# Process Solutions

**National Technical University Of Athens**

Research Team: Raw Materials Exploitation & Sustainable Energy Solutions

INFRASTRUCTURE

# 1600 $m^2$ of total laboratory space

- Section of Physicochemical Characterization of Materials
- Section of Hydro- Bio- & Electrometallurgical Processing
- Section of Pyrometallurgical Processing
- Section of Environmental Protection & Soil Remediation
- Section for Pilot Scale Technology Demonstrations

# Process solutions

OBJECTIVES

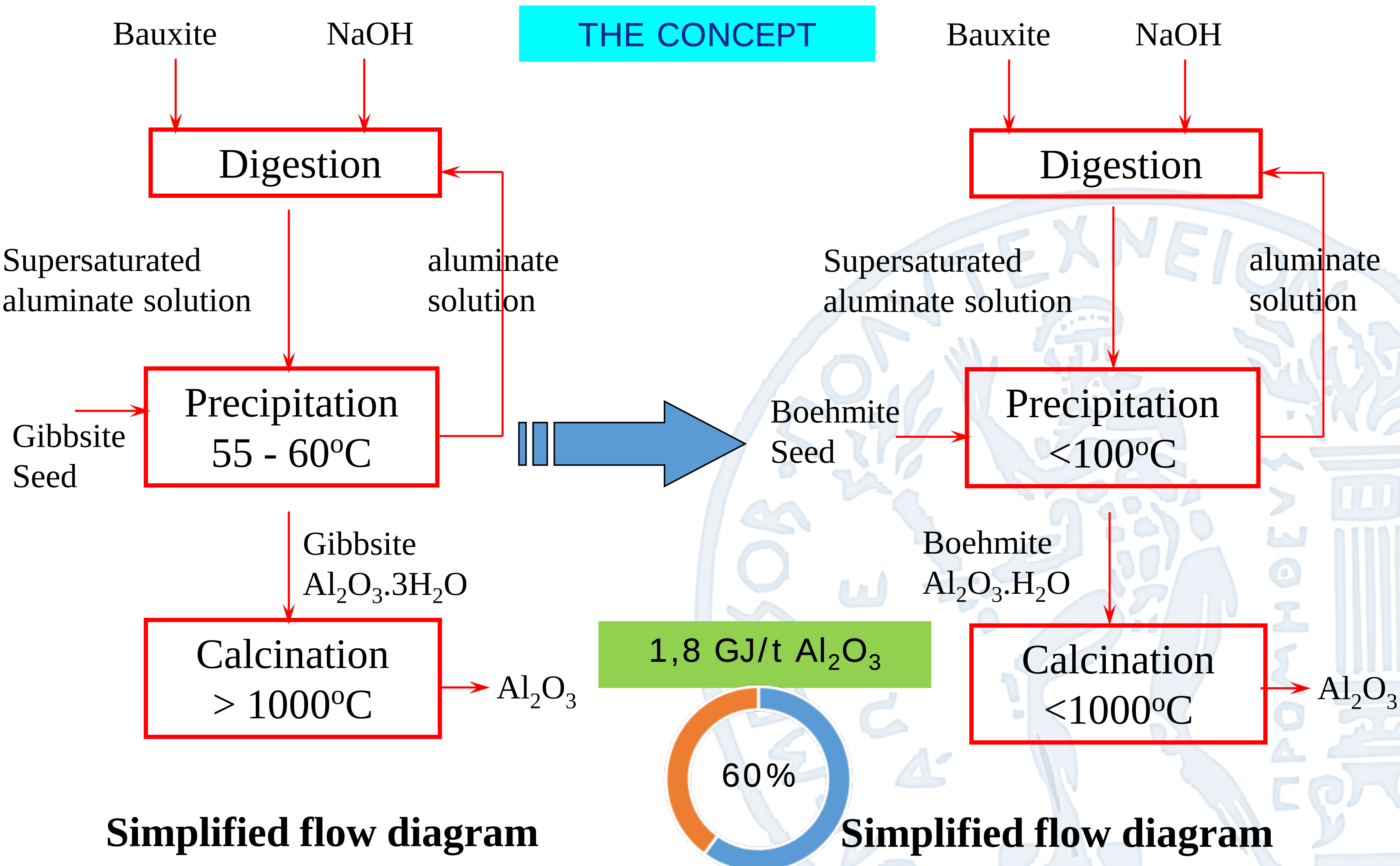
The development of Innovations in:

- Primary Metallurgy
  - Aluminum
  - FeNi
  - Gold
  - Copper

- Valorization of Metallurgical & Industrial Residues
  - Red Mud
  - FeNi Slags
  - Fly Ashes
  - Perlitic Wastes

# Innovations in Primary Aluminum Production

THE BOEHMITE PROCESS




**Simplified flow diagram of Bayer Process**

**Simplified flow diagram of new boehmite Process**

# Comparison of Bayer and Boehmite Processes

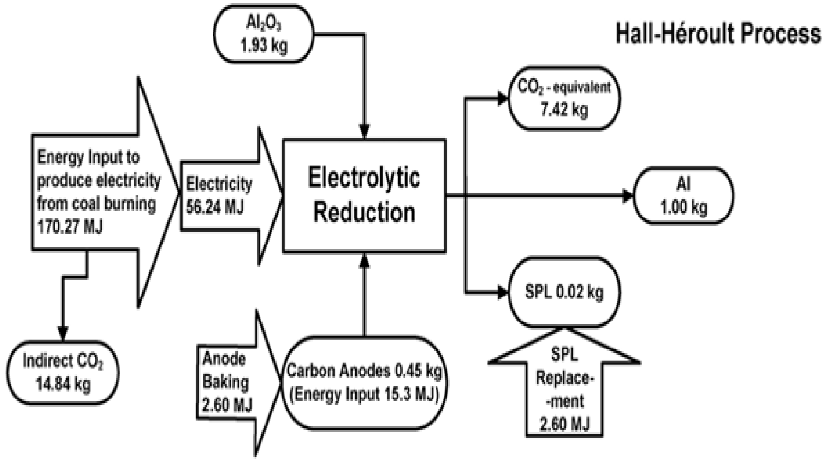


| Precipitation Stage | Bayer Process | Boehmite Process |
|---|---|---|
| Efficiency | 60 - 80g/L | 60 -70g/L |
| Retention Time | 24 - 72 h | 24 - 72 h |
| Initial RP | 1.1 | 1.1 |
| Initial Seed Ratio | 1 - 2 | 7 - 8 |
| Temperature | 55 - 60$^{o}$C | 90$^{o}$C |
| Calcination Stage | | |
| Temperature | 1100$^{o}$C | 700 - 900$^{o}$C |
| BET | > 80 $m^2/g$ | 30 - 80$m^2/g$ |
| L.O.I | < 1% | 1.2 - 1.8% |

The process patented but unfortunately never exploited commercially

# Innovations in Primary Aluminum Production

CARBOTHERMIC AL PRODUCTION




<u>Typical Aluminum Smelter</u>

- around 300 electrolytic cells
- 125.000 ton/y Al production

<u>New generation smelters</u>

400-500 kton/y Al production

Located in Middle East, China, Russia, India, Malaysia and Africa

## DRAWBACKS OF MOLTEN SALTS ELECTROLYSIS

- ❑ High Electrical Energy consumption (an upgraded energy form with high cost and exergy content) for production of chemical work and heat
- ❑ Increased Environmental Impact due to mainly $CO_2$ emissions
- ❑ Low volumetric efficiency due to 2 Dimensional Electrolytic Reactor. That means, for a given production capacity, a big number of cells and therefore big industrial space are necessary

# The Innovative Concept

## THE CONCEPT OF CARBOTHERMIC PROCESS

Cathode: $4Al^{3+} + 12e^{-} = 4Al$

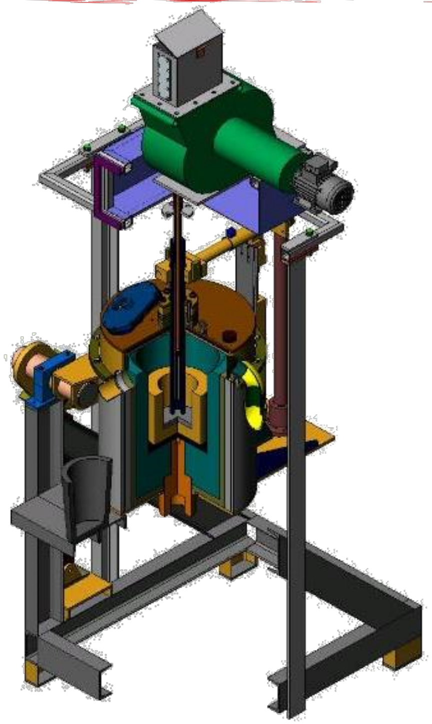
Anode: $6O^{2-} + 3C_{graphite} = 3CO_{2(g)} + 12e^{-}$

$$Al_2O_3 + 3C = 2Al + 3CO_{(g)}$$

## ADVANTAGES OF CARBOTHERMIC PROCESS

- Substitution of a part of Electrical Energy with the chemical and thermal energy of carbon
- Decrease of waste heat
- Potential for waste heat recovery
- Decrease of $CO_2$ emissions
- Higher volumetric efficiency due to 3 Dimensional Reactor
- For a given production capacity
  - smaller reactor size and thus industrial space
  - less capital cost

# Mode 1: High Temperature Carbothermic Process



Concept:

