MONTAN
UNIVERSITÄT
LEOBEN

EURECA-PRO
EUROPEAN UNIVERSITY ON RESPONSIBLE CONSUMPTION AND PRODUCTION

Selected topics of High Temperature Processing Technology for Responsible Production

Professor Harald Raupenstrauch

Technical University of Crete, Chania
15. November 2024

WHERE RESEARCH MEETS THE FUTURE

Univ.-Prof. Dipl.-Ing. Dr. techn. Harald Raupenstrauch

- Background: Chemical Engineering, Graz University of Technology
- Main research area: **Reactive Flow in Packed Beds**,
  especially at **high temperatures**
  including **safety** related topics and
  energy efficiency
- Full Professor at Montanuniversität Leoben since 2007
- Visiting Professorships:

  The Queen's University of Belfast, Northern Ireland
  Rutgers University of New Jersey, USA
  Delft University of Technology, The Netherlands
  The University of Zambia, Zambia
  University Lucerne, Switzerland

AIM

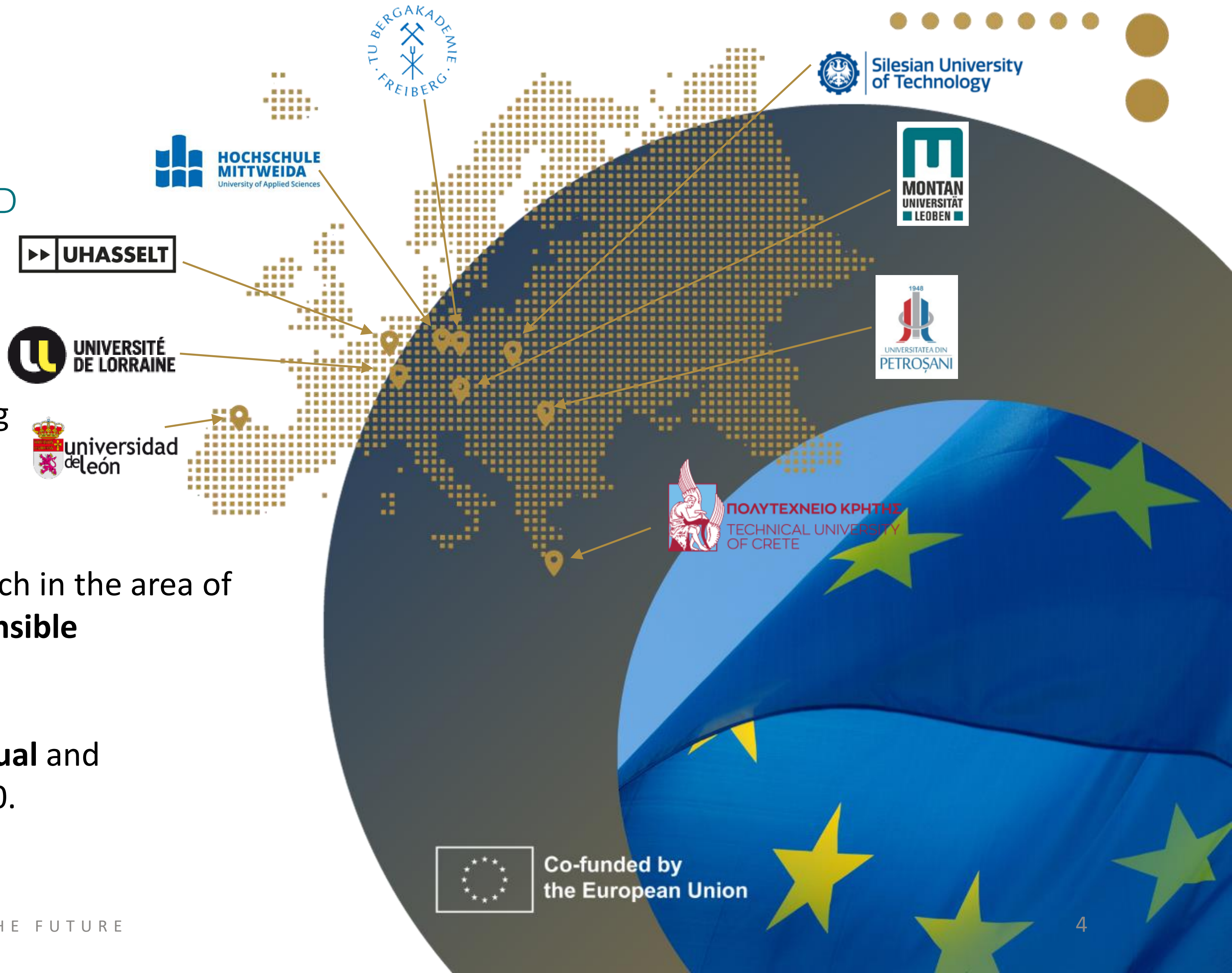
EURECA-PRO

EUROPEAN UNIVERSITY ON RESPONSIBLE CONSUMPTION AND PRODUCTION

EURECA-PRO is an **alliance**, consisting of 9 partners from 8 different **European countries**.

Objective: To study, teach and research in the area of **responsible consumption** and **responsible production**.

The long-term goal is a **common virtual** and integrated European **campus** by 2040.



AGENDA

- Montanuniversität Leoben
- Chair of Thermal Processing Technology
- Selected topics on High Temperature Processing Technology
- MSc programme Safety and Disaster Management

