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Unlocking the Potential of Metallurgical By-Products: A Comparative Exergy Analysis of Emerging Valorization Techniques

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ntua

technologies for sustainable metallurgy

Research group operating within the **Laboratory of Metallurgy** of the **National Technical University of Athens**, under the supervision of Prof. Panias.

Participation in EU Horizon 2020 and KIC EIT Raw Materials projects, in the field of:

- Base (Al, Fe, Cu) and Less common Metals (Sc & REEs, Ga, V) production with alternative processes and raw materials
- Valorization of industrial by-products (BR, Calcium aluminate slags, Fe-Ni slags, Fly ashes, MG-Si slags)
- GHG emissions friendly metallurgical processes (metallothermic reductions, electrometallurgical extraction)
- Novel inorganic & Cementitious materials (geopolymers, SCMs etc.)

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Assessment tools for developing new processes - Exergy Analysis

In the pursuit of developing new technologies towards sustainability and the green transition :

- It's easy to become narrowly focused on individual and technical aspects of the process
- optimizing specific reactions, reducing energy consumption, or increasing product yields → losing sight of the "big-picture"

EXERGY → quantifies the quality and not the quantity of energy

Exergy analysis is a thermodynamic based method used to evaluate the quality of energy within a system and understand how efficiently it is being utilized.

Exergy is the amount of the maximum useful energy that can be released if a substance comes into equilibrium with its environment

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Concept of Exergy Analysis

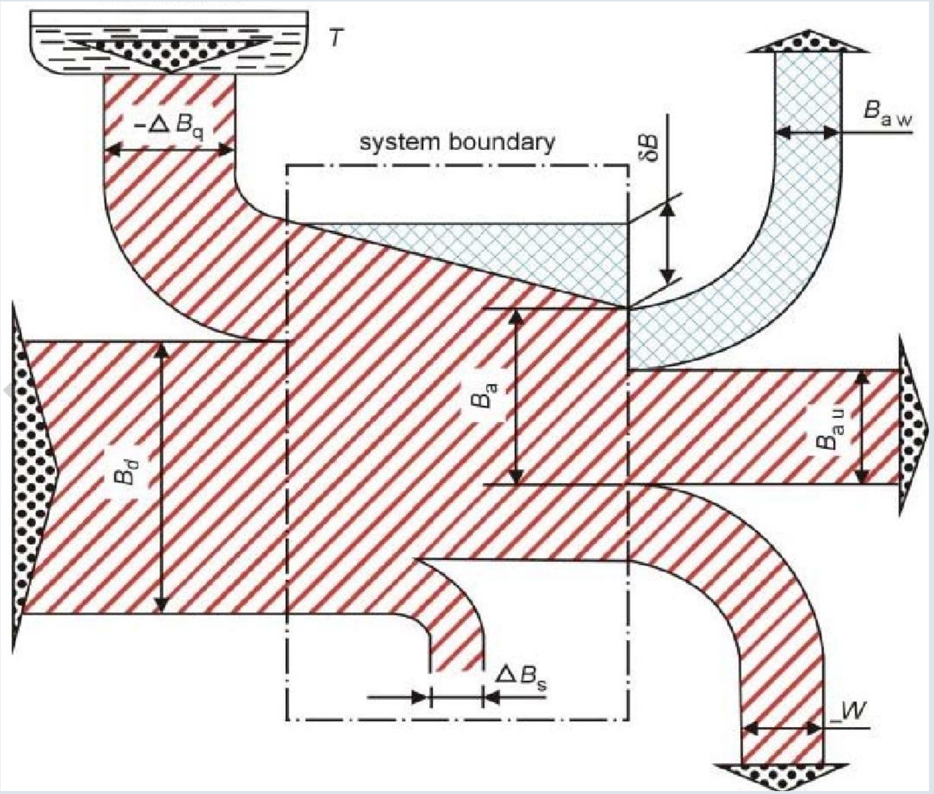
Exergy is the amount of the maximum useful energy that can be released if a substance comes into equilibrium with its environment

It helps us assess the efficiency and potential for improvement in terms of **energy consumption** and **resource utilization.**

(chemical reactions and thermal treatment)

- ✓ is a way to determine the maximum theoretical efficiency.
- ✓ identify the sources of inefficiencies and the potential for energy recovery and optimization.
- ✓ Exergy determines the contrast of a system with its environment. It helps understand the true environmental impact

Exergy balance



$$B_d = \Delta B_s + B_a + \sum \Delta B_q + W + \delta B$$

Exergetic efficiency "degree of perfection":

$$\eta_P = \frac{Exergy\ of\ useful\ products}{Feeding\ Exergy}$$

Bauxite Residue Production

The Aluminium production chain	Bauxite ore mining	Alumina Refinery	Aluminum smelter
	4 t Bauxite	2 t Alumina	1 t Aluminium

50- 60% Al_2O_3
20-30% Fe_2O_3
15% H_2O
5% Other oxides

The undissolved portion of the ore, forms the Bauxite Residue (BR) by-product

40- 45% Fe_2O_3
20-25% Al_2O_3
8-10% CaO
5-7% SiO_2
4-5% TiO_2
3-4 % Na_2O

Alumina Refinery
1.8 t Bauxite Residue

- ❑ 140 million tons of BR per year are produced globally
- ❑ 4 billion tons are already stockpiled
- ❑ Sites in Europe:
  - ❑ Greece, Ireland, Romania, France, Germany, Spain, Turkey, Bosnia Herzegovina

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Bauxite Residue Valorisation

- Stockpiling is not a solution and in some cases, not an option at all.
- Much research has been made in BR reuse:
  - Cement Industry (iron/alumina source in clinker)
  - Construction
  - Metal Recovery (Fe, Al, REEs)
- At the moment Greek BR is used for clinker substitution 1,5-3%
- Technical, Legislative, Financial and Social barriers impend wide valorisation of BR

❖ **BR centric recycling processes are needed <u>for added value products.</u>**

❖ **Multiple solutions / customers are needed to recycle the full BR produced**

RemovAL overcomes the barriers of economic viability by pooling together and integrating proposed stand-alone solutions, while adhering to the following principles:

- treat waste with waste
- recover valuable critical metals
- develop marketable products
- customise the solution to the industrial ecostystem of each alumina plant

near zero-waste processing, near break-even flowsheets

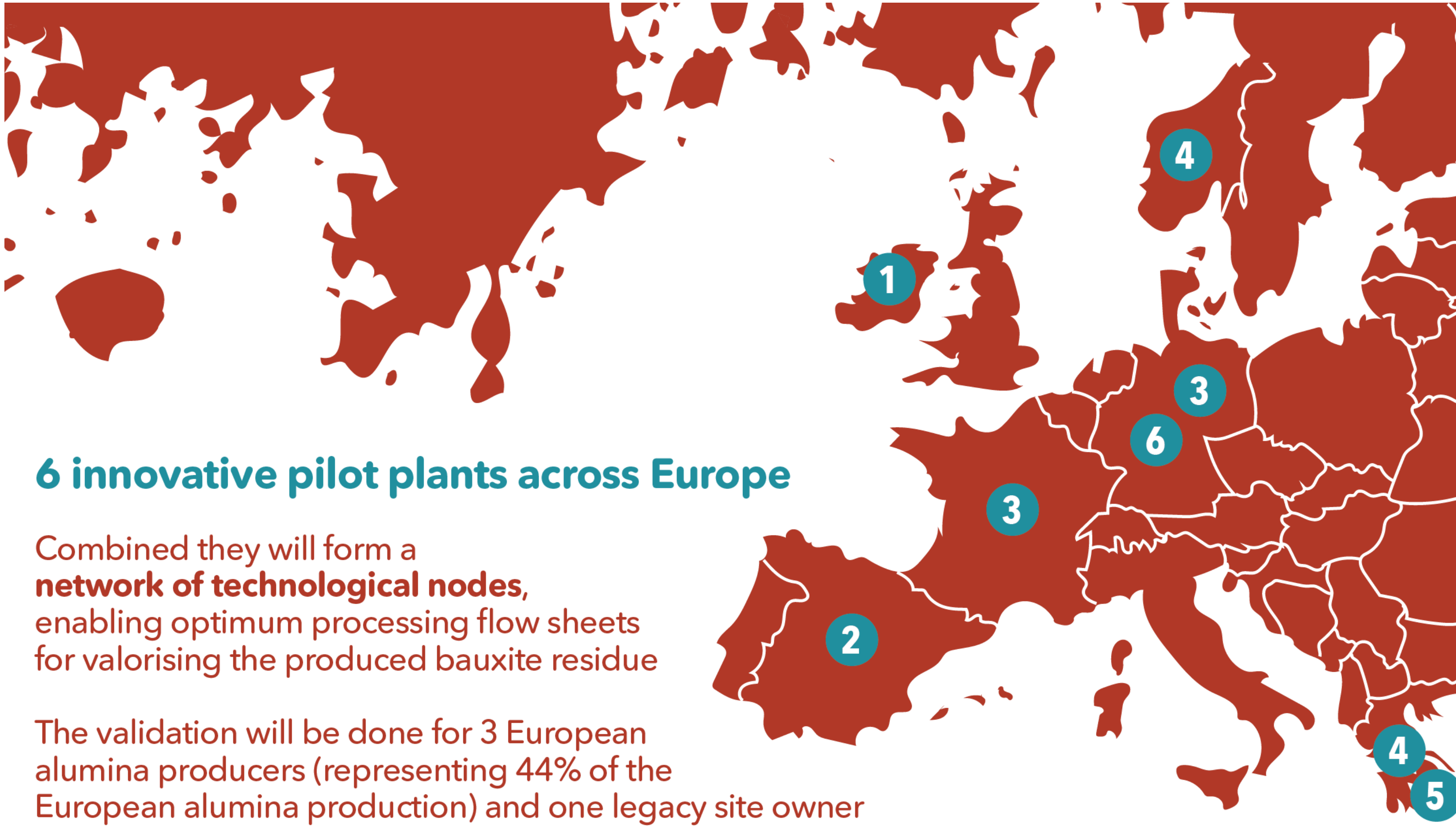
removAL

removing waste from alumina production

Processes developed and demonstrated in RemovAl

Technologies developed in removal

- Dealkalisation, removing the alkali-content
- Pig iron production
- Slag Valorisation
- REE Recovery
- Light-weight aggregates and high performance binders
- Soil-stabilizers



6 innovative pilot plants across Europe

Combined they will form a
network of technological nodes,
enabling optimum processing flow sheets
for valorising the produced bauxite residue

The validation will be done for 3 European
alumina producers (representing 44% of the
European alumina production) and one legacy site owner

- ❖ **There is not a stant-alone solution for BR treatment**

  100% reuse of BR through multiple products/process: near zero waste, near break-even, symbiotic with other industries
- ❖ **Combining process flowsheets is challenging, requires proper assessment tools**

removal
removing waste from alumina production

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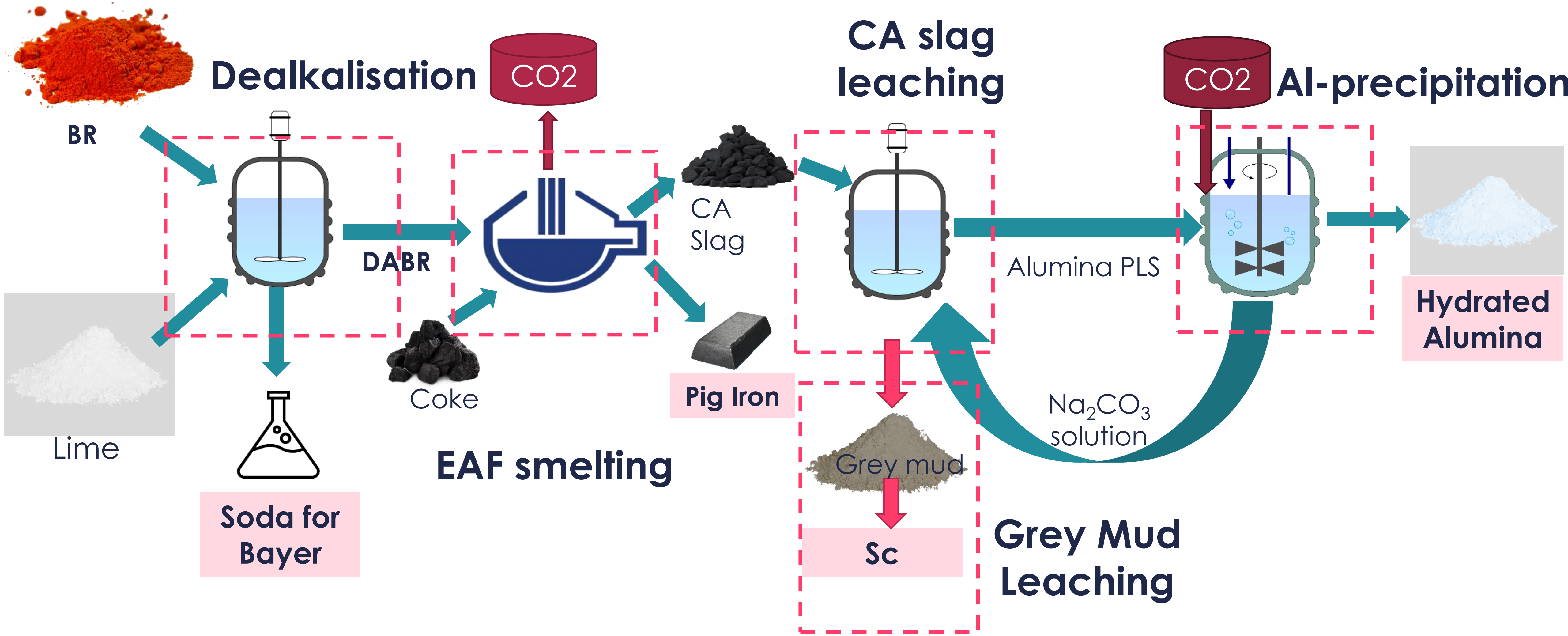
Conceptual flowsheet of complete BR valorization