Hollow electrode EAF

Feeding Alumina-Carbon pellets directly in the arc zone

Controlled feeding rate

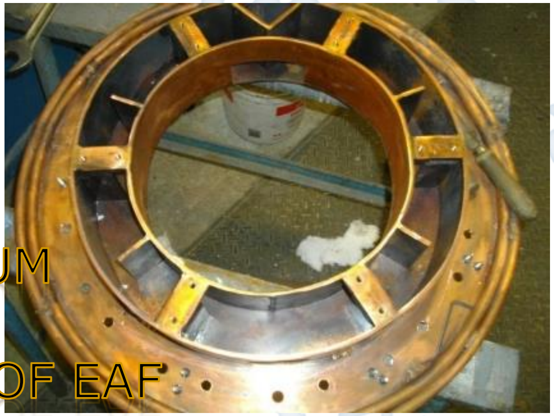
No liquid phase formation

Water cooled lid acts as condenser

Argon Overpressure

CHALLENGES

1. PROPER VERY FAST ALUMINUM CONDENSER
2. PLASMA FURNACE INSTEAD OF EAF

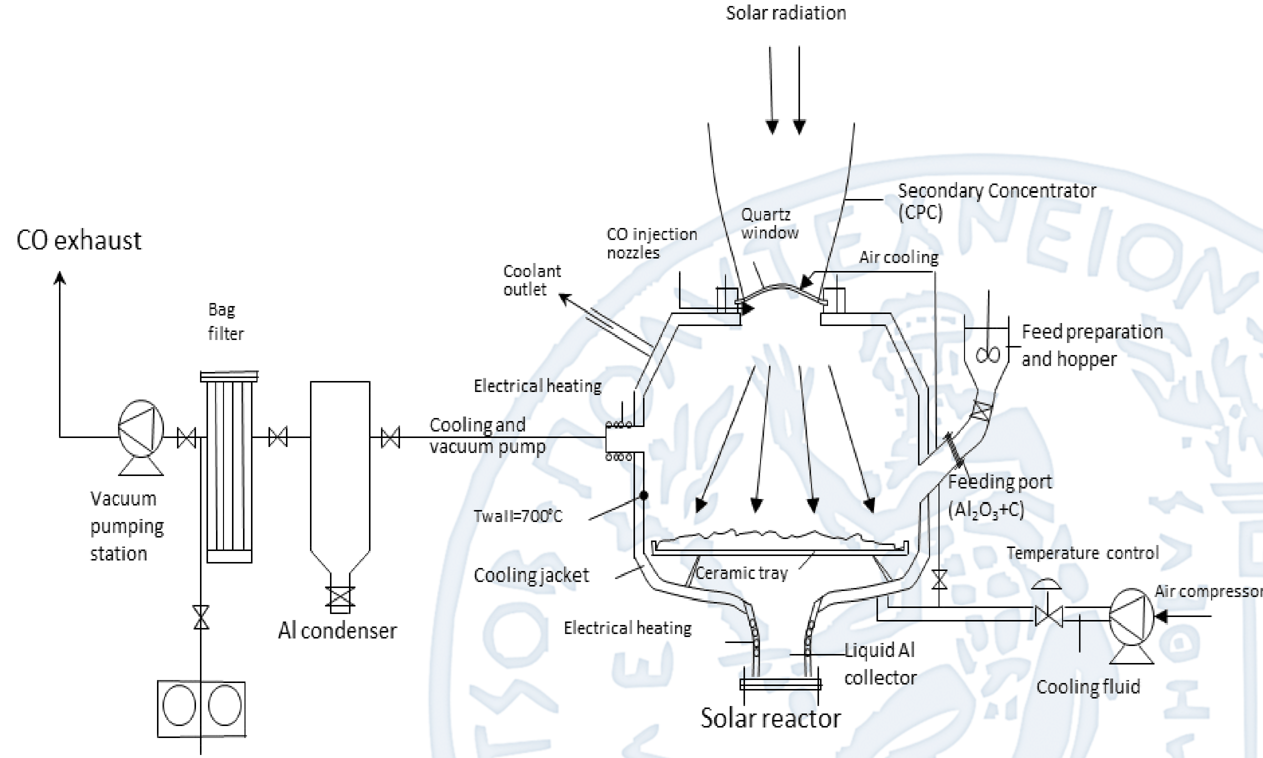


CFD Simulation (Rectangular Channel with Fins)

# Mode 2: Solar Vacuum Carbothermic Process

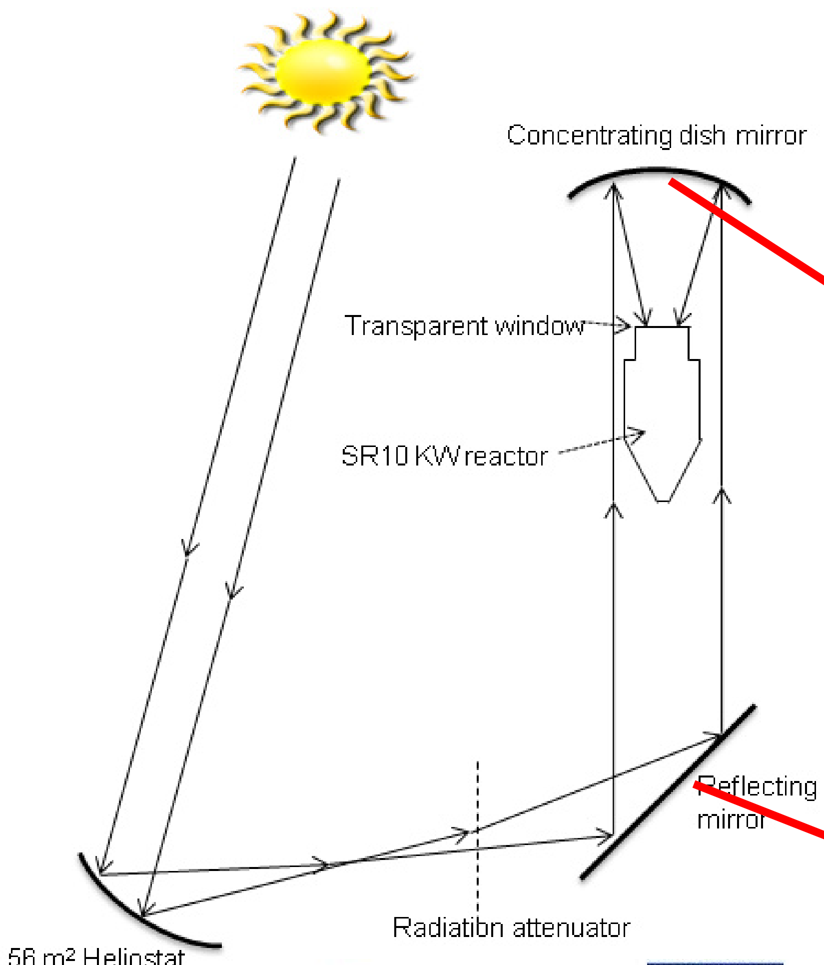
Concept:

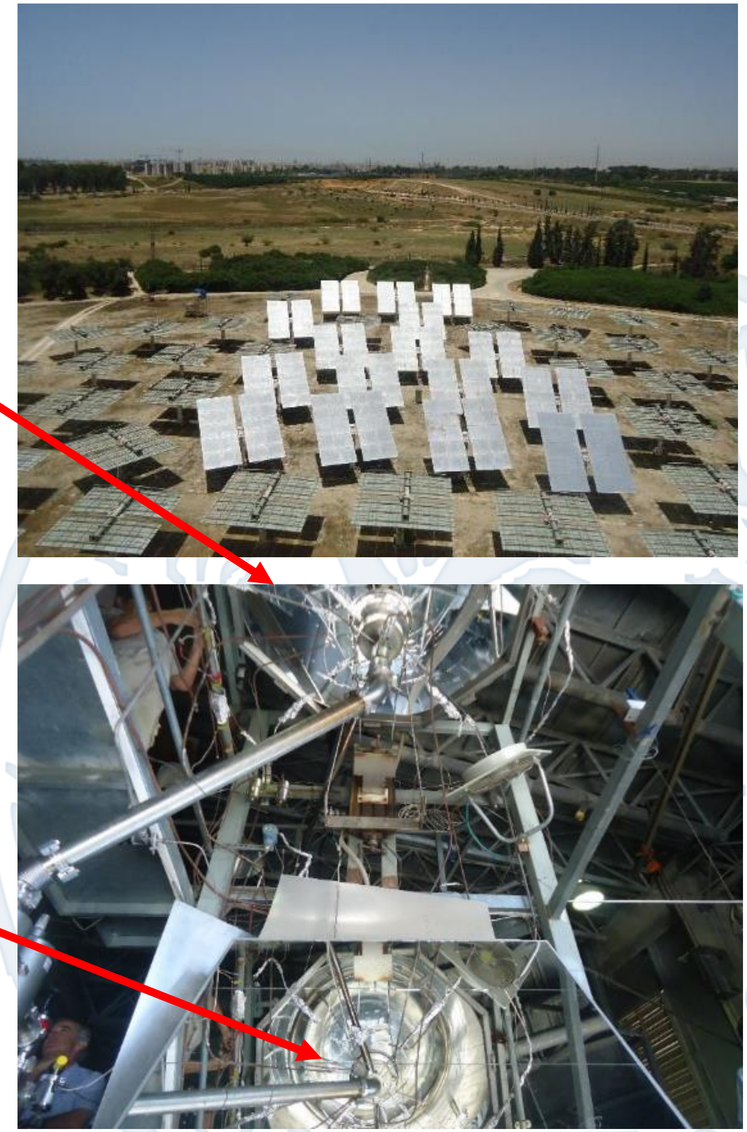
- Reactor under vacuum
- Concentrated Solar Radiation provides process heat
- Condenser before vacuum pumps collects the metal.