MONTAN UNIVERSITÄT LEOBEN

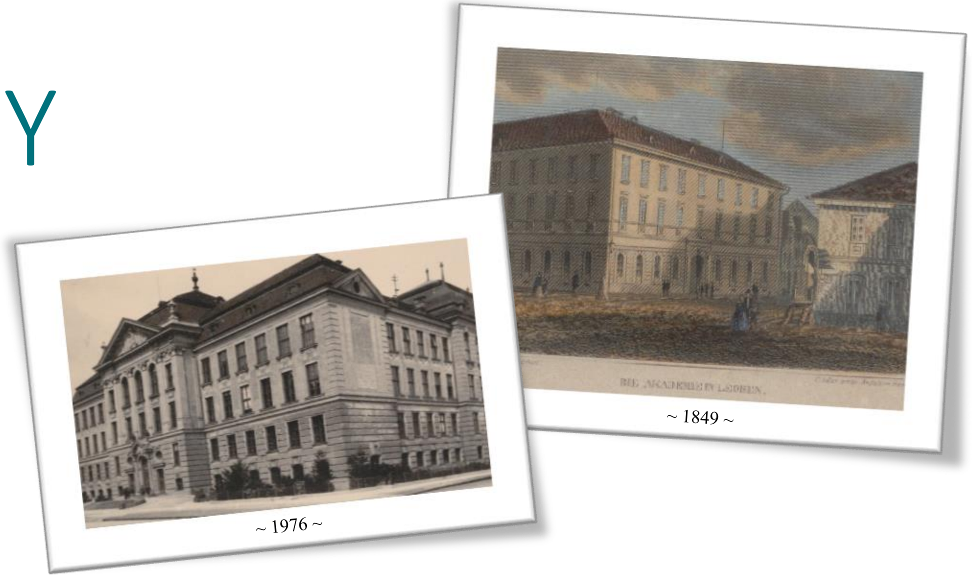
CAMPUS

A 1 .... **Main Building**, Franz-Josef-Straße 18
2 .... **Rittinger Building**
3 .... **Chemistry Building**
4 .... **Environmental Protection Building**
5 .... **Metallurgy Building**
6 .... **Workshops**
7 .... **Archduke Johann Buildng**

B .... **Peter Tunner Building**, Peter Tunner-Straße 5
C .... **Petroleum Engineering**, Parkstraße 27
D .... **Technology Transfer Centre**, Peter Tunner-Straße 25
E .... **Raw Materials and Materials Centre**, Erzherzog Johann-Straße 3
F .... **Materials Innovation Centre**, Roseggerstraße 12
G .... **Polymer Engineering Centre**, Otto Glöckel-Straße 2
H .... **Academy Montanuniversität Leoben**, Peter Tunner-Straße 15
I .... **Raw Materials Innovation Centre**, Roseggerstraße 11a
J .... **Parkstrasse 31**, Parkstrasse 31
K .... **Study Centre**, Peter Tunner-Straße 23
R .... **Centre for Applied Technology**, Peter Tunner-Straße 19
S .... **Austrian Foundry Research Institute**, Parkstraße 21
T .... **Austrian Academy of Sciences**, Jahnstraße 12

Photo : ©Wilfried Eichlseder

OUR HISTORY



Fotos: ©Bibliothek der MU Leoben

1840 - 1849	1849 - 1861	1861 -1904	1904 - 1975	SINCE 01 October 1974
STEIERMÄRKISCH-STÄNDISCHE MONTANLEHRANSTALT	K.K. MONTANLEHRANSTALT	K. K. BERGAKADEMIE	MONTANISTISCHE HOCHSCHULE	**MONTANUNIVERSITÄT LEOBEN**

POSITION & PROFILE MONTANUNIVERSITÄT LEOBEN 2030

The major social challenges of our time in the areas of resources, climate, energy and environment. At MU Leoben, these challenges are mainly being overcome with technical scientific methods.

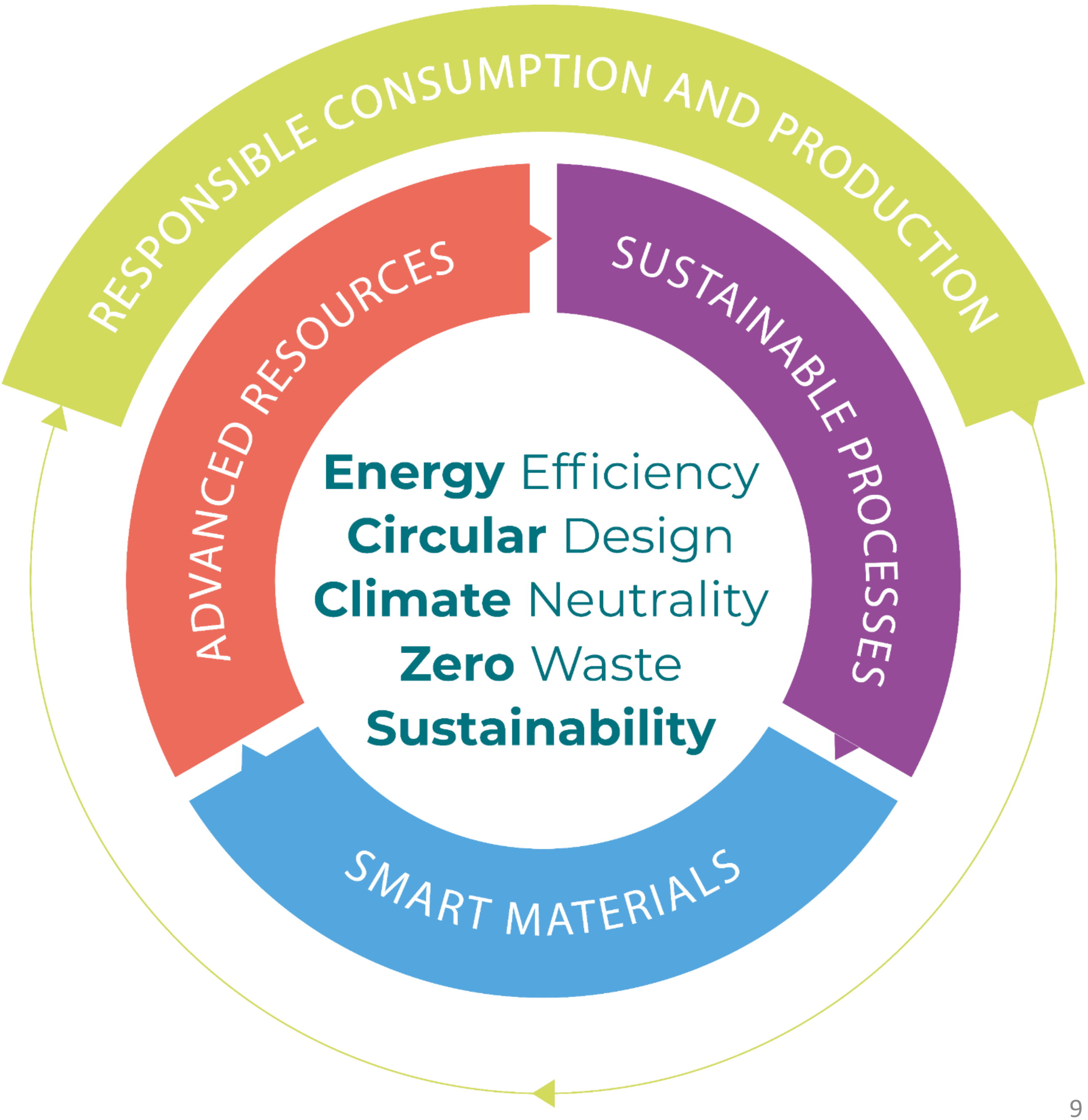
Montanuniversität Leoben considers it their purpose to make significant contributions to change the world for a better future through excellent science and outstanding education.

