5 largest ferronickel producers in the world.
- ❑ The company holds about **6% of the Fe-Ni European market share**

The “Greek” Metallurgical problem

- Both plants produce significant amount of by-products
  - ALSA: 650,000 tons of bauxite residues (red mud)
  - LARCO: 2 million tons of Fe-Ni slag
- Since 2012, sea disposal of by-products has been prohibited
- Potential for land disposal is limited due to geographical and other constraints

No proper areas (location and size) in short distances from plants

Proposed Solution

- Both by-products are chemically similar
  - Containing high amount of iron oxides (40-50%wt)
  - Containing at least 30% wt alumino-silicates

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

EAF Carbothermic Reductive Smelting

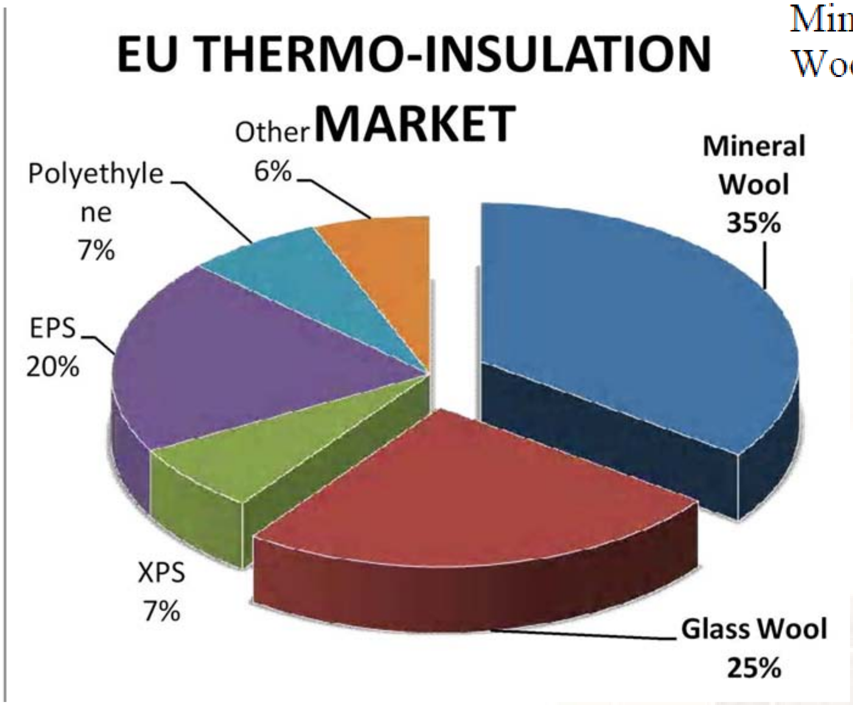
Produce Mineral Wool **Produce Pig-Iron** **= Zero Waste Process**

Mineral Wool production

Mineral wool

Is an excellent inorganic thermo- and sound- insulating material for commercial and industrial use

Material	Approx. Max Operating Temperature °C	Range of Bulk Density kg/m³	Range of Thermal Conductivity W/m.K
Glass Mineral Wool	230 to 250	9 to 120	0.032 to 0.040 (At 20°C)
Stone Mineral Wool	700 to 850	23 to 200	0.033 to 0.035 (At 10°C)



Mineral and glass wool currently dominate the thermo-insulation market in Europe

Loose Fill

Blanket

Carbothermic Reductive Smelting

- Process Design Issues:
  - Define conditions for optimum iron recovery (temperature, carbon addition)
  - Define physico-chemical properties of the slag through appropriate fluxes in order to produce a melt suitable for mineral wool production