Energy of the process = pumping work (electricity) + *concentrated solar radiation.*

# Mode 2: Solar Vacuum Carbothermic Process



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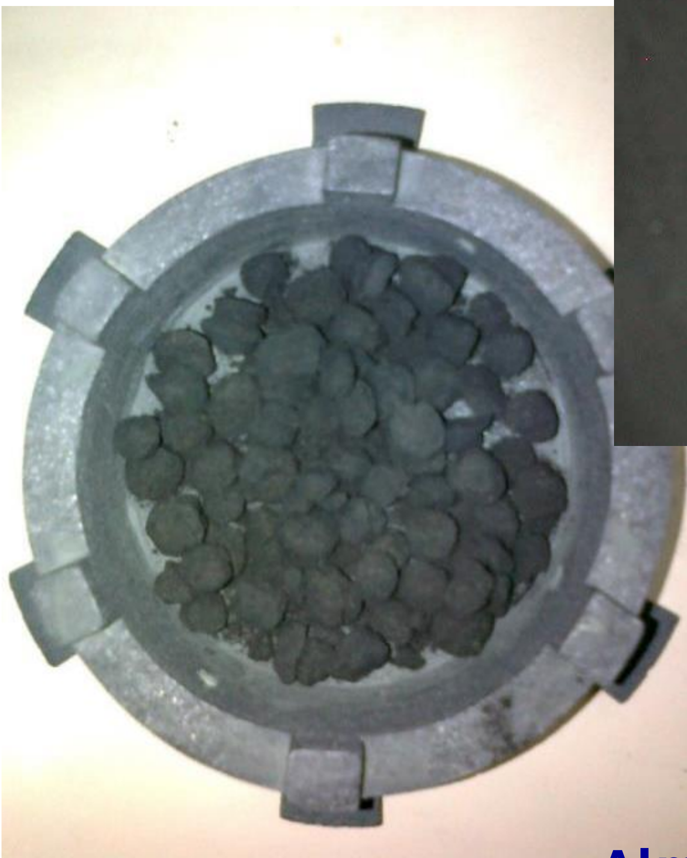
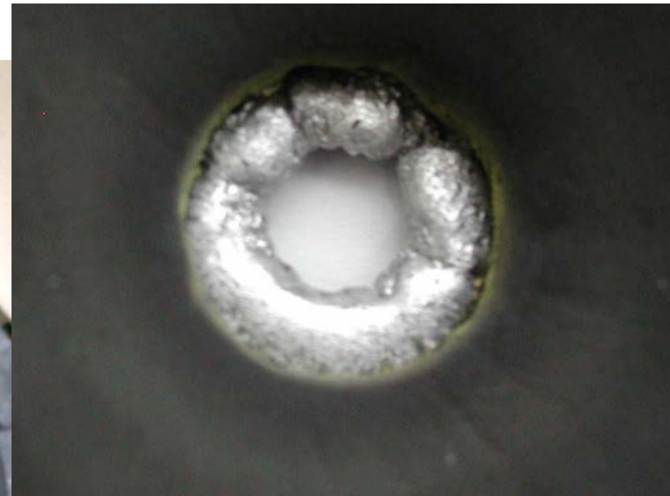
WEIZMANN INSTITUTE OF SCIENCE

# Mode 2: Solar Vacuum Carbothermic Process





Almost Pure Aluminum

Before test

After test

# Comparison of Processes

| Estimated gains of the new Alumina Smelter in Comparison to the Hall-Heroult | | | |
|---|---|---|---|
| **Energy Source** | **Energy Savings** | **Reduction in GHG Emissions** | **Exergy Efficiency Increase** |
| Coal based electricity | 16% | 35% | 3% |
| Hydroelectricity | 10% | 65% | 5% |
| Hydroelectricity for H-H and Concentrated Solar for New Smelter | 68% | 65% | 82% |

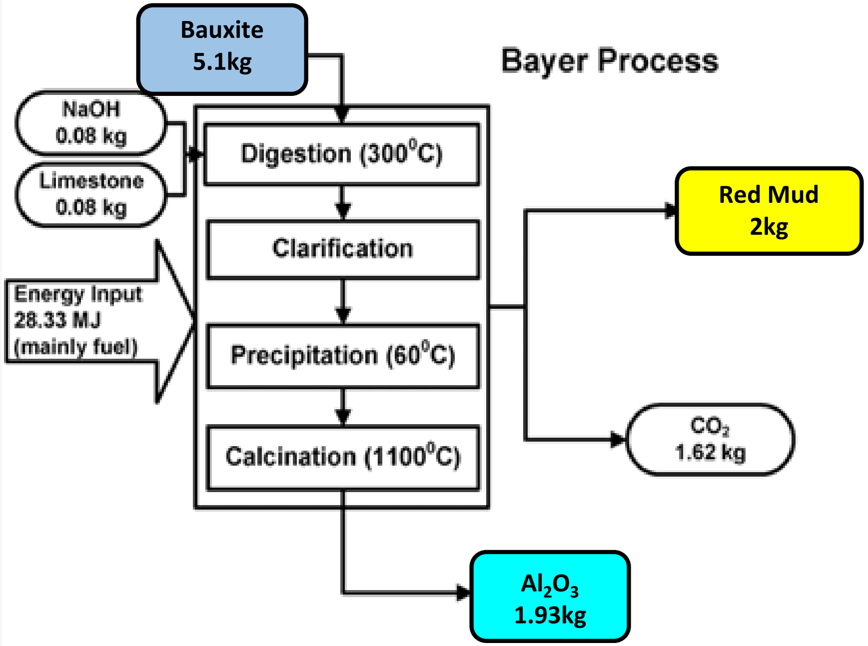
A SUSTAINABLE PERSPECTIVE FOR THE EUROPEAN ALUMINUM INDUSTRY

ALUMINUM MILLS VERSUS HALL-HEROULT MEGAPLANTS

# Innovations in Primary Aluminum Production

RED MUD VALORIZATION

## MASS & ENERGY BALANCES

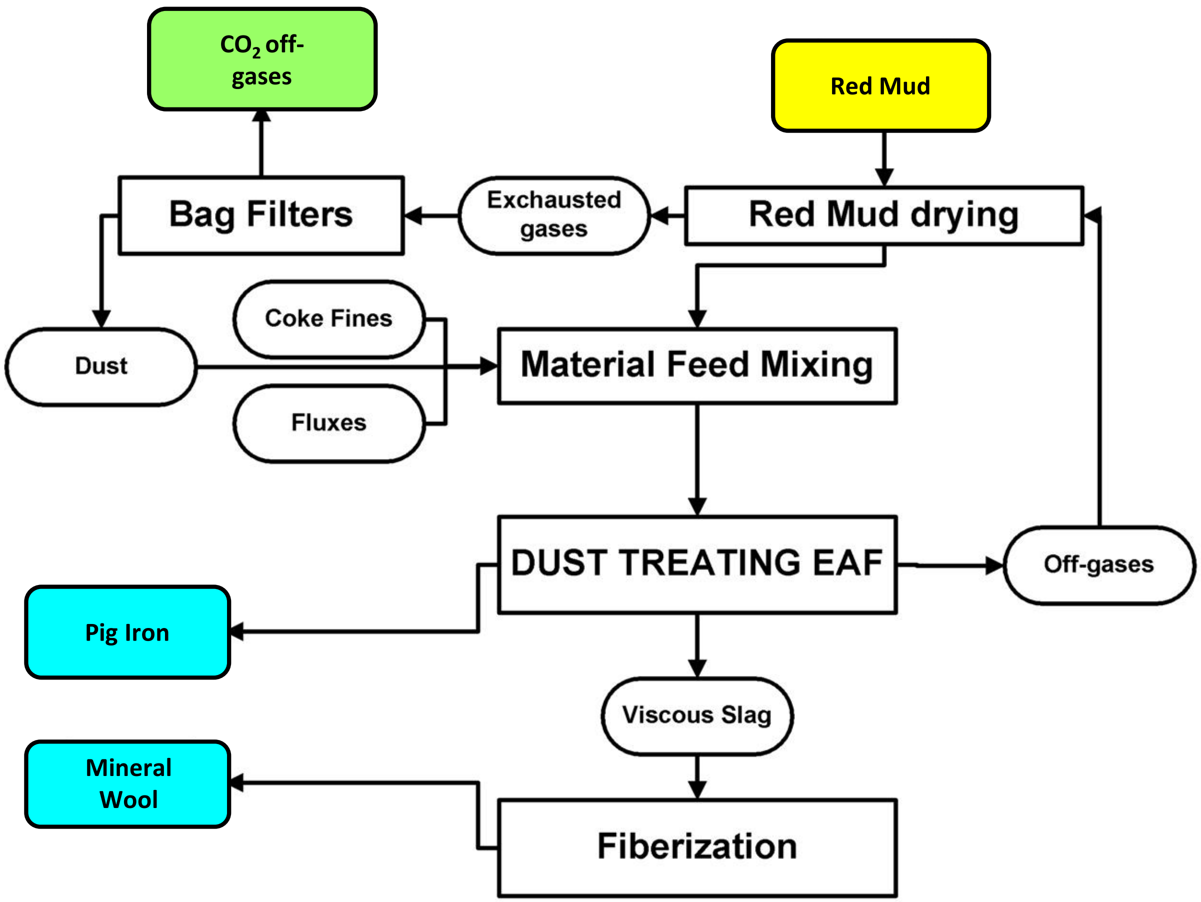



| Chemical Species | %wt (dry basis) |
|---|---|
| $Fe_2O_3$ | 47.74% |
| $Al_2O_3$ | 16.22% |
| $CaO$ | 10.73% |
| $SiO_2$ | 6.09% |
| $TiO_2$ | 5.93% |
| $Na_2O$ | 2.51% |
| $V_2O_5$ | 0.21% |
| $-SO_3$ | 0.60% |
| $-CO_2$ | 1.63% |
| $H_2O$(cry) | 8.35% |

**RED MUD IS A VALUABLE BY-PRODUCT AND NOT A WASTE**

# CONCEPT FOR RM VALORIZATION






Resource for Pig-Iron Production

# Innovations in Primary Aluminum Production

RED MUD VALORIZATION

## PILOT SCALE TESTING

1MVA dust treating AC EAF with 1 ton Batch Capacity

Melt Spinning Fiberizing Line

25 tons of RM has been treated

## PRODUCTS EVALUATION – PIG IRON

| Pig Iron | %w/w |
|---|---|
| Fe (%wt) | 93.44 |
| C (%wt) | 4.59 |
| S (%wt) | 0.07 |
| P (%wt) | 0.22 |
| Si (%wt) | 1.12 |
| Cr (%wt) | 0.50 |
| Total | 99.94 |

Used in Secondary Steel Industry as 21% w/w substitution of Steel scrap

White Iron Grinding Balls

# Innovations in Primary Aluminum Production

RED MUD VALORIZATION

## PRODUCTS EVALUATION – MINERAL WOOL

| wool | %w/w |
|---|---|
| $Fe_2O_3$ | 1.1 |
| $SiO_2$ | 26.5 |
| CaO | 23.4 |
| $Al_2O_3$ | 31.1 |
| $Cr_2O_3$ | 0.1 |
| MgO | 8.3 |
| $TiO_2$ | 6.1 |
| $Na_2O$ | 1.8 |