Foto: ©Hertha Hurnaus

MONTANUNIVERSITÄT LEOBEN DNA 2030

Montanuniversität Leoben stands for excellent science, outstanding education and top performance in the three competence areas Advanced Resources, Sustainable Processes and Smart Materials. These are embedded in the philosophy of Responsible Consumption and Production.

Five core values – our "DNA" – determine all our actions: Energy Efficiency, Circular Design, Climate Neutrality, Zero Waste and Sustainability.



RESEARCH NETWORKS

Networking with partners from **business and science** throughout Austria

MONTANUNIVERSITÄT LEOBEN

COMET
Competence Centres

Erich Schmid Institute

MCL
Materials Center Leoben

ÖGI
Austrian Foundry Institute

PCCL
Polymer Competence Center Leoben

ZAT
Center of Applied Technology

COMPETENCE CENTRES

COMET Competence Centres conduct application-oriented **cutting-edge research at the highest level**

47.5 % share

Materials Center Leoben Forschung GmbH

Specializes in metallic and non-metallic materials, their manufacturing and processing methods and innovative applications

35 % share

Polymer Competence Center Leoben GmbH

The leading Austrian centre for cooperative research in the area of polymer engineering and science

35 % share

K1-MET

One of the leading international metallurgical competence centres for ferrous and non-ferrous metallurgy

5% share

LEC EvoLET

One of the leading research facilities in the world for large-motor technologies. Development of innovative solutions for sustainable energy and transport systems

Resources Innovation Center Leoben (RIC)

Bundles national and international **resource innovation and sustainability activities** of the university in research, education and industrialization

ric Leoben

Sustainable raw materials supply

Strengthening of the raw materials supply for a green Europe

Sustainable planet

Raw materials, climate protection and sustainability in research and teaching

Climate research

Innovation for carbon-free economy and climate-resistant society

Education

Development of innovative education concepts for the raw materials community

ZENTRUM AM BERG - ZAB

Underground **research**, **development**, **training** and **education** on 1:1 scale

ZaB ZENTRUM am BERG

Photos: ©Zentrum am Berg

STUDY PROGRAMME

7 SEMESTER

4 SEMESTER

YEAR OF STUDY TOGETHER

- Basics in natural sciences and engineering sciences
- The same applies to all beginning students

BACHELOR`S PROGRAMMES

- Introduction to field of study
- Mandatory internship
- Bachelor's thesis
- Acad. degree: BSc

MASTER´S PROGRAMMES

- Solid education and training
- Master's thesis
- Acad. degree: Dipl.-Ing. (MSc)

THE 1ST YEAR TOGEHTER

- ✓ Completion of the 1st year without delay
- ✓ Easy option for changing field of study

1st YEAR

1st semester WS

- Introductory module (STEOP)
- Key competences for engineers
- Introduction to study programme
- Digital competences & statistics

2nd semester SS

- Key competences for engineers
- Introduction to study programme
- Digital competences & statistics

Let`s start together!

Introductory modules (at beginning of semester) — **10 ECTS**
Boot Camp and MINT introduction

Basics are forever!

Key competences for engineers — **32 ECTS**
Mathematics, physics, chemistry, mechanics

Digital competences & statistics — **12 ECTS**
Data modelling, algorithms, programming, statistics

Exciting start

Introduction to study programme — **6 ECTS**
Bachelor's fundamentals
Do-it Lab for the respective programme

BACHELOR´S PROGRAMMES

ADVANCED RESOURCES //DE

- Applied Geosciences
- Energy Engineering
- Geoenergy Engineering
- Mineral Resources Engineering

SMART MATERIALS //DE

- Materials Science and Technology

SUSTAINABLE PROCESSES //DE

- Industrial Data Science
- Industrial Logistics
- Mechanical Engineering
- Recycling Technology
- Metallurgy and Metal Recycling
- Environmental and Climate Protection Technology

RESPONSIBLE CONSUMPTION AND PRODUCTION //EN

- Circular Engineering
- Responsible Consumption and Production (EURECA-PRO)

MASTER´S PROGRAMMES
Dipl.-Ing. (Msc)

ADVANCED RESOURCES

- Applied Geosciences //EN
- Geoenergy Engineering //EN
- Mining and Tunnelling//EN
- Raw Materials Engineering //EN
- International Study Program in Petroleum Engineering //EN
- Energy Engineering //DE
- Industrial Management and Business Administration //DE

SUSTAINABLE PROCESSES

- Metallurgy //DE+EN
- Mechanical Engineering //DE
- Industrial Logistics //DE
- Industrial Data Science //EN
- Environmental and Climate Protection Technology//DE
- Recycling //DE

SMART MATERIALS

- Materials Science //DE
- Polymer Engineering and Science //DE

MASTER´S PROGRAMMES MSc

ADVANCED RESOURCES

- International Master of Science in Advanced Mineral Resources Development //EN
- International Master of Science in Building Materials and Ceramics //EN
- International Master in Petroleum Engineering //EN
- International Master of Science in Applied and Exploration Geophysics //EN
- EM Joint Master in Sustainable Mineral and Metal Processing Engineering //EN