Pig iron standards	
%C	~ 4%
%S	<0.02%
%P	<0.05%
%Si	0.4-0.8%

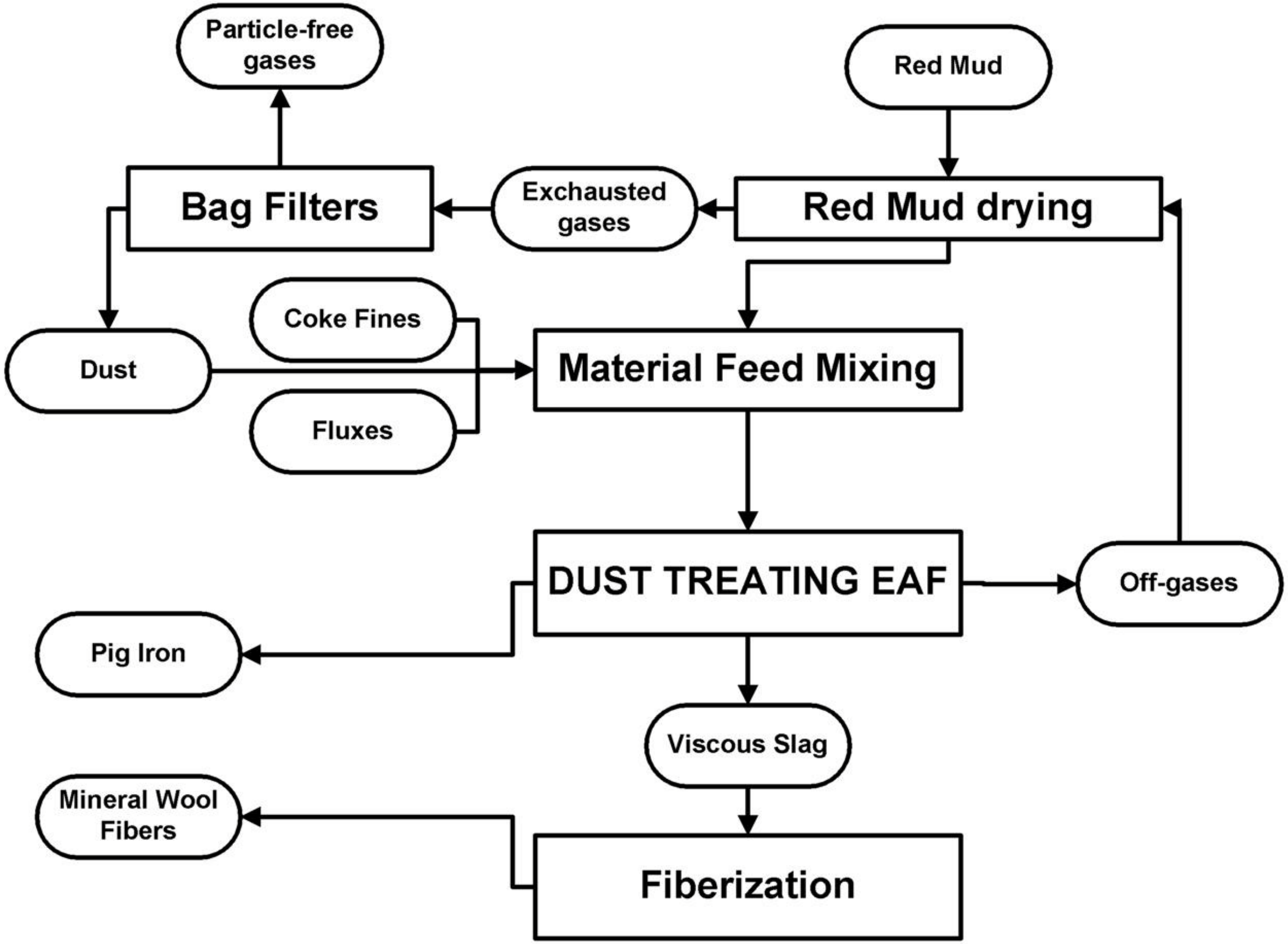
Empirical indexes for mineral wool production	
A = $(SiO_2 + Al2O_3 + TiO_2)/(CaO+MgO;$	< 1.8
P = $4.9/[(MgO+CaO+Fe_2O_3 + Na_2O + TiO_2)/(SiO_2 + Al_2O_3)] - 0.45$	< 15
k2 = $[100 – (SiO_2 + Al_2O3)]/(SiO_2 + Al_2O_3)$	0.8 -1
SHG = $(SiO_2 + Al_2O_3)/(1.4\ MgO + 0.4\ Fe_2O_3 + CaO + TiO_2)$	1.3 - 1.4
KNB = $Na_2O + MgO + CaO$	30 – 40
N = Na_2O	< 5%
F = Fe_2O_3	> 5%