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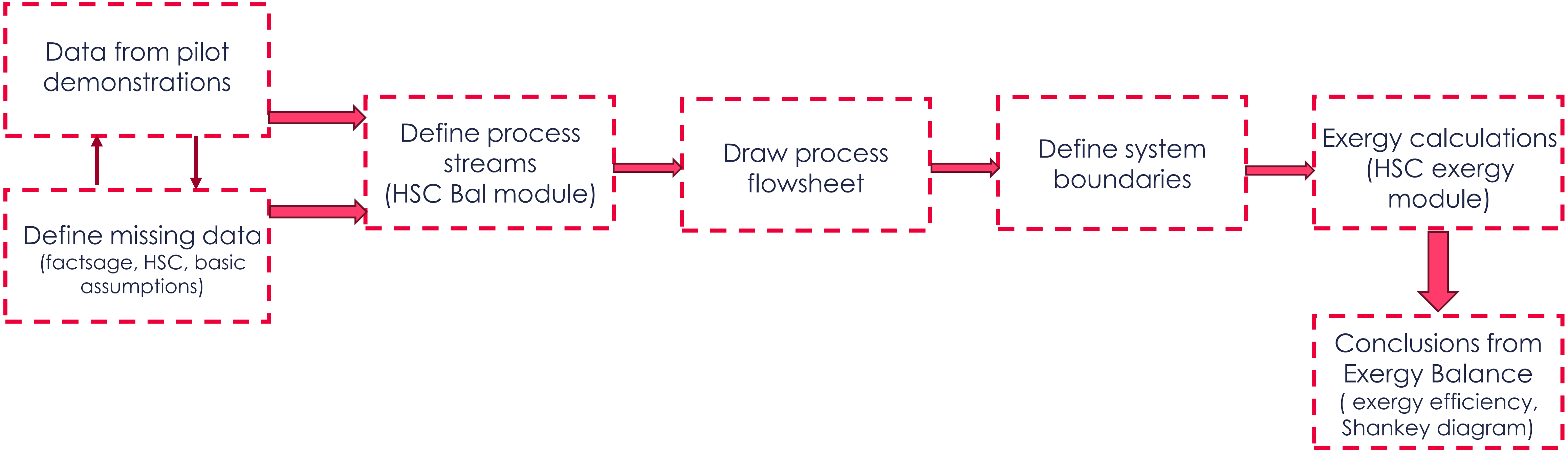
Methodology for Exergy Analysis



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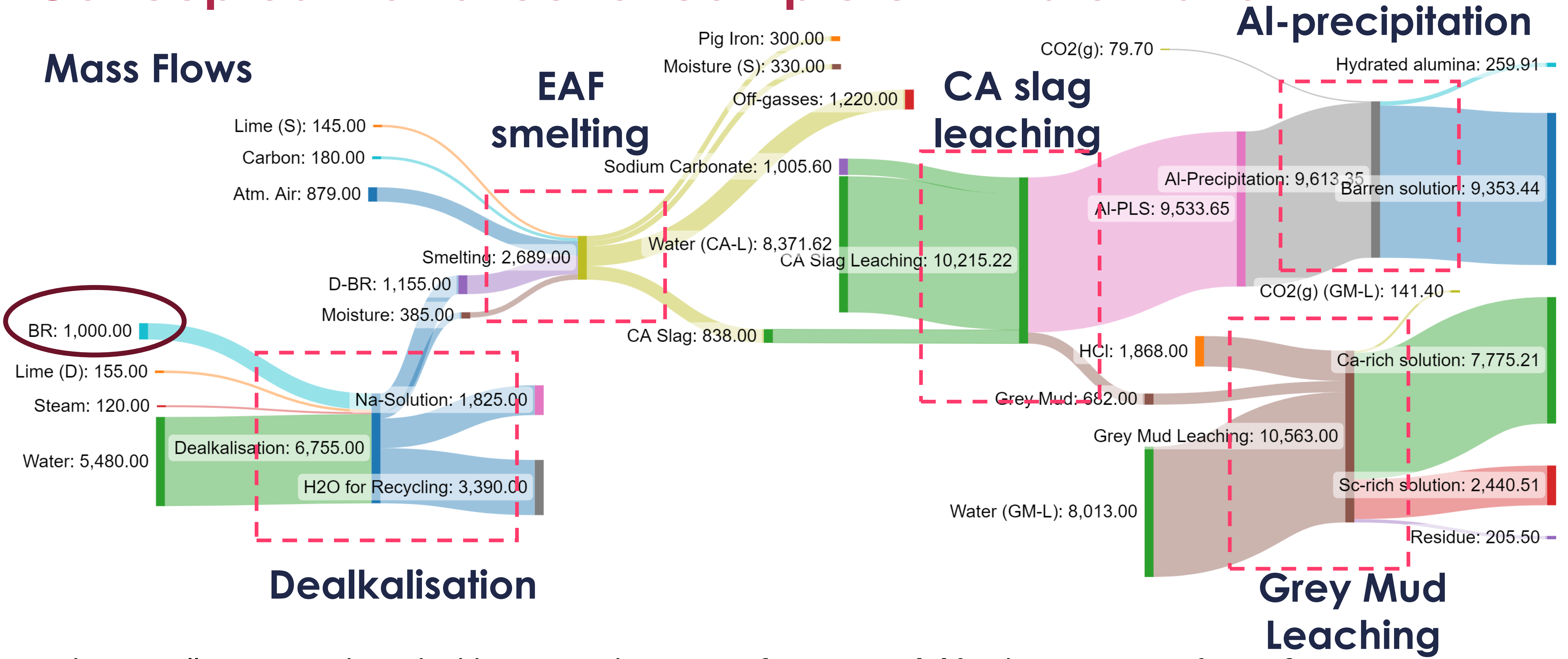
Conceptual flowsheet of complete BR valorization