SMART MATERIALS

- Advanced Materials Science and Engineering (AMASE) //EN

SUSTAINABLE PROCESSES

- International Master in Sustainable Materials //EN
- Safety and Disaster Management //EN

RESPONSIBLE CONSUMPTION AND PRODUCTION

- Circular Engineering //EN
- Responsible Consumption and Production (EURECA-PRO) //EN

INTERNATIONAL MASTER´S PROGRAMMES

ADVANCED RESOURCES

- International Master of Science in Advanced Mineral Resources Development (AMRD) //EN
- International Master of Science in Building Materials and Ceramics (BMC) //EN
- International Master of Science in Applied and Exploration Geophysics (IMAGE) //EN
- Joint International Master Program in Petroleum Engineering (JIMP) //EN
- EM Joint Master in Sustainable Mineral and Metal Processing Engineering // EN

SMART MATERIALS

- Advanced Materials Science and Engineering (AMASE) //EN

SUSTAINABLE PROCESSES

- Sustainable Mineral and Metal Processing Engineering (PROMISE) //EN
- International Master in Sustainable Materials (SUMA) //EN

RESPONSIBLE CONSUMPTION AND PRODUCTION

- Responsible Consumption and Production (EURECA-PRO) (RCP) //EN

FACTS & FIGURES

Montanuniversität Leoben has an above-average rating of 7 out of 10 points by ist students (Universum Survey)

(Universum survey)

13 BACHELOR`S PROGRAMMES

26% of students are female

3.000 students from 89 different countries

75 Startups

80% Success Rate

300 laboratories & workshops form an excellent research infrastructure

29 golden buttons on the miner's coat

About a tenth of the students work at Montan-universität Leoben

164 km from Vienna

25 MASTER`S PROGRAMMES

154.659 m² campus area

5:1 ratio students : teacher

71 Sport courses at the USI

DEPARTMENT FÜR

Umwelt- & EnergieverfahrensTECHNIK

Department of Environmental and Energy Process Engineering

Head: Professor Harald Raupenstrauch

ThermoprozessTECHNIK

Chair of Thermal Processing Technology

Head: Professor Harald Raupenstrauch

AbfallverwertungsTECHNIK & AbfallWIRTSCHAFT

Chair of Waste Processing Technology and Waste Management

Head: Professor Roland Pomberger

VerfahrensTECHNIK des industriellen Umweltschutzes

Chair of Process Technology and Industrial Environmental Protection

Head: Professor Markus Lehner

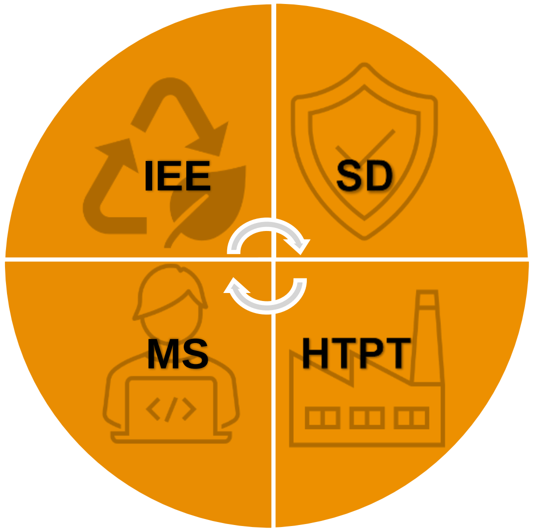
EnergieverbundTECHNIK

Chair of Energy Network Technology

Head: Professor Thomas Kienberger

Chair of Thermal Processing Technology

- employees: ~45 including K1-MET (incl. 4 Senior Scientists, 9 PhD students)
- Publications: https://pure.unileoben.ac.at/en/organisations/chair-of-thermal-processing-technology-580/publications/



- IEE – Industrial Energy Engineering
  - Energy Efficiency
- MS – Modelling and Simulation
  - Computational Fluid Dynamics, Industrial Furnaces and burners
- SDS – Safety and Disaster Studies
  - Safety Engineering
- HTPT – High-Temperature Processing Technology
  - Recovery and Recycling Processes

HTPT – High Temperature Processing Technology

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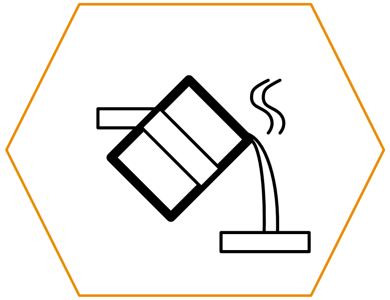
HTPT

- Introduction
  - The desired **defossilisation** and **climate neutrality** of energy-intensive industries requires the reduction of the CO_2 intensity of products and the development of adequate technologies
  - The "High-Temperature Process Technology" working group (HTPT) focuses on **promoting a sustainable circular economy**
  - Our research concentrates on the **resource-efficient valorisation of residues** using high-temperature processes **above 1000 °C**

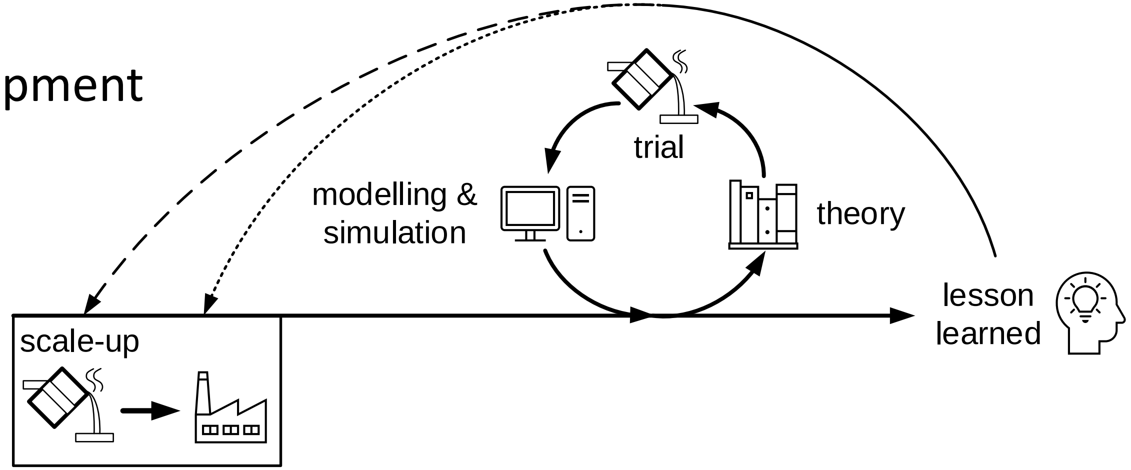
HTPT

- Objectives
  - Defossilisation and climate neutrality of energy-intensive industries
    - reducing the CO_2 intensity of products
    - development of adequate technologies
  - Promoting a sustainable circular economy
    - resource-efficient valorization of residues using high-temperature processes
  - Collaboration scientific and/or industrial partners
  - Education for sustainable development