Case Study with Bauxite Residues

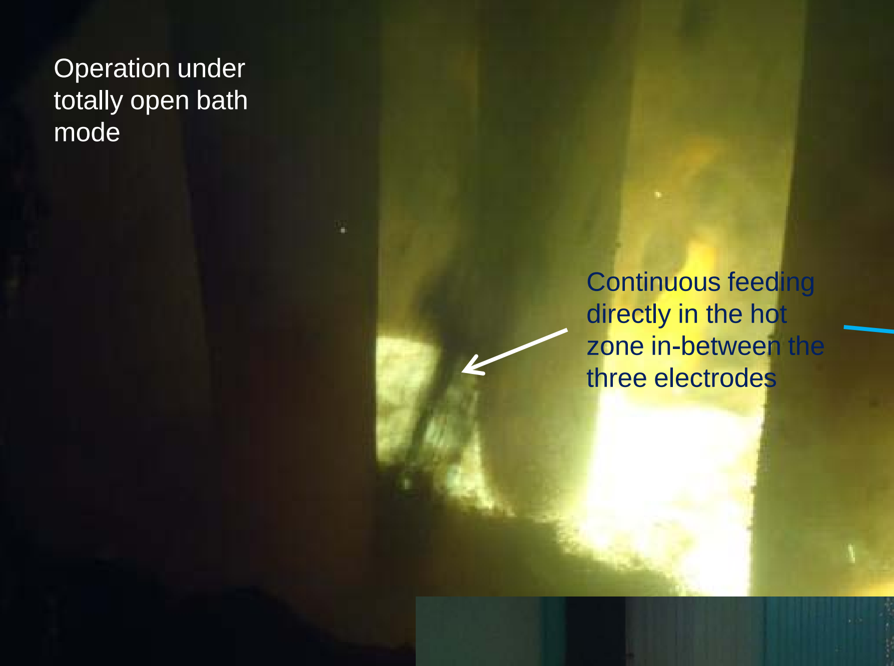
- Bauxite residues in ALSA :
  - Annual production is approximately 650,000 tons
  - Over the last years four (4) filter Presses are used for drying residues to moisture content close to optimum value (28% w/w dry basis) (considered as BAT)

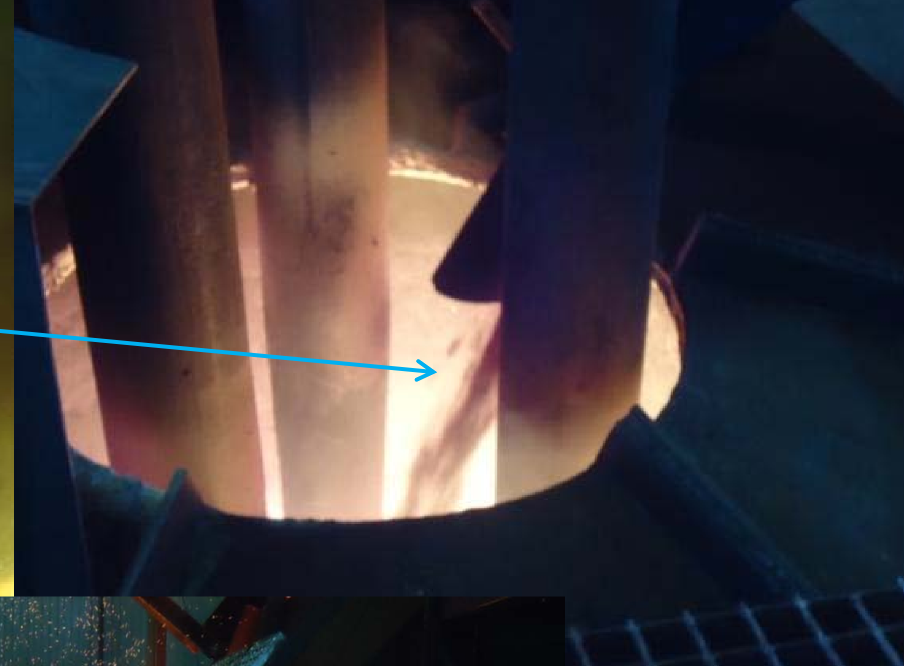
- Processing issues :
  - Red mud is an extremely fine material (d_{50} ≈ 5μm) Dust treating EAF
  - It still necessitates drying prior to be fed in an EAF Double skin dryer
  - It contains almost 0,5% Na_2O which can cause damages to the refractories EAF with high area to height ratio in relation to a blast furnace