- The overall resources input in this process is ***26.3tn of raw material*** for the treatment of **1tn of BR**
- 83% (21.9tn) of which is the water demand and could be significantly reduced with water recycling and the rest 17% (4.4tn) is the raw material.
- The **18.35%** come out of this process as useful products.

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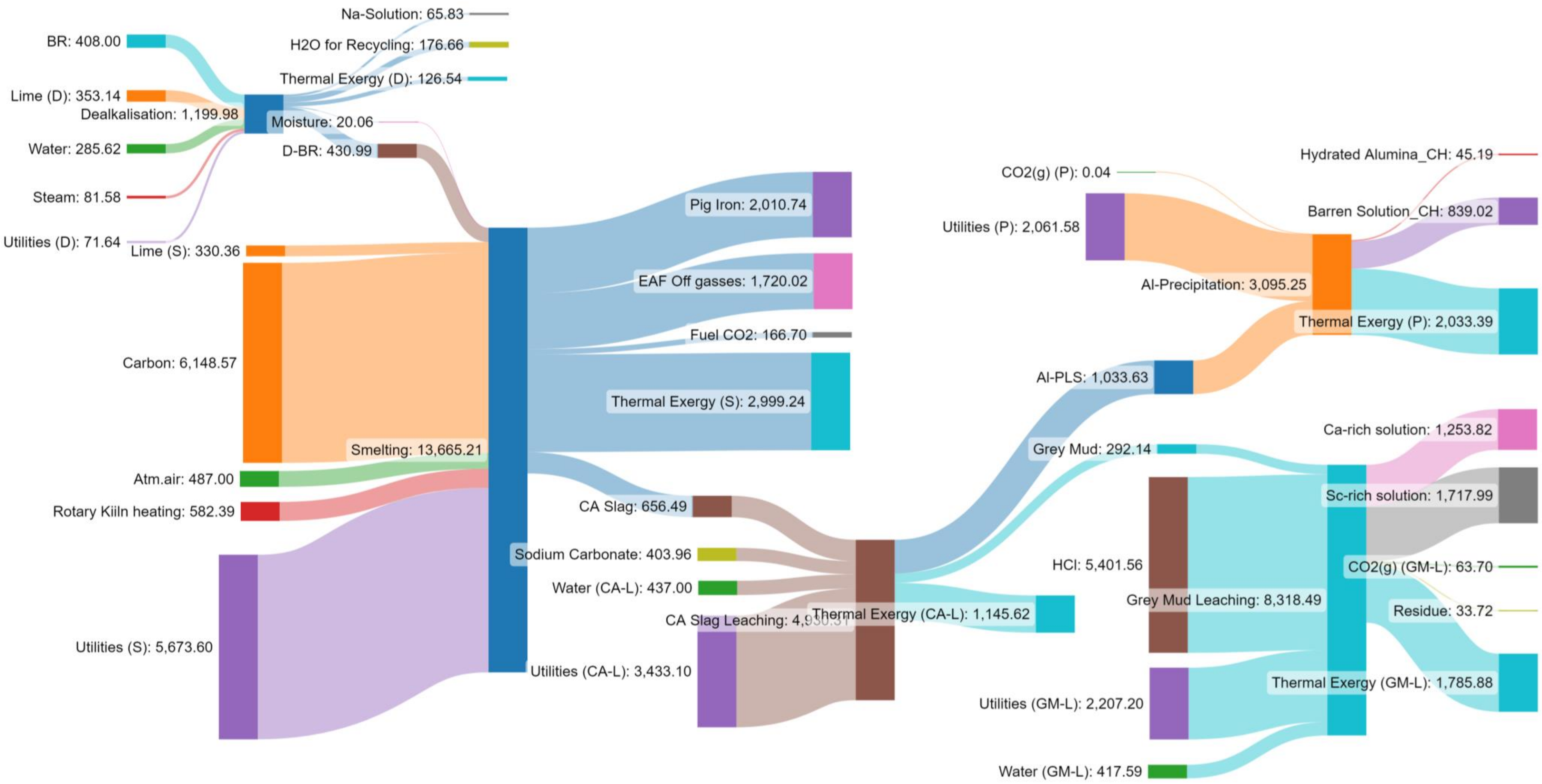
Conceptual flowsheet of complete BR valorization