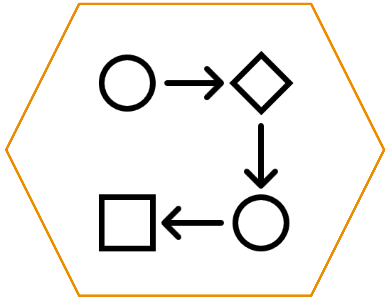
HTPT



- Scientific Competences
  - material characterization
    - physical & chemical properties
  - high-temperature processes
    - process development & optimization
  - modelling & simulation
    - prediction model development



HTPT



- Current Projects – Excerpt

acronym (link)	project
H2PlasmaRed	Hydrogen Plasma Reduction for Steelmaking and Circular Economy
BitKOIN	CO_2-reduced Binding Agents through Thermochemical Conversion of Mineral Wool Waste Combinations
Recover-Met-Binder	Valuable Metal Recovery and Binder Provision from the Electric Furnace Route as a Contribution to Cross-Sector Circular Economy
UpcycSlag-Binder	Upcycling of slag residues to new, sustainable binders in the construction materials cycle
ReMFra	Recovering Metals and Mineral Fraction from Steelmaking Residues
FuLIBatteR	Future Lithium Ion Battery Recycling for Recovery of Critical Raw Materials

Funded by the European Union
Horizon Europe Grant Agreement No. 101138228

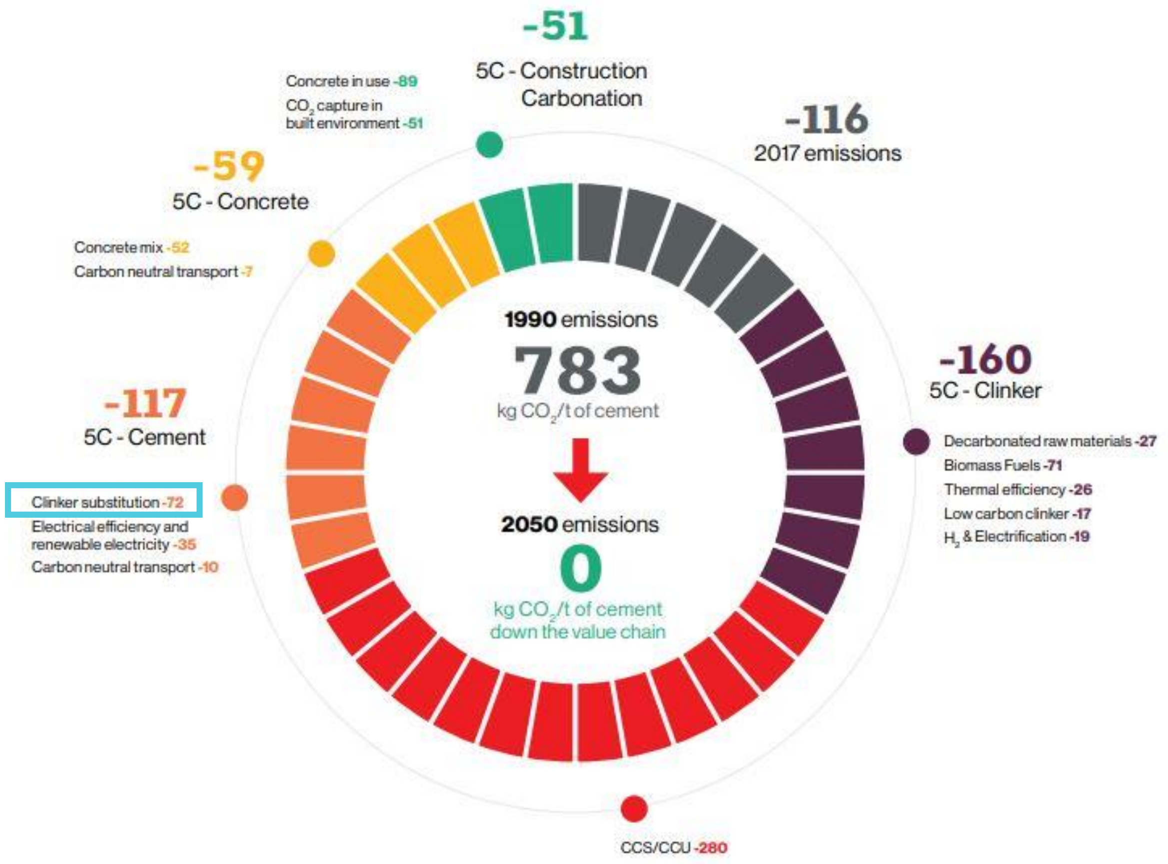
Funded by the European Union
Horizon European Clean Steel Partnership Grant Agreement No. 101058362