**Wool of excellent quality**

- ❑ $\lambda$ = 0,034 W/m.K
- ❑ Mean Fiber Diameter 7 μm
- ❑ Bright white color (low Mn content)
- ❑ High Mechanical resistance due to high $TiO_2$

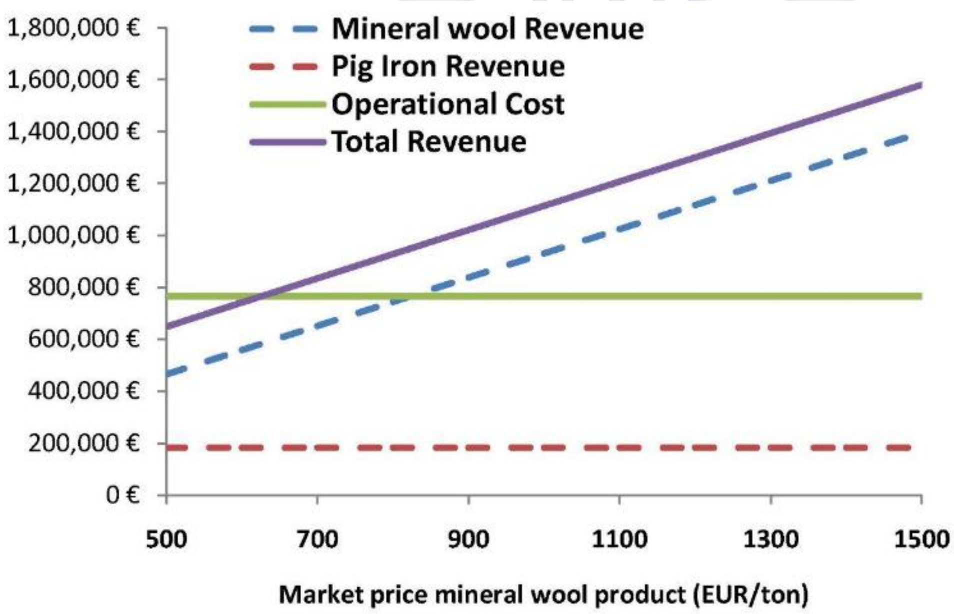
Industrial pipes insulation

# Innovations in Primary Aluminum Production

RED MUD VALORIZATION

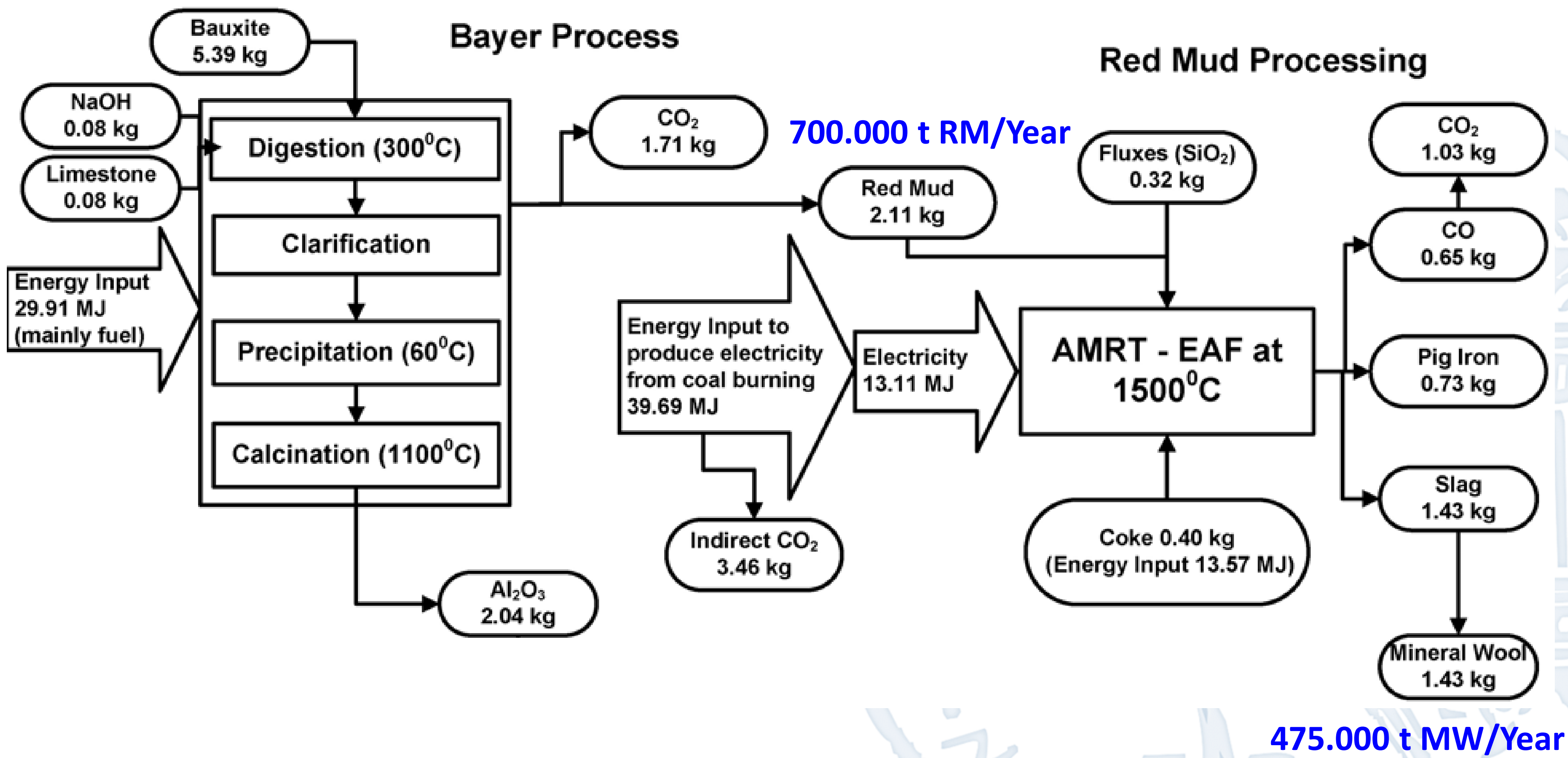
## PROCESS ECONOMIC EVALUATION

- 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)



# Innovations in Primary Aluminum Production

## The new bayer process




**IS MORE RESOURCE EFFICIENT AND SUSTAINABLE PROCESS**

# Current NTUA research activities on Bauxite residue.

eu 57-71 Rare sustainable exploitation

Developing a sustainable production of REE from European primary and secondary resources

EU MSCA-ETN REDMUD

European Training Network for Zero-Waste Valorisation of Bauxite Residue (Red Mud)

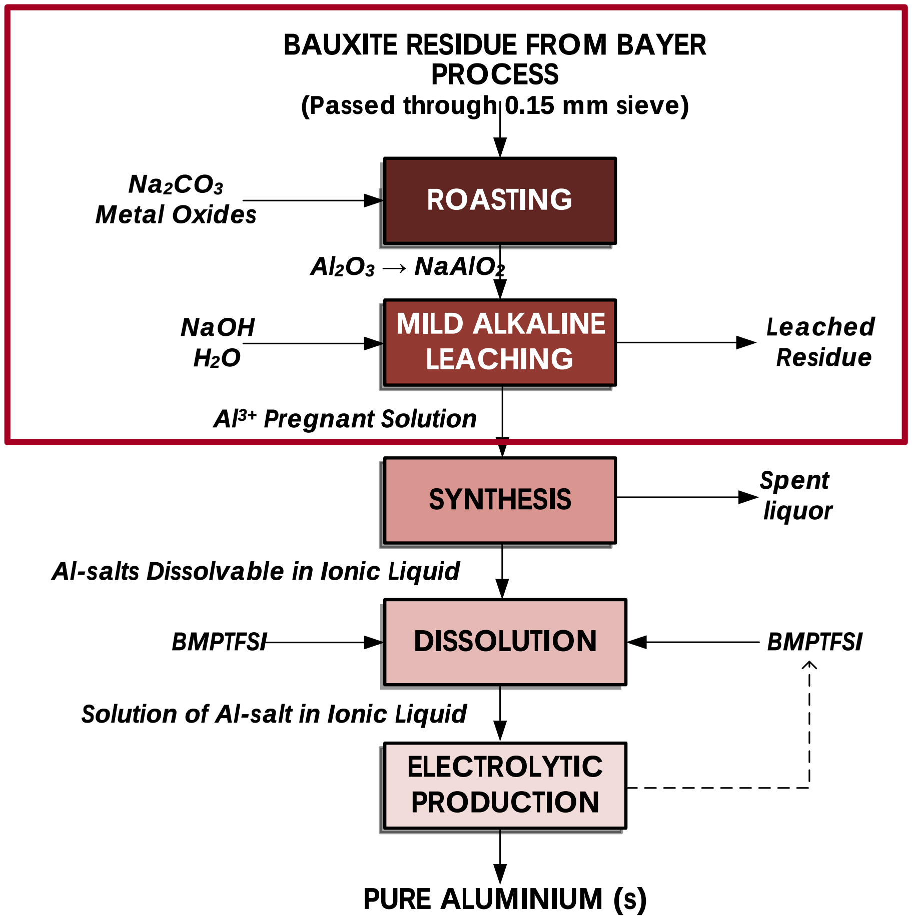
scale SCANDIUM ALUMINIUM EUROPE

Production of Scandium compounds and Scandium Aluminum alloys from European metallurgical by- products