Exergy Flows



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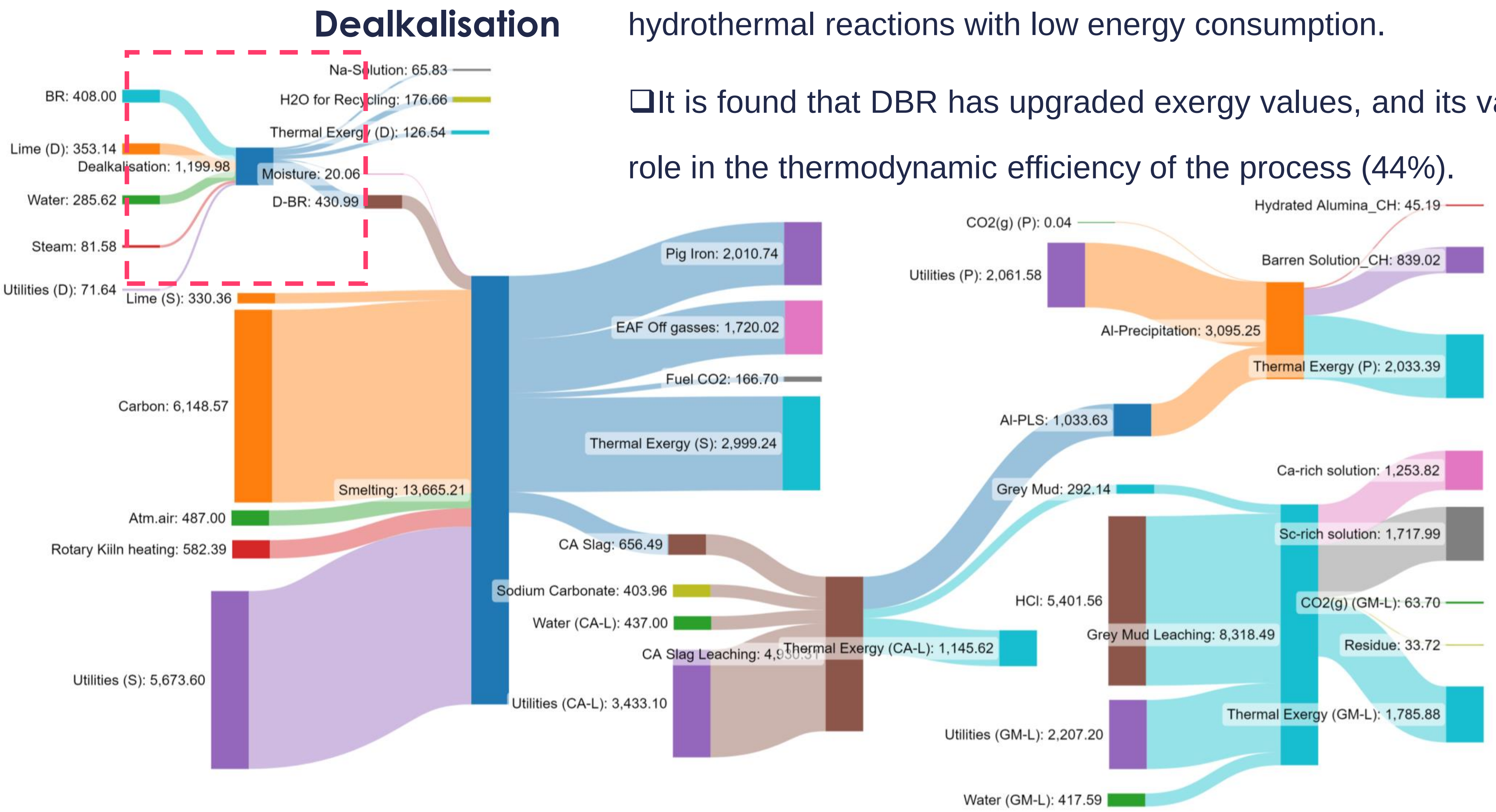
Conceptual flowsheet of complete BR valorization

Exergy Flows

❑Dealkalisation has low exergy demand (996MJ) because it is based on hydrothermal reactions with low energy consumption.

❑It is found that DBR has upgraded exergy values, and its valorization has important role in the thermodynamic efficiency of the process (44%).



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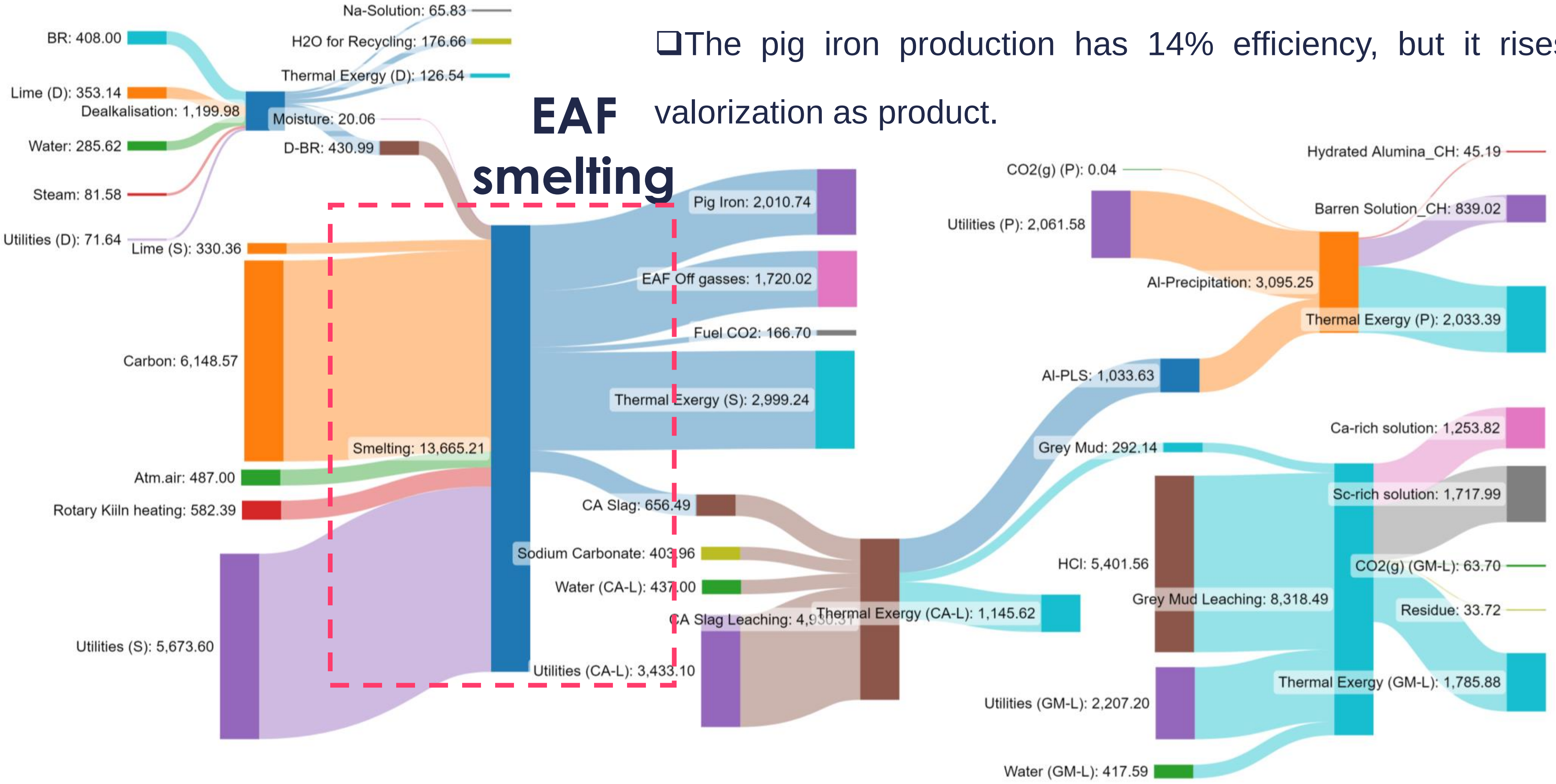
Conceptual flowsheet of complete BR valorization