Carbothermal Treatment and Cooling of Metallurgical Residues

- Introduction
  - **Cement Industry**
    - Worldwide production of 4.3 Gt cement (2021)
    - 2.42 Gt of CO_2 emissions, mainly due to the clinker burning process at high temperatures:

$$\mathbf{CaCO_3 \rightarrow CaO + CO_2}$$

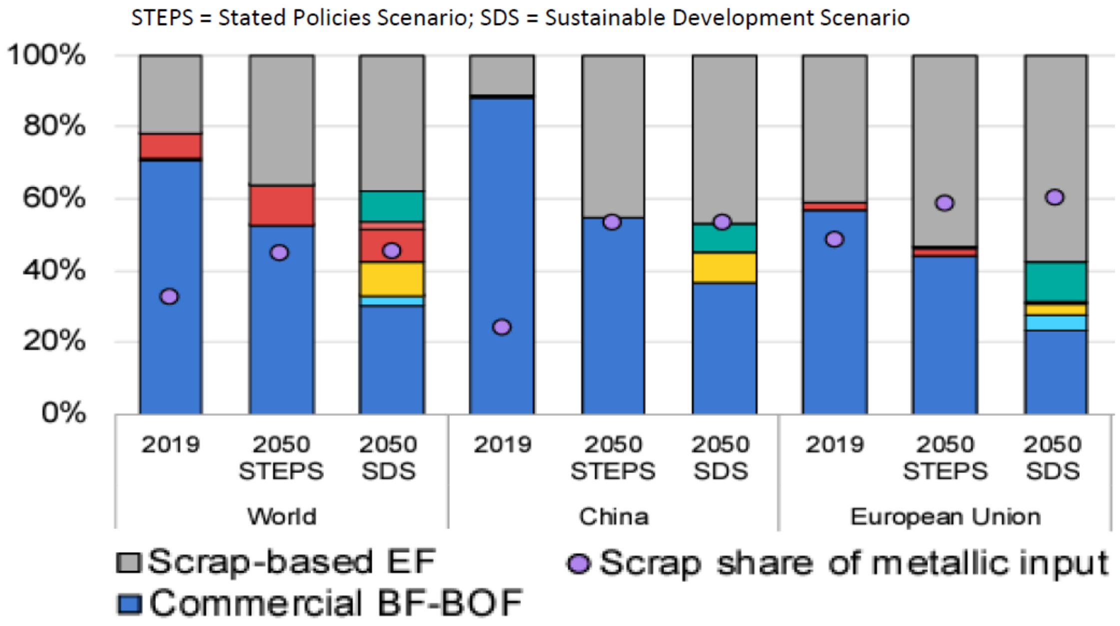
    - At the moment: **clinker substitution** with <u>granulated blast furnace slag</u> and <u>fly ash from coal combustion</u>



IEA-International Energy Agency (2018): Low-CarbonTransitionintheCementIndustry.Hg. v. IEA - International Energy Agency. Paris. Online verfügbar unter https://www.iea.org/reports/technology-roadmap-low-carbon-transition-in-the-cement-industry

Carbothermal Treatment and Cooling of Metallurgical Residues

- Introduction
  - **Iron and Steel Industry**
  - Worldwide production of 1.9 Gt crude steel (2021)
  - 2.62 Gt of CO_2 emissions, mainly due to the energy demand
    - **Shift from blast furnace/basic oxygen furnace route towards electric steelmaking and other green technologies**
  - Slags as by-product:
    - 390 – 560 kg/$t_{crude\ steel}$ (BF/BOF Route)
    - 185 – 265 kg/$t_{crude\ steel}$ (EAF Route)



IEA (2020), Iron and Steel Technology Roadmap, IEA, Paris https://www.iea.org/reports/iron-and-steel-technology-roadmap (adapted)

world steel association (2023): World Steel in Figures. Brussels. Online verfügbar unterhttps://worldsteel.org/wp-content/uploads/World-Steel-in-Figures-2023-4.pdf

Carbothermal Treatment and Cooling of Metallurgical Residues

The conversion of iron and steel production in the course of defossilisation means that **blast furnace slag** that is needed to make the cement industry climate-neutral, **is no longer available**.

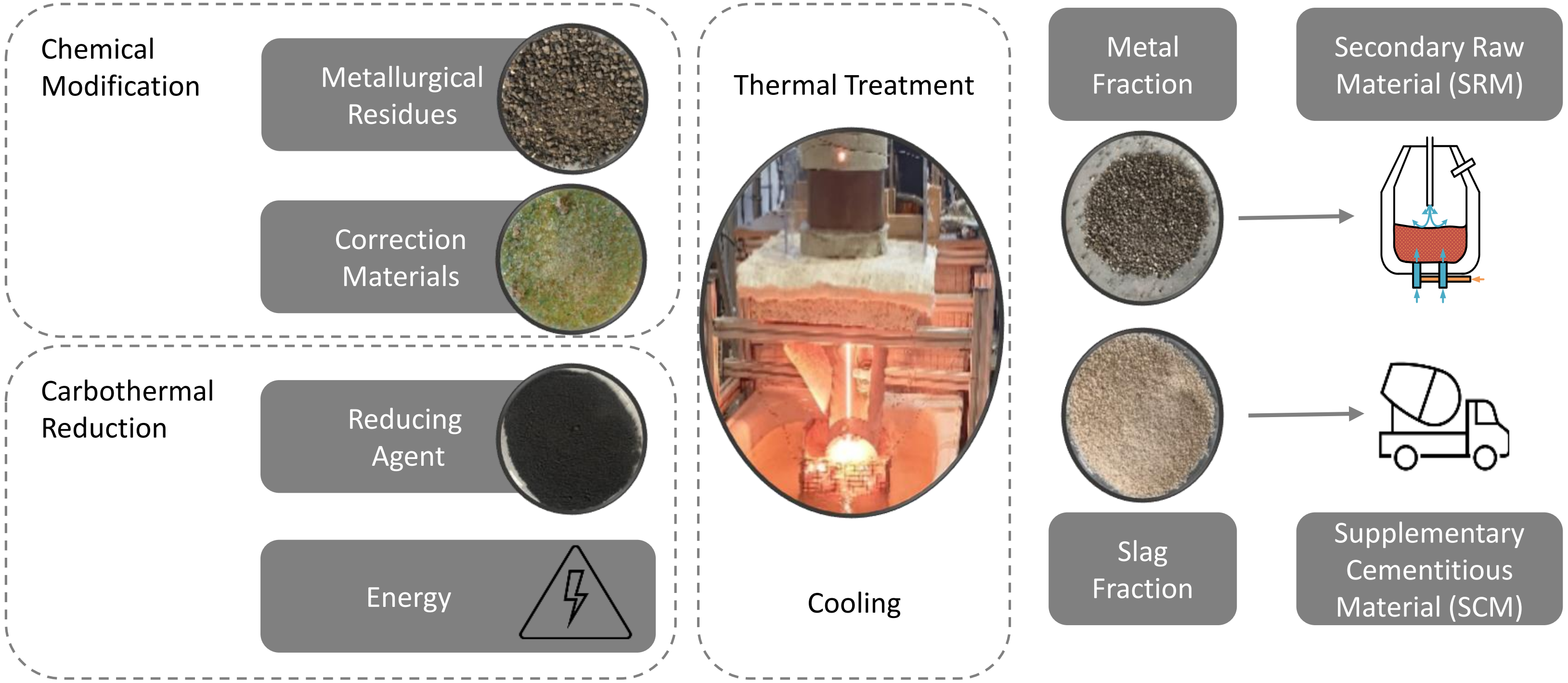
New types of slag are emerging that are still **unexplored**, which means that it has not yet been possible to present a suitable utilization strategy in the sense of sustainable circular economy.