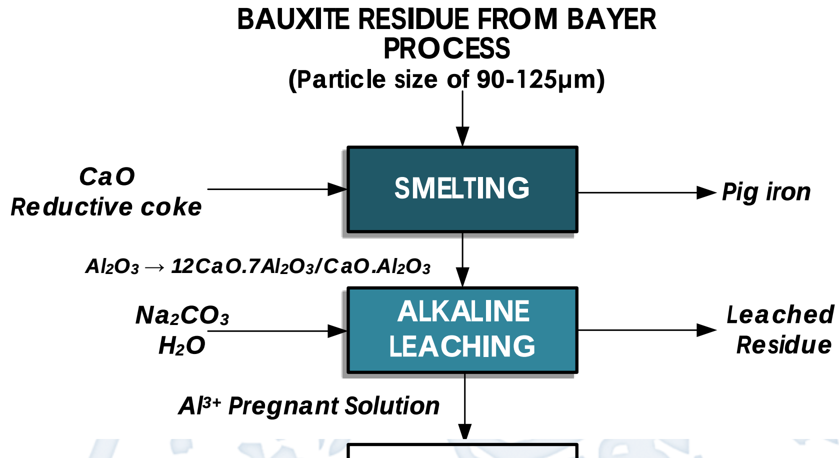
RECOVER

Red mud and Copper slag Valorisation in Engineered Products

# Recovery of aluminium from bauxite residue




## Recovery of Aluminium Species from Bauxite Residue (BR)




Identification of the aluminium minerals lost in the Bayer process in BR

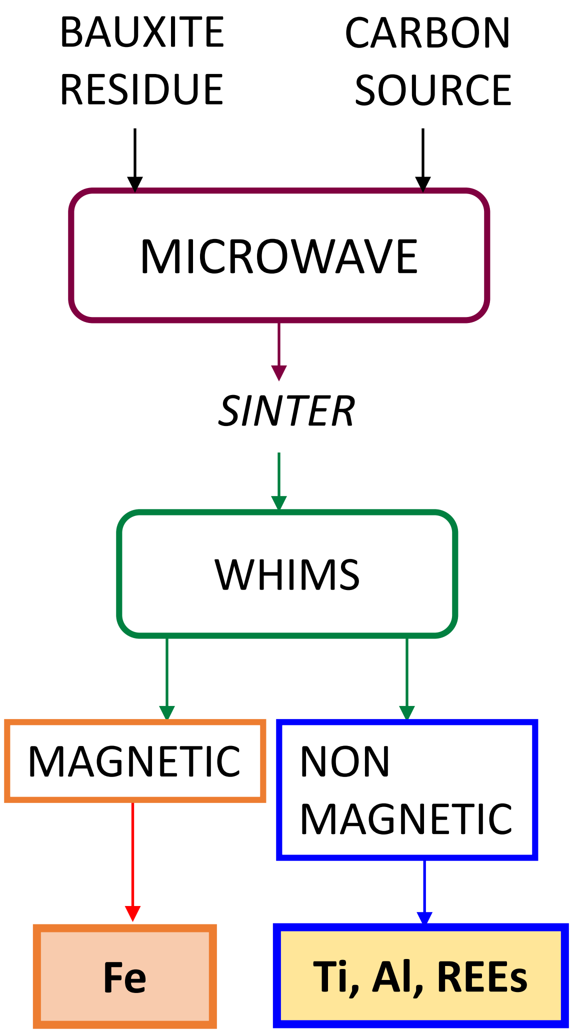
- Simple minerals: Gibbsite, Boehmite, Diaspore,
- Complex minerals: Hydrogarnet and Cancrinite (via desilication step of Bayer route)

<u>Soda Sintering Process</u>

- Sintering of soda and mild caustic leaching proposed to recover aluminium from bauxite residue.
- Optimisation results for 900°C sintering **up to 70% Al recovery (14% Si)** at 50% excess reagent or more with **leachable solid solution in Na-Al-Si phases formed** (Confirmed by Bruckard et al 2010)

# Iron oxide removal from Bauxite Residue through microwave roasting and magnetic separation

EU MSCA-ETN REDMUD

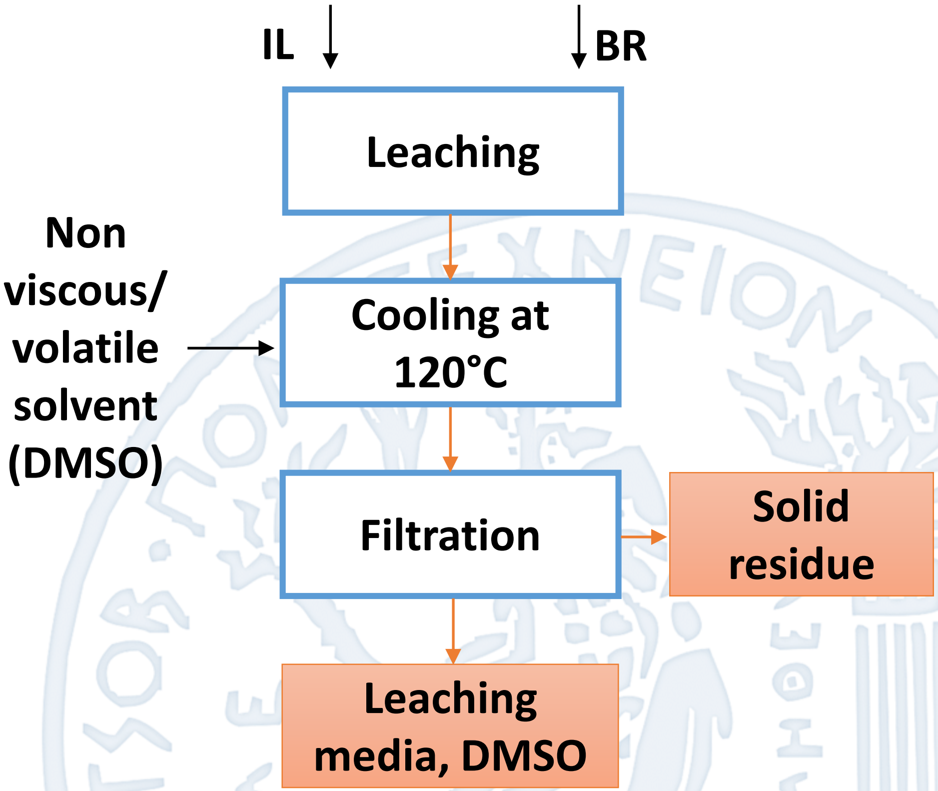



- ✓ **0.6 KW** are used to roast **10 g** of BR mixed with a carbon source by microwave radiation;
- ✓ hematite ($Fe_2O_3$) and goethite (FeOOH) are totally reduced after **3 minutes** to iron magnetic phases, allowing a magnetic separation of the Fe content through wet high intensity magnetic separator (WHIMS);
- ✓ the residue from microwave carbothermic reduction is enriched in Ti and REEs.

# Ionic Liquid leaching for reactive metals (Ti, Sc, REEs) recovery

EU MSCA-ETN REDMUD

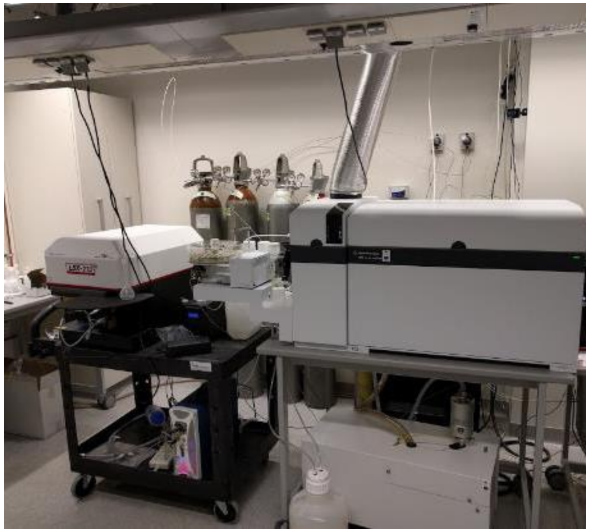

- Development of a leaching process to dissolve metals from BR by using the hydrophilic ionic liquid Emim[$HSO_4$] ;
- High recovery yields of Sc, Ti and Fe (75, 90 and 100%wt. respectively), almost 100%wt. of Si and Ca and 70% of Al and Na remain in the residue after leaching.

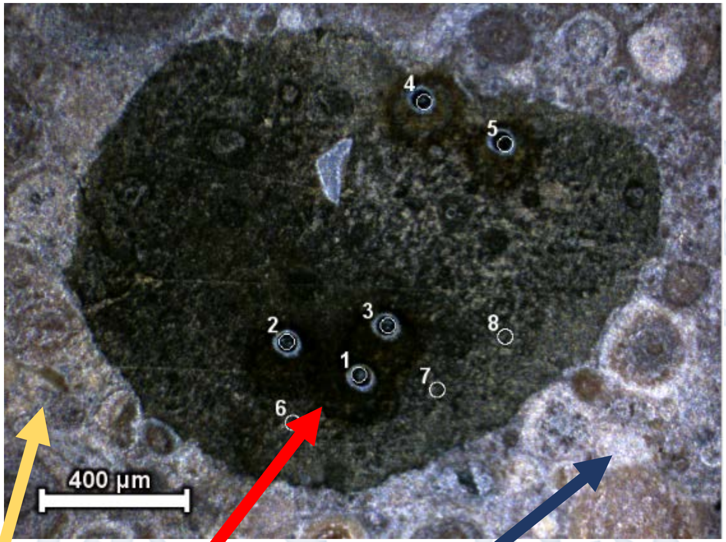


EU MSCA-ETN REDMUD

# Scandium/REE occurrence modes in bauxite

Laser ablation ICP-MS in-situ measurements demonstrate the close correlation of **iron** oxide phases with **scandium** in Greek **bauxites**