Exergy Flows

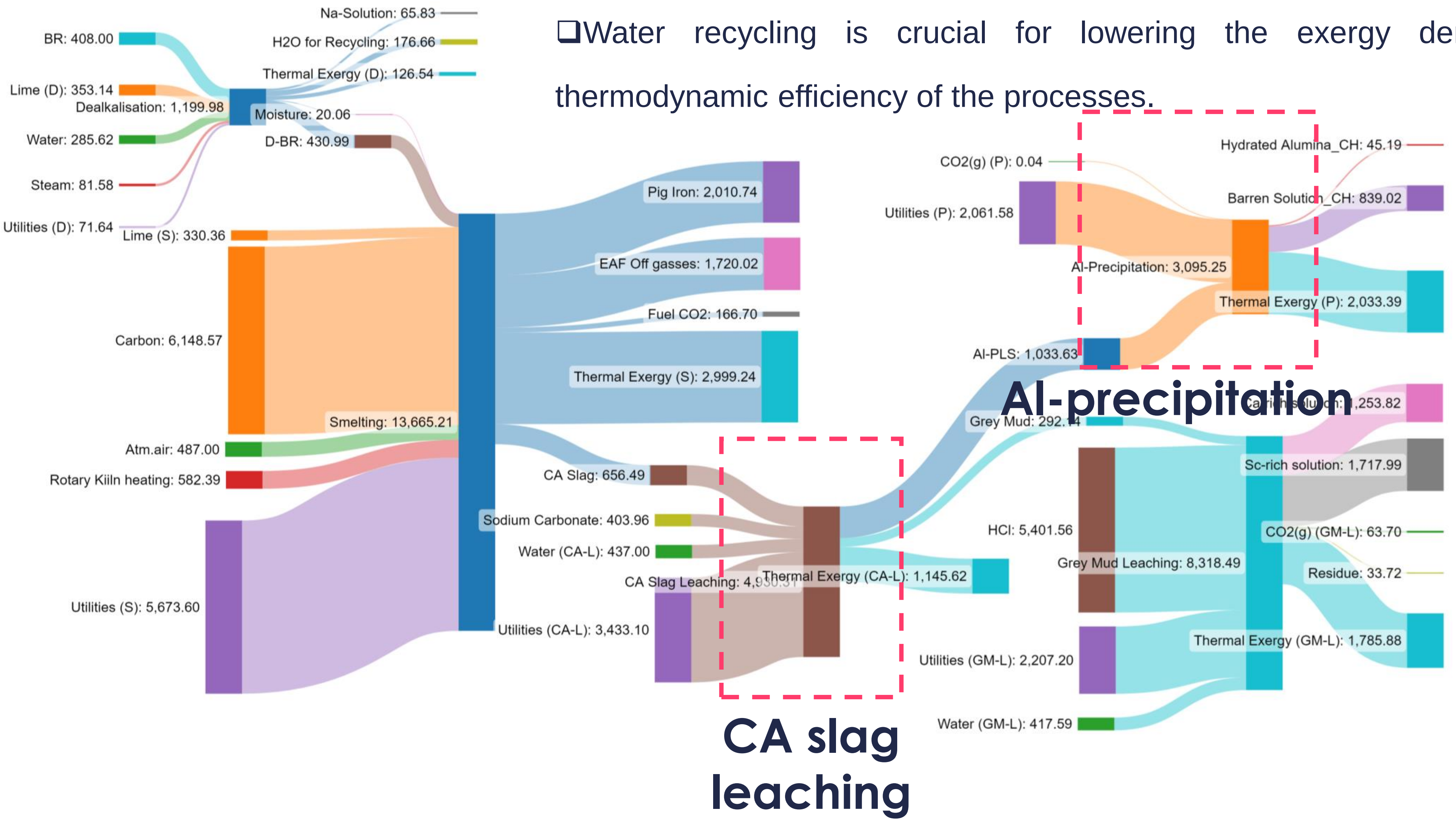
- ❑High exergy demand ~14*10^{3}MJ, which is due to the high use of carbon and electricity.
- ❑The pig iron production has 14% efficiency, but it rises 19% due to CA slag valorization as product.



Conceptual flowsheet of complete BR valorization

Exergy Flows

- ❑Alumina leaching has 20.96% exergy efficiency, while the precipitation has only 1.46% due to low thermodynamic value of the $Al(OH)_3$ product.
- ❑Water recycling is crucial for lowering the exergy demand and improve the thermodynamic efficiency of the processes.