Research Objectives

- **Recovery of valuable metals** (Fe, Mn, Cr) as a secondary raw material for scrap-based steel production
- Development of **alternative supplementary cementitious materials** as a substitution for granulated blast furnace slag
- **Avoidance of landfilling** of metallurgical residues and promoting a circular economy
- Investigation of the **possible energy recovery** through dry slag granulation
- **Characterisation and development of new slag types**

Carbothermal Treatment and Cooling of Metallurgical Residues

- Materials & Methods



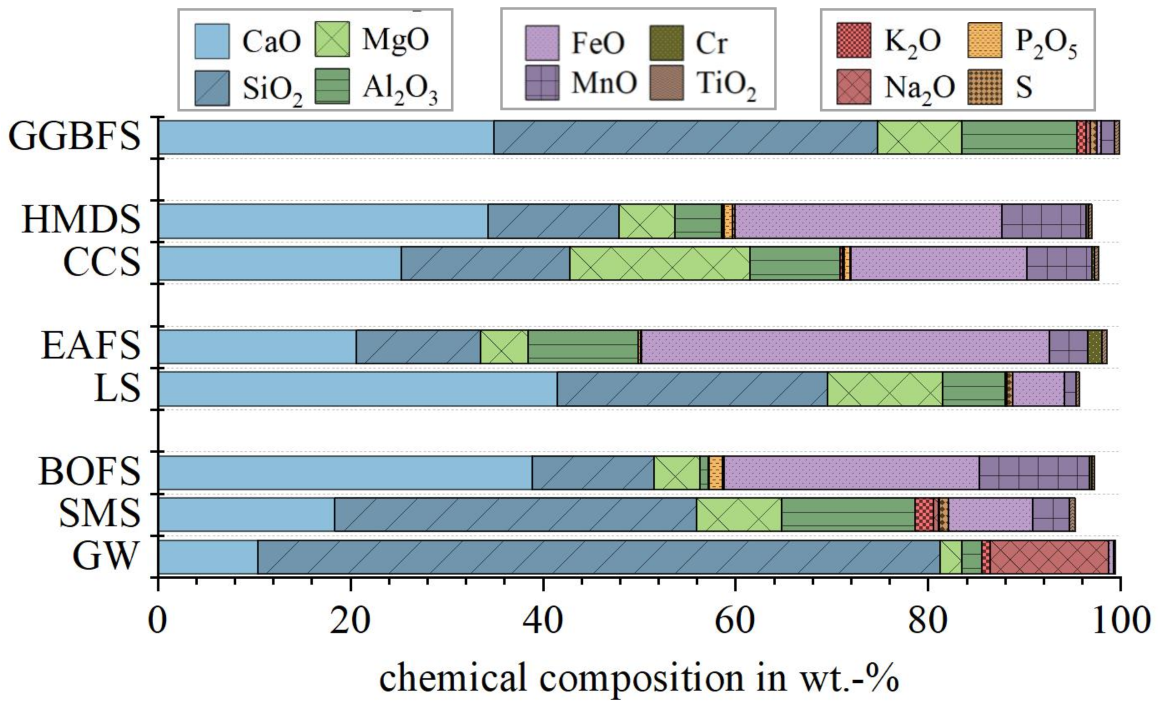
SUSTAINABLE DEVELOPMENT GOALS
9 INDUSTRY, INNOVATION AND INFRASTRUCTURE
12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Doschek-Held, K, Krammer, A, Doschek-Held, K, Steindl, FR, Gatschlhofer, C, Wohlmuth, D & Sorger C, (in press.2024), Thermochemical treatment of iron-, calcium- or silica-rich residues from the iron and steel industry: recovery of valuable metals and alternative binder components. in Proceedings of the 6th EMCEI. Euro-Mediterranean Conference for Environmental Integration, Marrakesh, Marokko, 15/05/24.

Carbothermal Treatment and Cooling of Metallurgical Residues

- Materials & Methods
  - Reference Material: Ground Granulated Blast Furnace Slag (GGBFS)

  - Integrated Steelmaking Slags
    - Hot Metal Desulphurization Slag (HMDS)
    - Continuous Casting Slag (CCS)
  - Electric Steelmaking Slags
    - Electric Arc Furnace Slag (EAFS)
    - Ladle Slag (LS)
  - Correction Materials
    - Basic Oxygen Furnace Slag (BOFS)
    - Siemens-Martin Slag (SMS)
    - Glass Waste (GW)