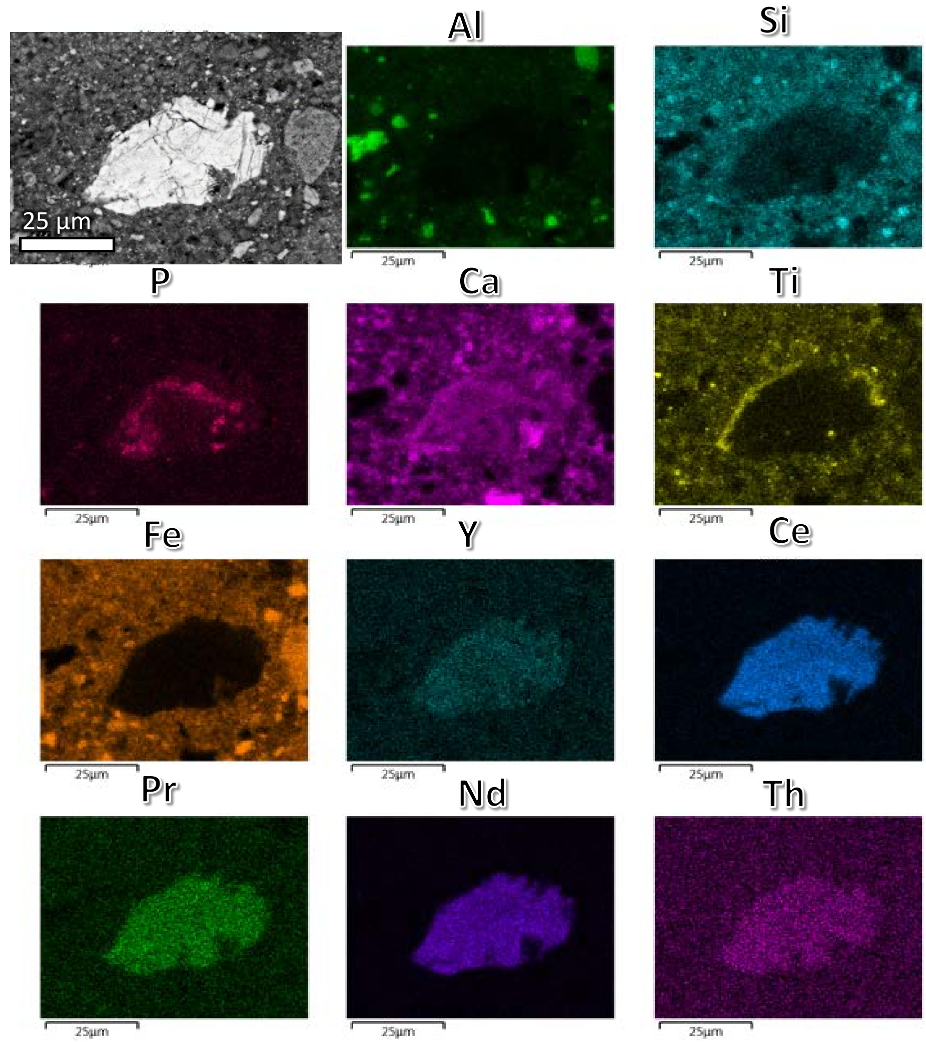





- **AlO(OH) — ~15 mg/kg Sc**
- **Hematite — ~200 mg/kg Sc**
- **Bauxite matrix — ~50 mg/kg Sc**

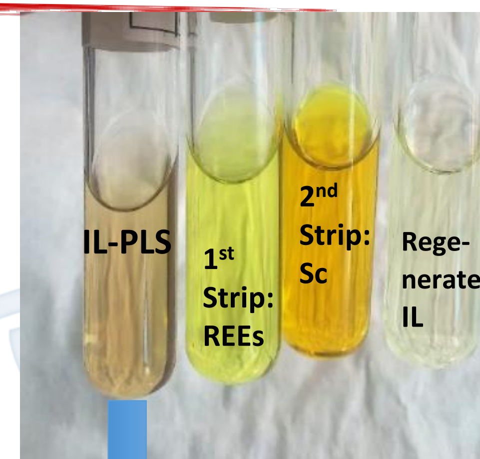
# Scandium/REE occurrence modes in bauxite

- Surprisingly large mineral grains
- Various occurrence modes
  - Primary, inherited from bauxite
  - Secondary, created during the Bayer process
- Light and heavy rare earth phases

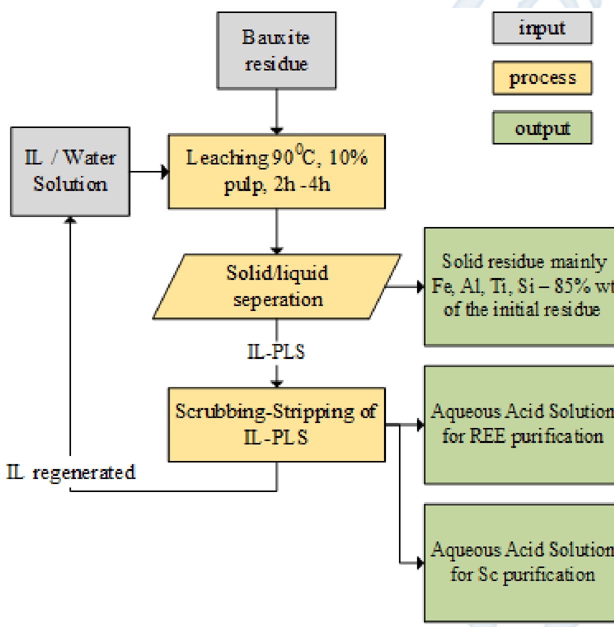


# Selective leaching of Sc/REE with Ionic liquids

- Selective recovery of REEs against Fe, Si, Ti
- The structure of the IL remains intact from the whole process of leaching and regeneration
- **Aqueous Strip solution produced is suitable for Sc extraction** (Sc up-concentrates 8-12 times from the IL-PLS)
- Pilot Scale tests under way for multiple cycles of IL regeneration