Case Study with Bauxite Residues

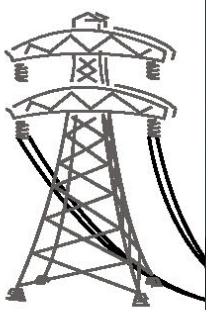


- 100% Utilization of Red Mud **- no solid wastes**
- Production of two marketable products





Grid Powe



AC Transf

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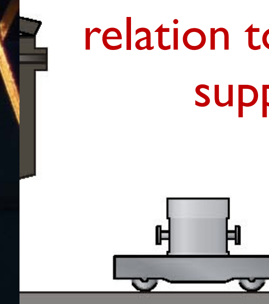
processing of dusty material (<10 mm) by regulating the rate of feeding in relation to power supply



Case Study with Bauxite Residues

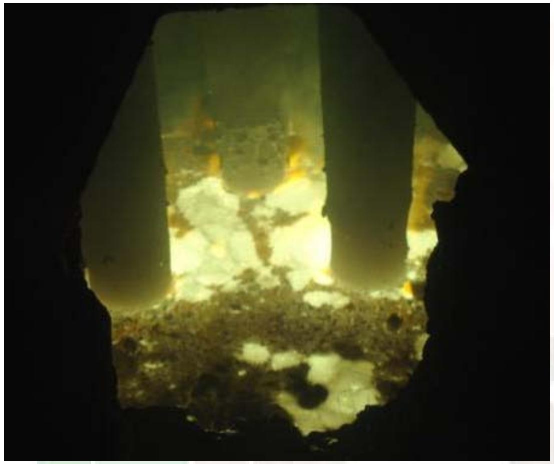
Experiments in the 400 kVA AMRT EAF

Total charge:550 kg

Fluxes: 351kg/tn RM

Molar ratio C:Fe = 2.43 [Stoicheometirc reduction ratio C:Fe = 1.5]

(%wt CaO+ %wt MgO) / (%wt SiO2) = 0.94 [Neutral Slag = 1.0]



Experimental conditions

Pre heat slag: 200kg

Feeding Rate: 3kg/ min

Smelting time: 3.5 h

Optical Pyrometry

Around Electrodes 1700 -2400 C

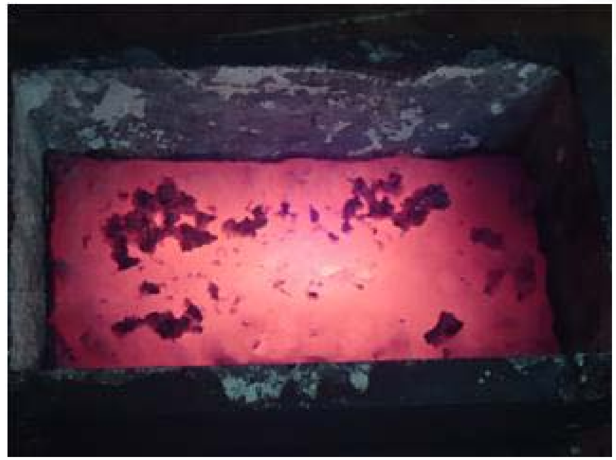
Melt surface T = 1400 -1600 C

“Crust surface” T = 900-1100 C

Case Study with Bauxite Residues

Pig iron	Exp %wt
%Fe	87.09%
%C	4.05%
%S	0.05%
%P	0.20%
%Si	1.70%
%Ti	0.45%
%V	0.28%
%Cr	4.43%
TOTAL	99.83%
Pig Iron Phase	**120 kg**
Fe % Recovery	**97%**