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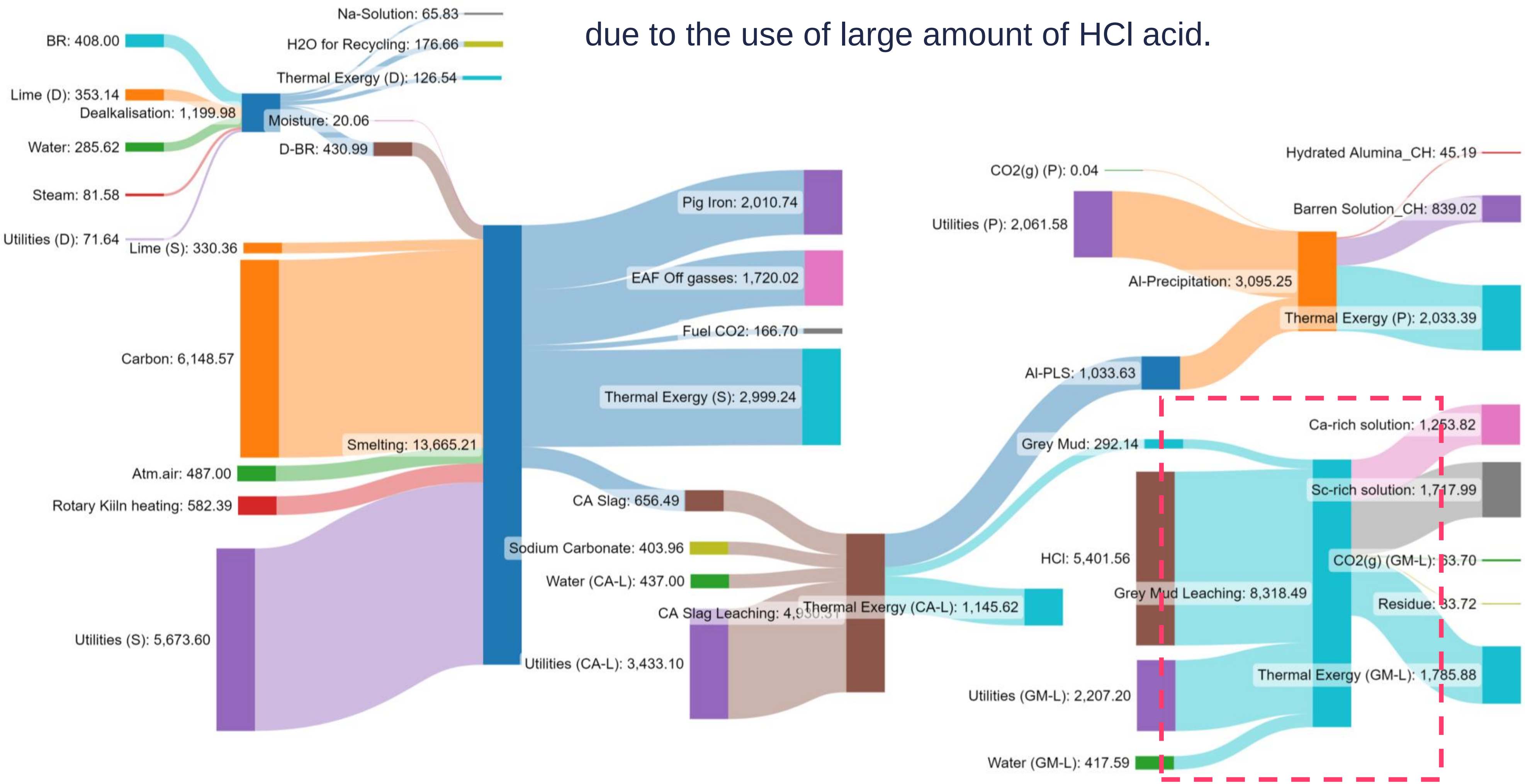
Conceptual flowsheet of complete BR valorization

Exergy Flows

❑Grey Mud Luaching has 20.65% exergy efficiency.

❑Even though it is also a hydrometallurgical process, has high exergy demand (8.318MJ) due to the use of large amount of HCl acid.



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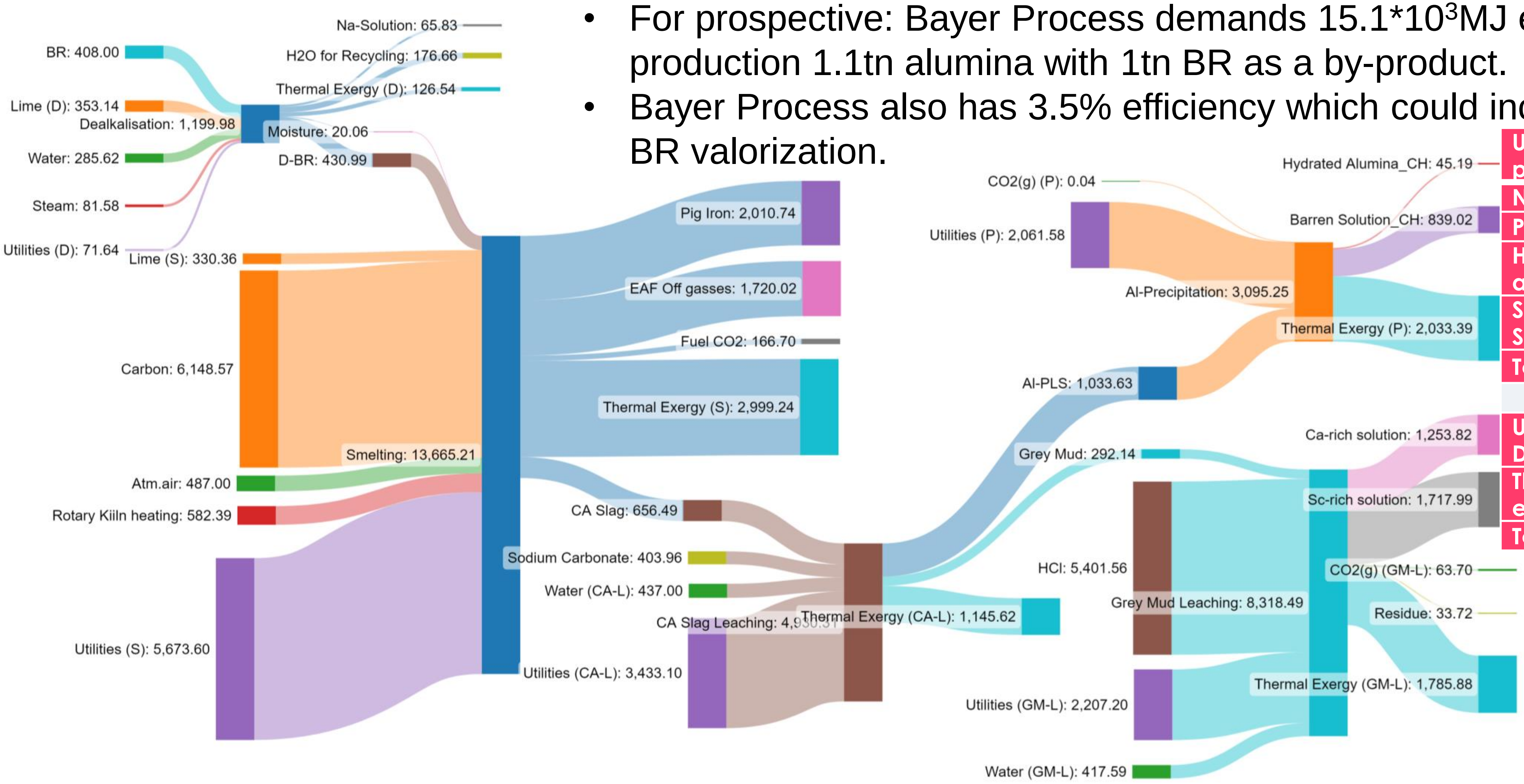
Conceptual flowsheet of complete BR valorization

Exergy Flows

- The overall exergy demand in this process is **28.8*10^3 MJ exergy** for the complete treatment of **1tn of BR**
- For prospective: Bayer Process demands 15.1*10^{3}MJ exergy for the production 1.1tn alumina with 1tn BR as a by-product.
- Bayer Process also has 3.5% efficiency which could increase plus 1.5% with BR valorization.