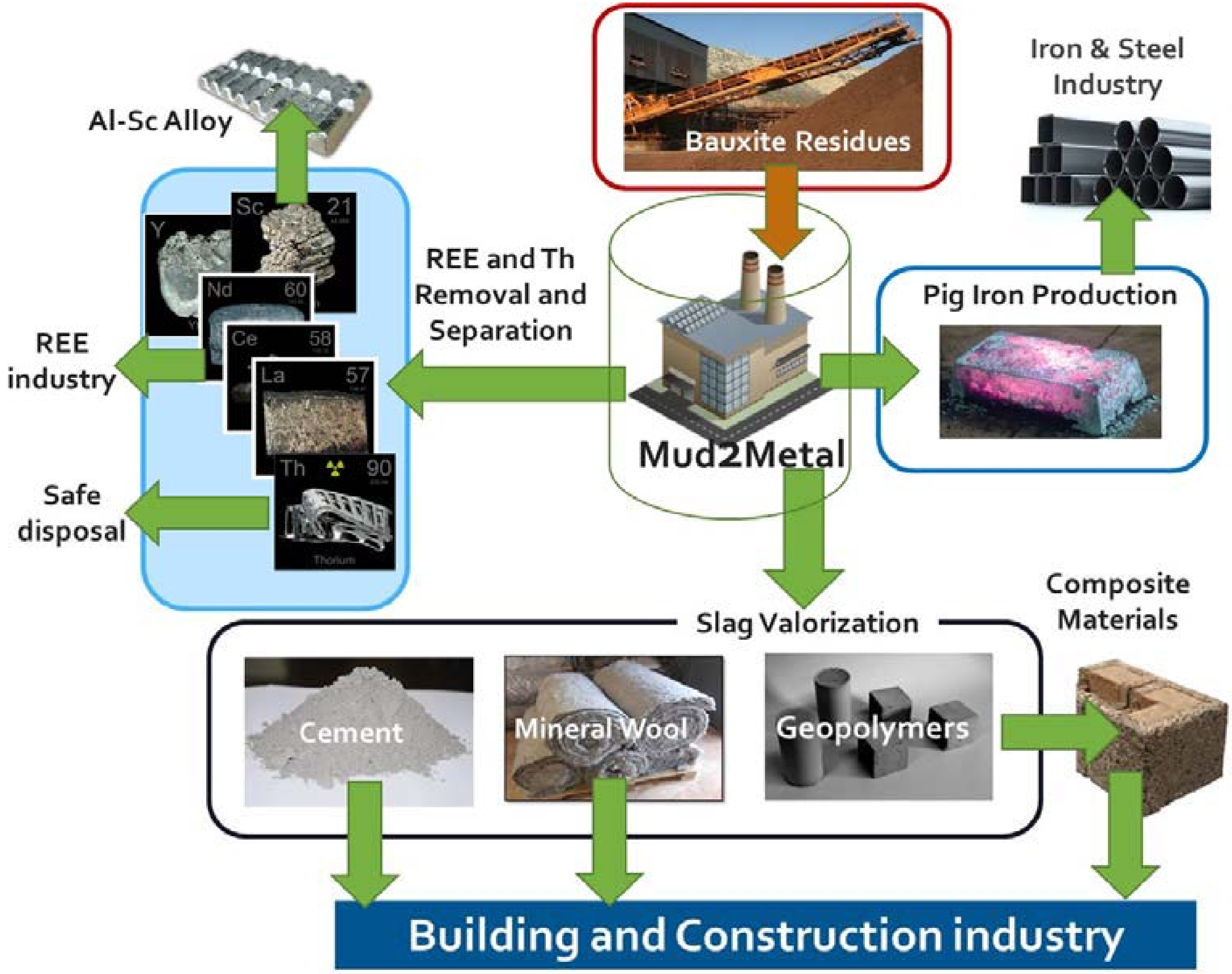



**IL-PLS contains 60-80% BR's REE, 30% of Al and 4% of Fe, almost 100% Ca and Na**

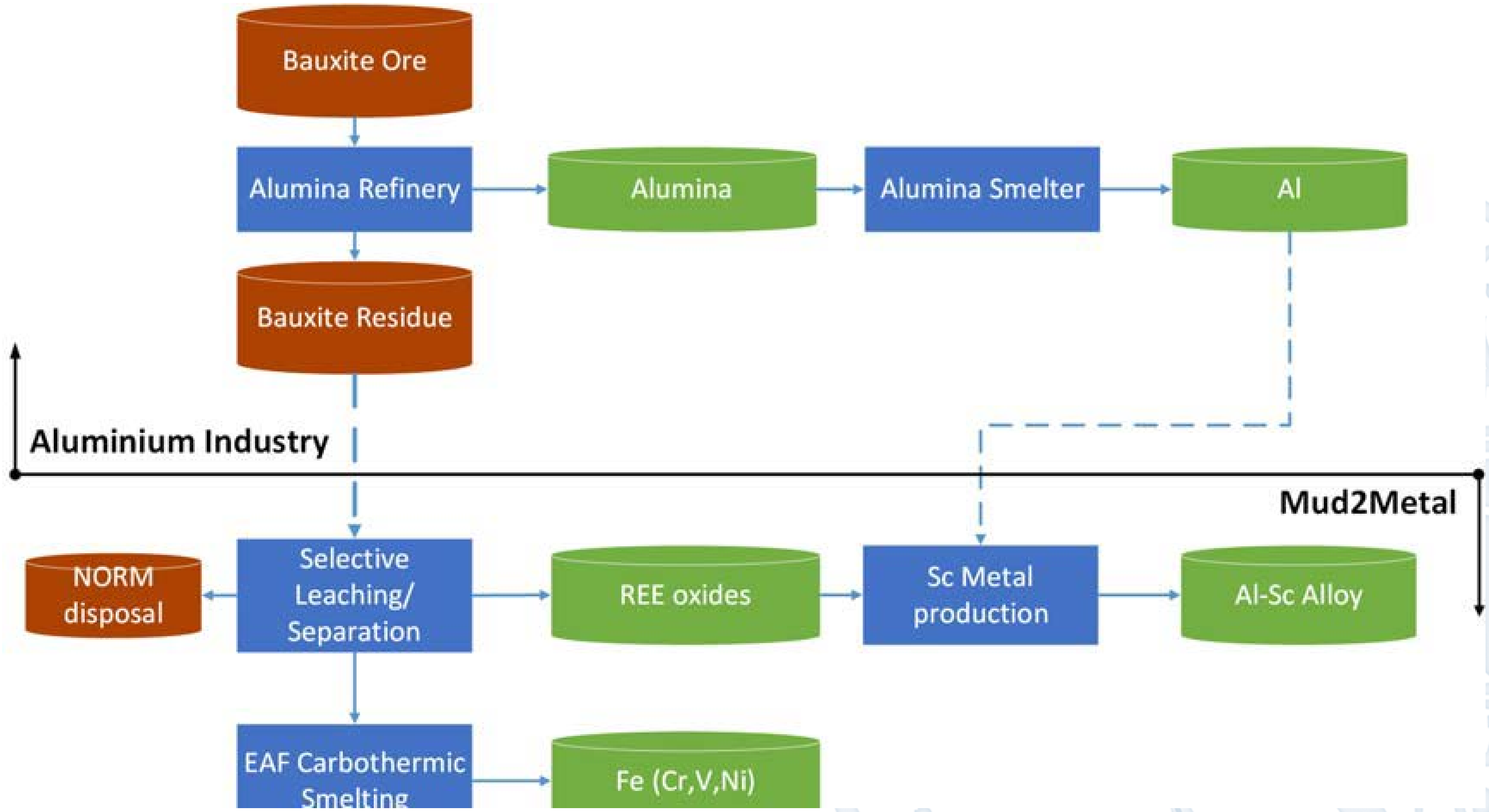



**Solid Leach residue BR² contains 56% Iron oxides, 12% alumina, 7% titania and 6% silica**

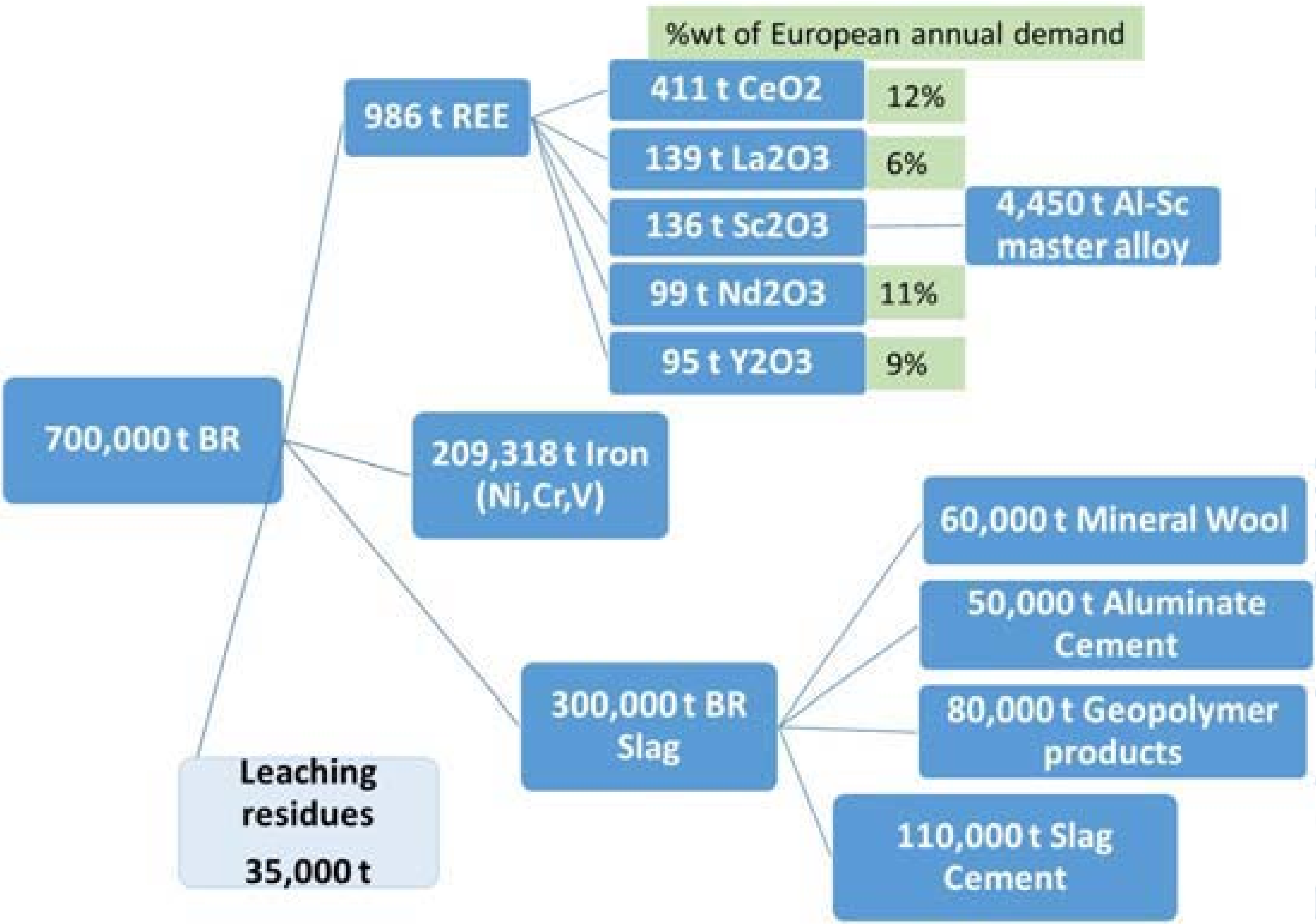
# Mud2Metal Approach



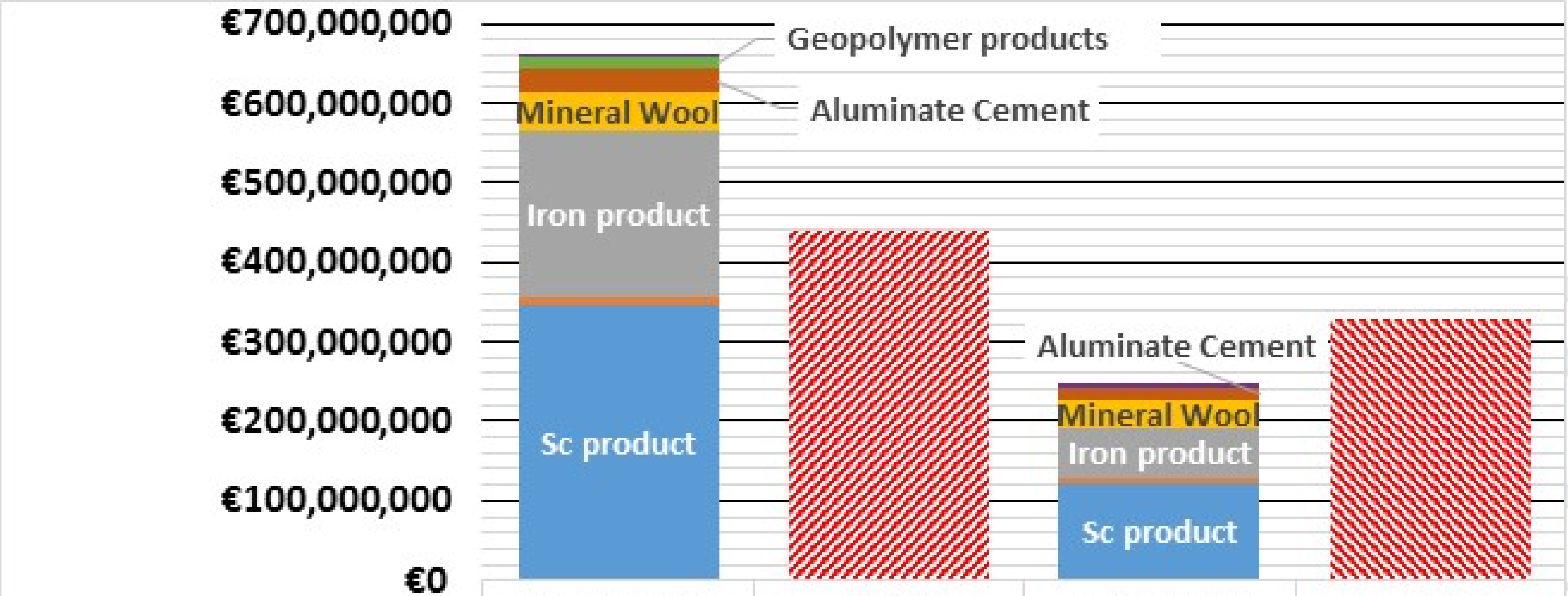
# The Future Greek Aluminum Industry



# The Mud2Metal Target



# The Economy




| | Optimistic | OPEX | Pessimistic | OPEX |
|---|---|---|---|---|
| Operational Cost | | €438,480,000 | | €329,000,000 |
| Slag cement | €2,200,000 | | €3,800,000 | |
| Geopolymer products | €16,000,000 | | €- | |
| Aluminate Cement | €30,000,000 | | €15,000,000 | |
| Mineral Wool | €48,000,000 | | €36,000,000 | |
| Iron product | €209,318,000 | | €62,795,400 | |
| REOs | €8,756,457 | | €6,373,154 | |
| Sc product | €347,134,788 | | €122,843,381 | |