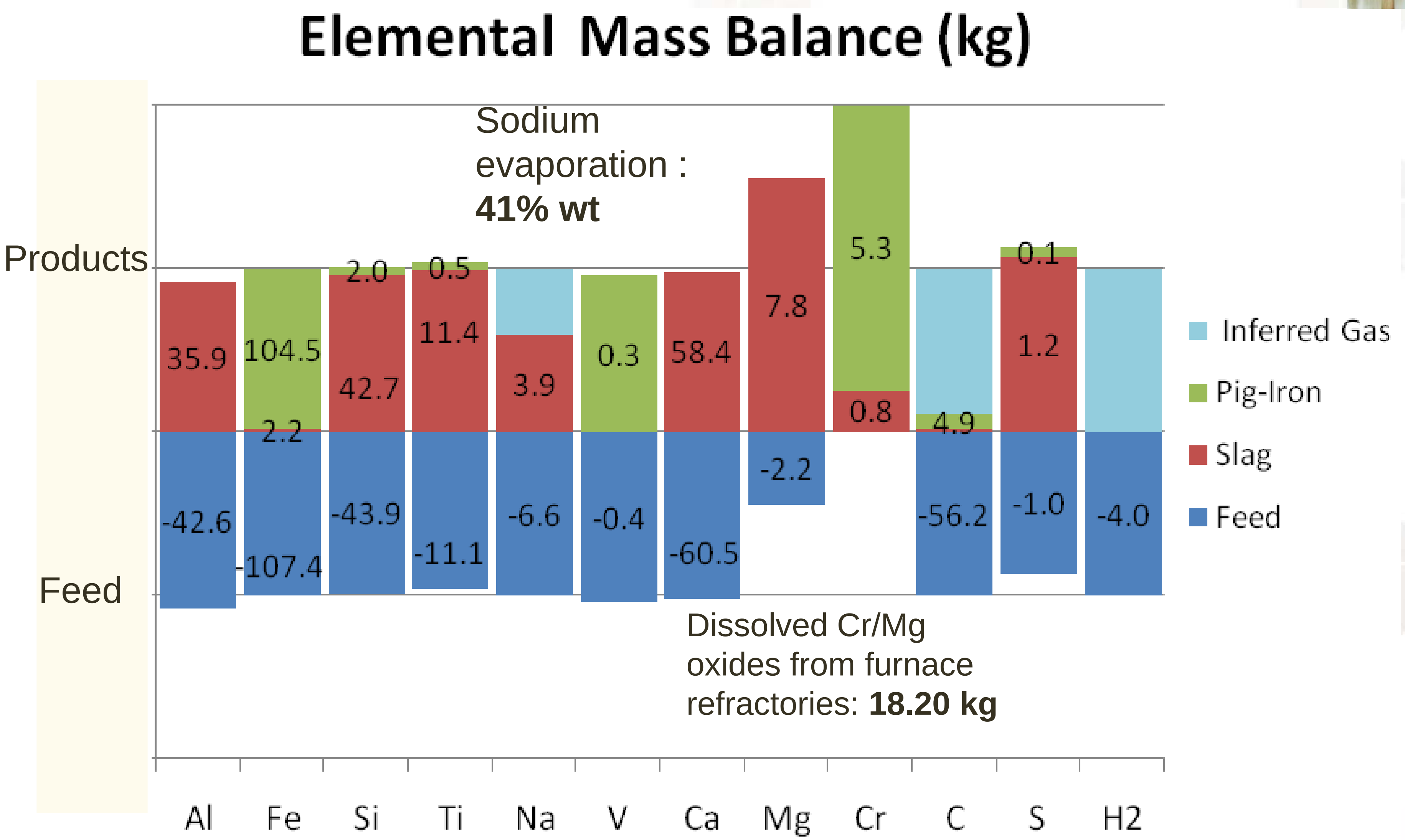
Contains **31%wt** of the initial Red Mud



Slag	Exp %wt
% Na_2O	1.89%
%MgO	4.65%
% Al_2O_3	24.23%
% SiO_2	32.62%
% - SO_3	1.09%
% CaO	29.65%
% TiO_2	6.79%
% Cr_2O_3	0.41%
% Fe_2O_3	1.11%
%C	0.49%
TOTAL	102.43%
Slag Phase	**280 kg**
Basicity	**1.05**

Contains **43% wt** of the initial Red Mud

Case Study with Bauxite Residues



Carbothermic Smelting of red mud

➢The pig iron produced was used to substitute 16% scrap in white iron production (high Cr content)