Usefull products	MJ	% of total demand
Na-solution	66	0.23
Pig Iron	2011	7
Hydrated alumina	45	0.16
Sc-Rich Solution	1718	6
Total	**3840**	**13**
Utilites Demand	10596	37
Thermal exergy losses	6945	24
Total Exergy demand		28784

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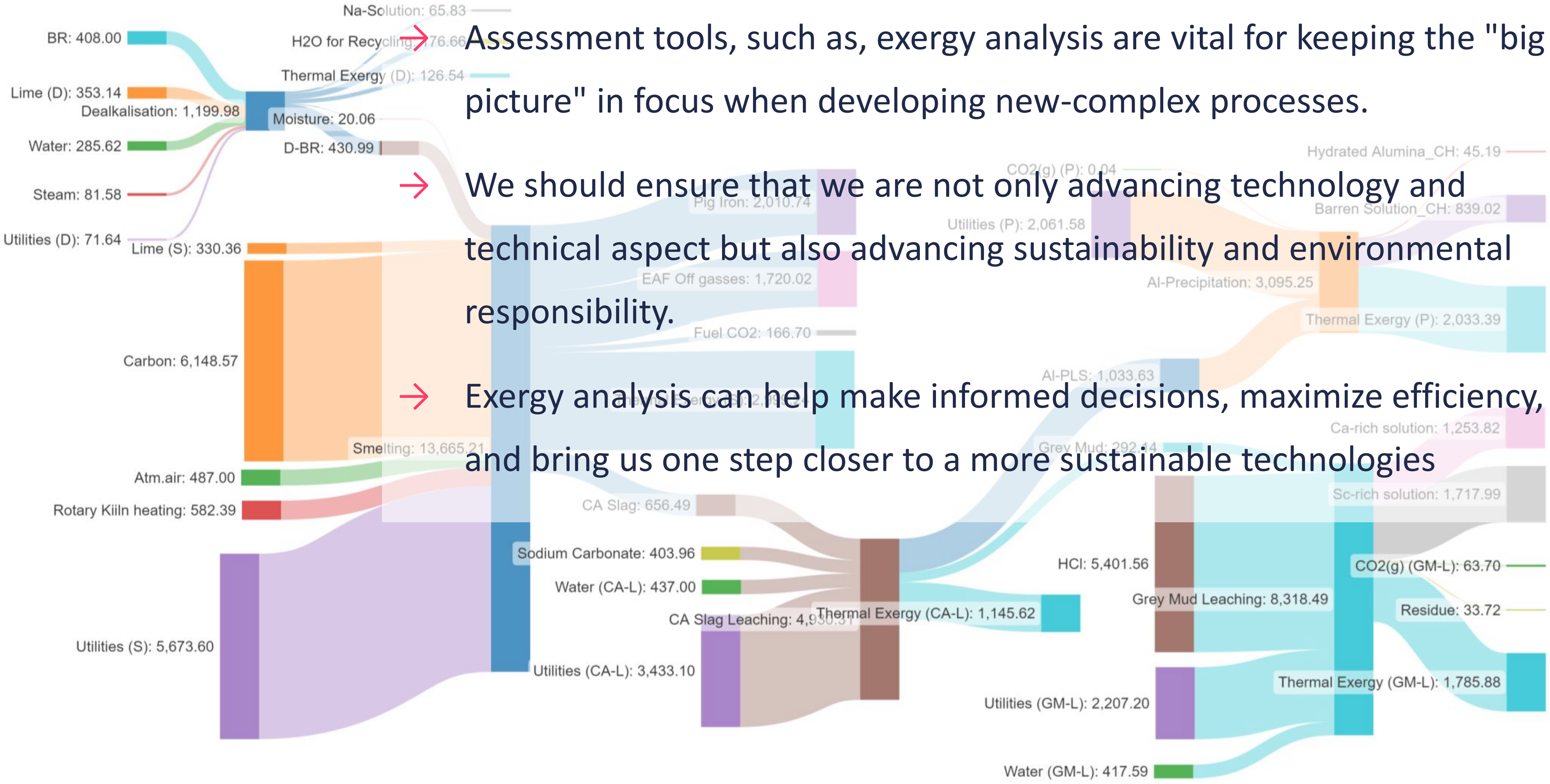
Take away notes



- → Assessment tools, such as, exergy analysis are vital for keeping the "big picture" in focus when developing new-complex processes.
- → We should ensure that we are not only advancing technology and technical aspect but also advancing sustainability and environmental responsibility.
- → Exergy analysis can help make informed decisions, maximize efficiency, and bring us one step closer to a more sustainable technologies

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HEPHAESTUS PROJECT

Heavy and Extractive industry wastes PHASing out through ESG Tailings Upcycling Synergy

Aims to develop a set of scalable and tuneable unit operations, to be built as integrated processing plant featuring the capacity to treat multiple process wastes deriving from primary mineral and metallurgical (primary and secondary) streams.

HEPHAESTUS

- **Clean-Tech electric furnace**, to transform the EAF and AOD dust into metal alloy to be immediately remelted, process supported with streams of fines by-products from the mineral primary extractions (construction, aggregates and dimensional stone)
- **EZINEX process**, to extract the zinc present in the dust of the furnace
- **Fibre drawing**, for mineral wool manufacturing out of the process slag in molten state
- **Catalytic conversion of CO_2 gas into methanol or formic acid**
- Ammonia-ammonium carbonate (AAC) and methanesulfonic acid (MSA) based hydrometallurgical processes, to produce a recyclable Fe-rich residue and to recover metals (e.g.e.g., ZnS) from EAF dust

HEPHAESTUS PROJECT

Heavy and Extractive industry wastes PHASing out through ESG Tailings Upcycling Synergy

HEPHAESTUS

- Investigate the potential use of various by-products of pyrometallurgical processes

Raw Materials

EAF Slag

Option I: Fe-alloy (pig iron), supplement cementious material (SCM)

Option II: Fe-Si alloy, geopolymer precusor

Converter and R/K dusts

✓ Option I: Fe-Ni alloy, $FeO\text{-}SiO_2$ type of slag

ISP Slag

✓ Option I: Fe alloy (pig iron), supplement cementious material (SCM)

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THANK YOU FOR YOUR ATTENTION
Questions?

https://www.removal-project.com/

https://hephaestus-horizon.eu/

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