# THE ENEXAL BAUXITE RESIDUE TREATMENT PROCESS

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## Novel Technologies

**for enhanced energy and exergy efficiencies in primary aluminium production industry**

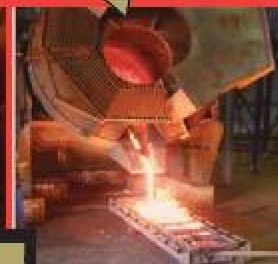
The ENEXAL research project is co-financed by the European Commission in the Seventh Framework Programme (FP7), under the cooperation theme: [FP7-ENERGY-2009-2] / Energy efficiency in energy intensive industry

The Bayer process for the production of metallurgical alumina requires on average globally 2.7 kg of bauxite ore to produce 1 kg of alumina, while the remaining amount of the ore is removed from the process as a red slurry. This by-product, called Bauxite Residue (BR consists of various metal oxides like Fe, Al, Ti, Si, Na, Ca, V and others. On a global scale BR amass to a total of 150 million tonnes annually.Due the lack of an economically viable processing method all BR are currently disposed in artificial ponds or landfills, resulting both in brownfield land creation and mineral resource squander.

Through EAF carbothermic smelting the BR are fully converted into two marketable products: pig iron and mineral wool. The pig iron is used in the secondary steel industry as a steel scrap substitute, while the mineral wool can be used for the production of variety of thermo-acoustic insulating products used in the construction and manufacturing industry.
No solid or liquid by-products are produced in the process, and thus in conjunction with the alumina refinery plant, complete exploitation of the bauxite ore can be achieved.
This novel process has been applied for more than a year in AoG's industrial scale pilot plant housing a 1MVA EAF and a melt fiberizing line.

1

Dry Bauxite Residues (BR) are treated with carbon and fluxesin Electric Arc Furnace (EAF)

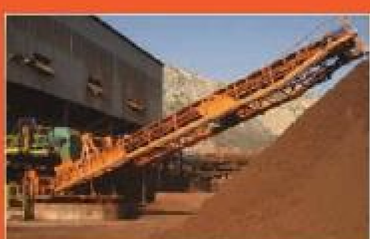


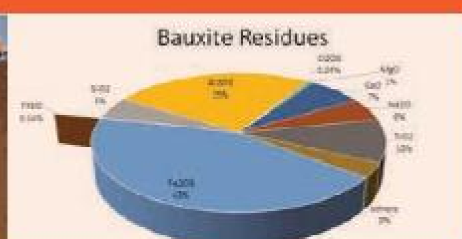
2

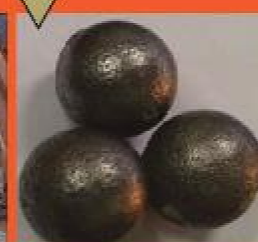
An aluminasilicate slag and pig-iron metal phase are produced

3

The slag is fiberized in-situ, producing mineral wool insulation products





4

The metal is cast in ingots and used in secondary steel mills

**25 tons of BR have been treated in ENEXAL producing 5 tons of pig iron**

57-71

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SLU

GTK

NGU Norges geologiske undersøkelse Geological Survey of Norway

brgm Geoscience for a sustainable Earth

British Geological Survey NATURAL ENVIRONMENT RESEARCH COUNCIL

Kemakta Konsult AB

Outotec

MEAB

LCM less common metals

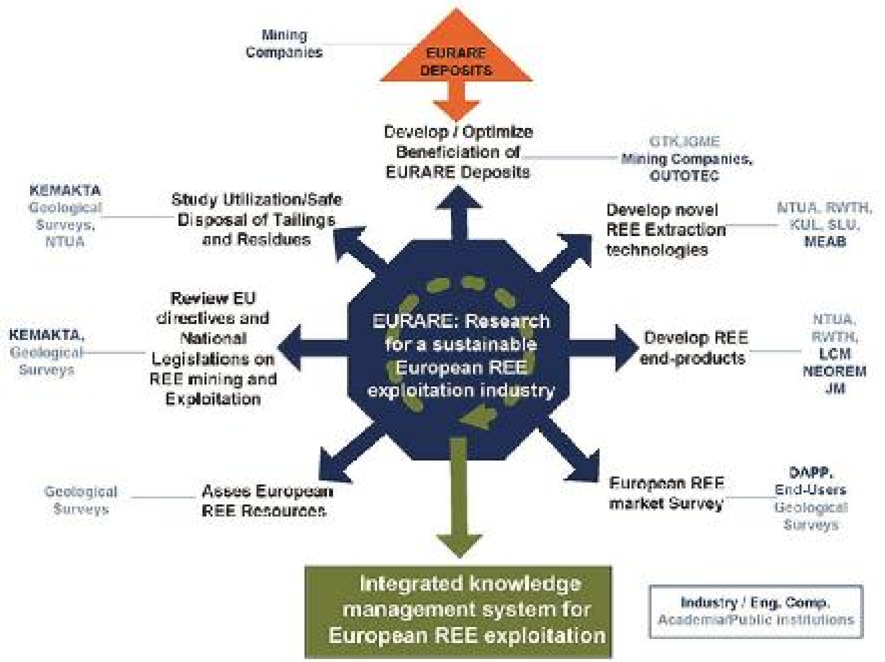
JM Johnson Matthey

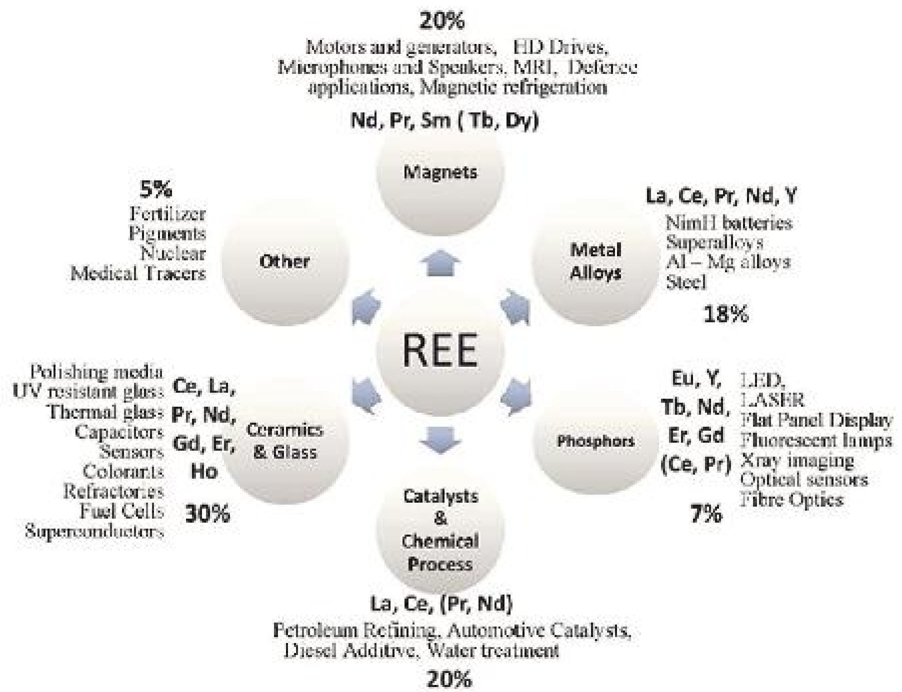
TANBREEZ

SGU Sveriges geologiska undersökning Geological Survey of Sweden

The EURARE project has received funding from the European Community Seventh Framework Programme ([FP7 / 2007 2013 ]) under grant agreement num. 309373. This publication reflects only the author view exempting the Community from any liability

SEVENTH FRAMEWORK PROGRAMME




The rare-earth metals or elements (REEs) are a unique group of chemical elements that exhibit a range of special electronic, magnetic, optical and catalytic properties. They have hundreds of applications. Their use in components manufactured from a wide range of alloys and compounds, can have a profound effect on the performance of complex engineered systems.
App. 300 kg of REES are needed for a 3.5 MW wind turbine, 1 kg are needed for 1 hybrid car, and 2.4 g of REEs are needed for one laptop computer.

The REE are found in a wide range of minerals, including silicates, carbonates, oxides, and phosphates. Around 270 minerals are known to contain the REE as an essential part of their crystal structure, but only a small number are ever likely to have commercial significance. The majority of production has come from a small number of minerals, most importantly bastnäsite, monazite, and xenotime with China in Bayan Obo being the world's main producer of REE.
With numerous European industries heavily depended on imported REE raw materials, there is a need for EU to secure a viable supply of REE minerals as well as develop from the ground up the currently non-existent

European REE extraction and processing industry. The goals of the EURARE project are:

› To characterize the potential REE resources in Europe.

› To research, develop, optimize and demonstrate technologies for the efficient and economically viable exploitation of currently available European REE deposits with minimum consequences to the environment.

In the EURARE project, the mineral processing technologies currently used for the REEs minerals will be investigated for representative European REE ores, with a tendency for improvement by adopting new approaches for the complete ore utilization and minimal environmental consequences, establishing integrated mineral processing systems, with zero or close to zero tailings.

The current state-of-the-art processes for REE extraction follows complicated, energy and resource intensive technologies. The EURARE project aims in developing novel cost-effective and resource-efficient REE extraction process, tailored specifically for European REE ore deposits as well as for European health, safety and environmental protection standards.

The main goal of the EURARE project is to set the basis for the development of a European REE industry that will safeguard the uninterrupted supply of REE raw materials and products crucial for the EU economy industrial sectors, such as automotive, electronics, machinery and chemicals, in a sustainable, economically viable and environmentally friendly way.

For more information about our work please visit us at **www.eurare.eu**