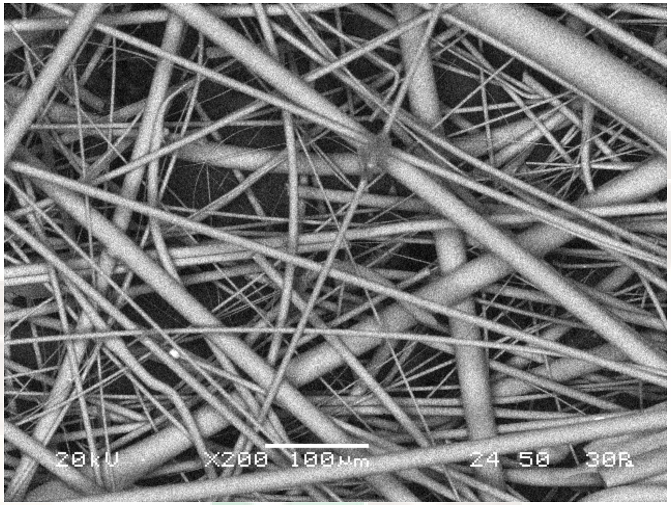
By changing the furnace refractories to Magnesia carbon bricks, a chrome-free pig iron will be produced

➢The Chrome free pig iron could be uses as feedstock in the secondary steel production industry, substituting **up to 20% of steel scrap.**

Pig iron	Fe	C	Si	Mn	P	S	Cr
0%	98.95	0.19	0.19	0.64	0.012	0.017	0.00
5%	98.92	**0.21**	0.22	0.62	0.015	0.017	0.00
10%	98.89	**0.23**	0.24	0.61	0.018	0.017	0.00
15%	98.86	**0.25**	0.27	0.59	0.021	0.018	0.00
20%	98.82	**0.27**	0.29	0.58	0.024	0.018	0.00
25%	98.79	**0.29**	**0.32**	0.56	0.027	0.018	0.00
30%	98.76	**0.31**	**0.34**	0.55	0.030	0.019	0.00

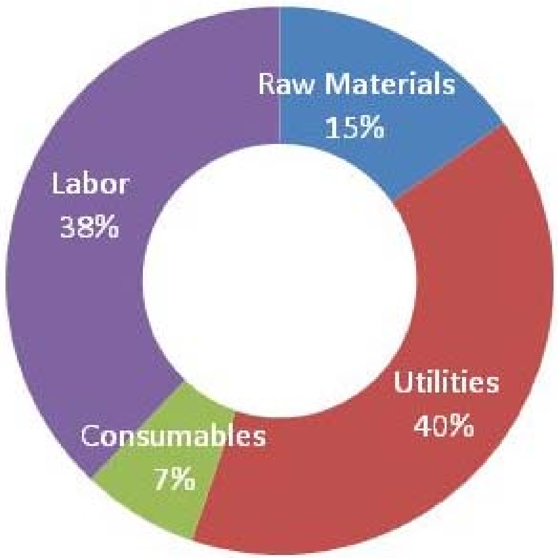
Case Study with Bauxite Residues

Slag fiberization

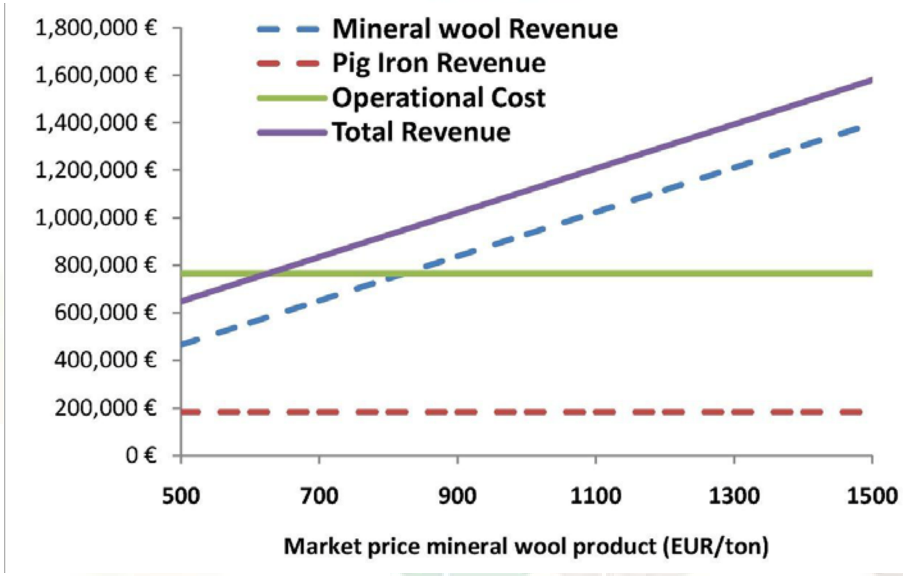


- ➢Preliminary slag blowing tests has shown that the slag produced can be fiberized.
- ➢ The chemical composition of the slag is within mineral wool industry's specs.

Preliminary Economic Evaluation



- Extrapolation for a 5.0 MVA EAF treating 1300 tons of bauxite residues and producing 442 tons of pig iron and 931 tons of mineral wool per month
- Pig Iron revenues (calculated at a market price of 415€/t) amount to 25% of operational costs
- Mineral wool revenues depend on market price (depends on product quality and market demand)



Case Study with Bauxite Residues

Next Step: Industrial Demonstration

➢Tests on the 1MW AMRT EAF in Aluminion of Greece

➢ A year long campaign is foreseen under ENEXAL

The industrial demonstration of the process is expected to prove its industrial applicability

Case Study with Fe-Ni slag

- Fe-Ni Slags in LARCO :
  - Annual production is approximately 2 million tons
  - There are no special processing issues
  - Treating the slag in-situ, before cooling would mark significant energy savings.

Pig Iron (wt%)	Model		Slag (wt%)	Model
%Fe	89.49		Al_2O_3	29.65
%C	1.98		CaO	32.64
%Cr	5.11		SiO_2	24.23
%Ni	0.25		MgO	6.78
%Si	3.17		FeO	4.65
			Cr_2O_3	1.89
Total weight	**31.03 kg**		**Total weight**	**84.63**
Fe Recovery	**99.79%**		**Slag basicity**	**1.07**

Market Barriers

- Pig iron product : No market barrier
- Mineral wool product: Mineral wool is produced at 2:1 mass ratio to pig iron and including fluxes may weight 70 -80 % of the initial by-product – hence large amounts of mineral wool would be produced if all by-products were converted in the process
- Mineral wool transportation costs limit its potential markets to nearby regions

Other complimentary methods have to be consider for complete by-product treatment

Bauxite Residue Geopolymeric Tiles/Bricks

Bauxite Residues 85% - Metakaolin 15%
S/L=2.9g/mL [NaOH]=8M [SiO_2]=3.5M
Curing: 60°C – 3 days – RH70%

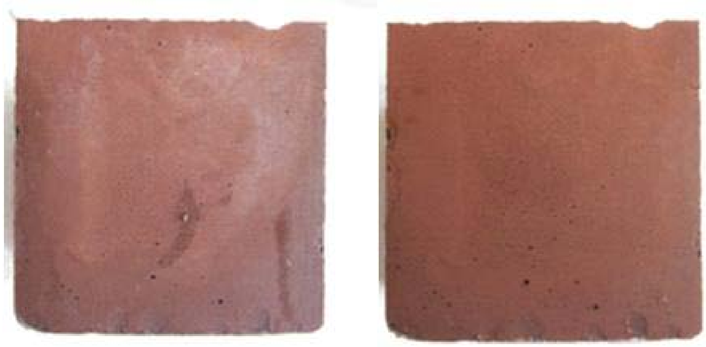
- Compression Strength: 20,5 MPa - MW (Moderate Weathering Conditions)

- Bending strength : 600 N (good for tiles)
- Water Absorption 1.28%
- Negligible water permeability
- *Low resistance to Freezing-Thawing Cycles*

Suitable building material for moderate climates (e.g. Mediterranean)

Combined Geopolymers for Bricks and Tiles

Bauxite Residues 50% - FeNi Slag 50%
S/L=4g/mL [NaOH]=7M [SiO_2]=4M
Curing: 60ºC – 6h – RH70%



- Excellent Mechanical properties

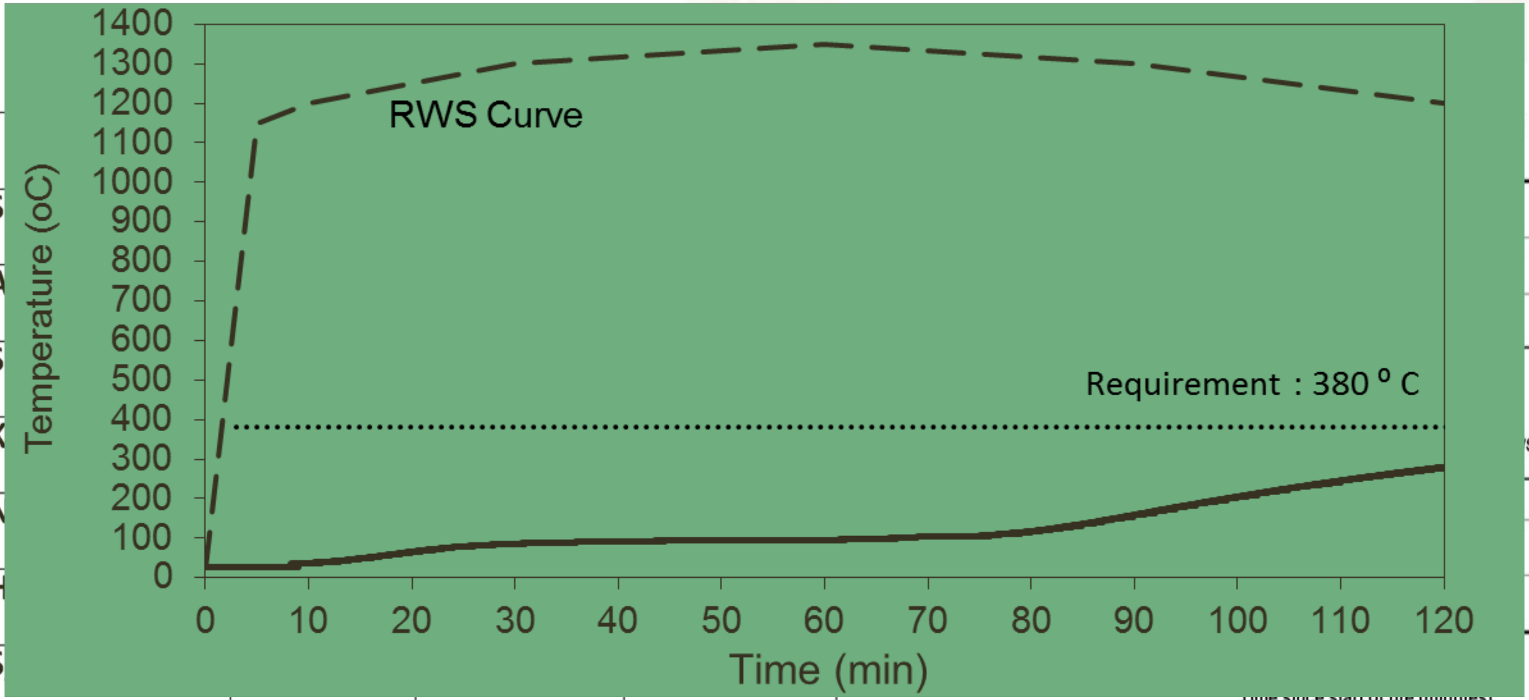
  Comp. Strength: > 40MPa

  Bending Strength: 4MPa

- Density: 2350 kg/m^3
- Water absorption: 0.57%
- Water permeability: Negligible
- High resistance to Freezing-Thawing Cycles

Suitable building material for almost any climate

Fe-Ni Slag Fire Resistant Geopolymers



S			
A			
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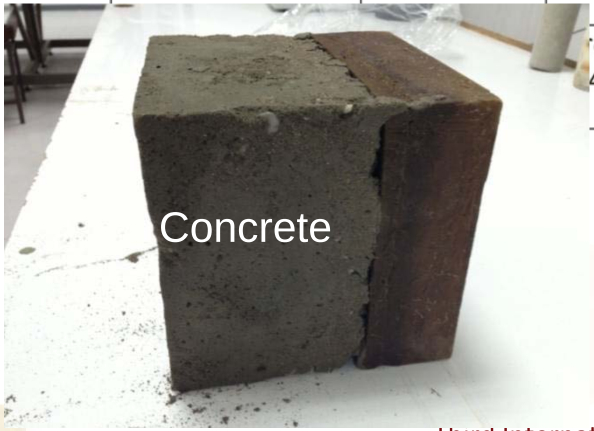
Curing(°C/h)	(25/4)	(50/4)	(70/4)

Before **Fire Testing** **After**



Conclusions

- Both by-products can be treated with the same pyrometallurgical technology for the production of pig-iron and mineral wool
- Additional technological solutions like Geopolymerization can provide the necessary **products diversity** which will allow complete valorization of these by-products
- Now, a critical mass of alternative treatment technologies for the Greek metallurgical by-products exists offering viable solutions to the Greek Metallurgical Industry and improving substantially its environmental performance

Thank you for your attention

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