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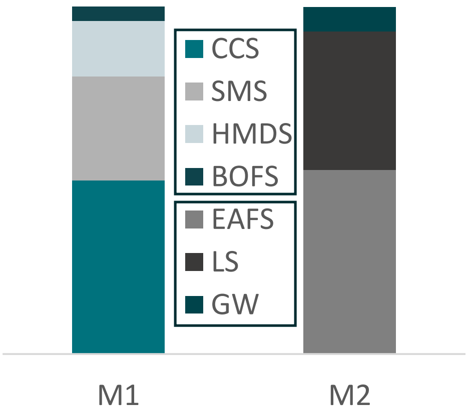
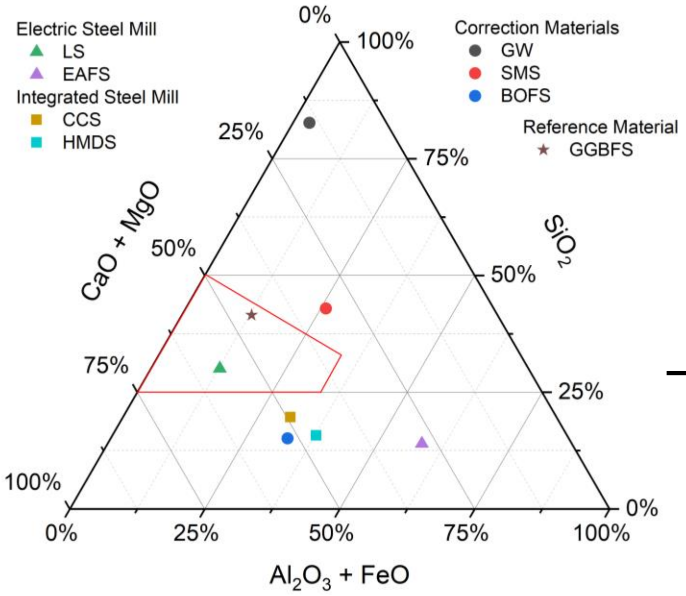
Carbothermal Treatment and Cooling of Metallurgical Residues

- Materials & Methods
  - Mixture Calculation
    - Microsoft Excel Spreadsheet Model using a Solver Add-In
      - Transfer Coefficients: Mathematical Separation into the Mineral Fraction (SCM), Metallic Fraction (SRM) and Gas Fraction
      - European Standard for GBFS (EN 15167-1): Limitation of Chemical Properties for the Mineral Fraction

Mixture (M) Composition





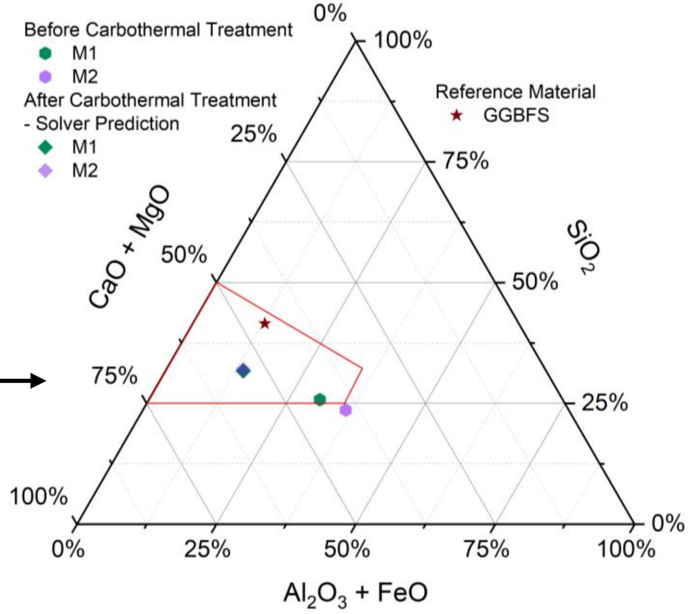
SCM Limitation (EN 15167-1)

SiO_2 content > 25 wt.-%

$CaO + MgO + SiO_2$ > 66 wt.-%

$\frac{CaO+MgO}{SiO_2} > 1$

Mixing, Carbothermal Treatment and Cooling



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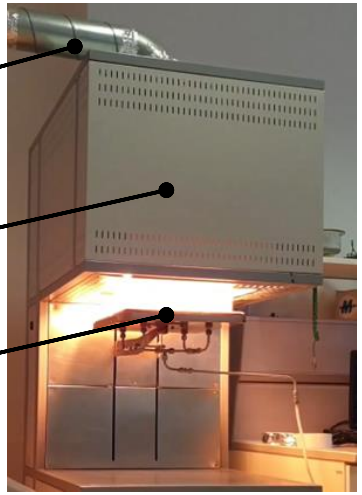
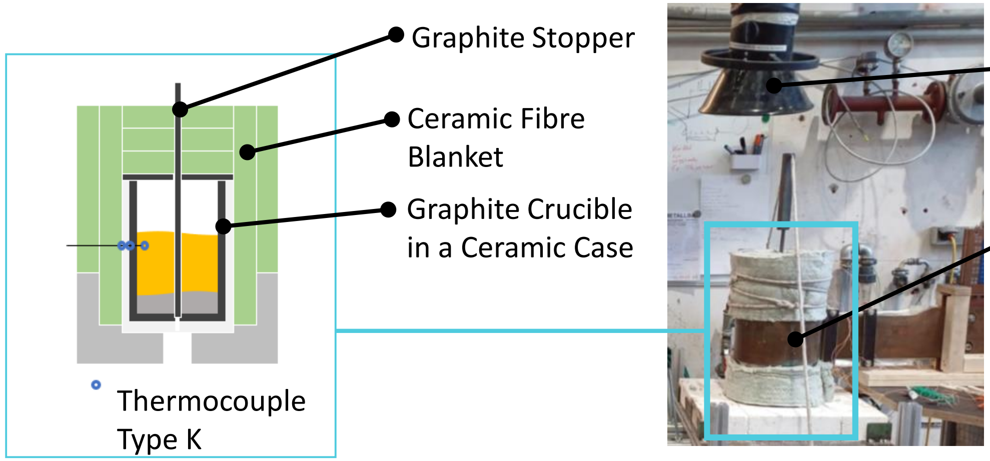
Carbothermal Treatment and Cooling of Metallurgical Residues

- Materials & Methods
  - Carbothermal Treatment
    - Melting and Reduction in a Graphite Crucible and Addition of Carbon Powder
    - Resistance Elevator Furnace (EF)
      - Sample Quantity: 200 - 250 g
      - Heating: 500 K/h up to 1600°C
      - Atmosphere: Argon, (CO, CO_2)
      - Cooling: Water Quenching
    - Inductively Heated Crucible Furnace (ICF)
      - Sample Quantity: 1300 - 1600 g
      - Heating: 600 K/h to 1400 – 1600 °C
      - Atmosphere: O_2, CO, CO_2
      - Cooling: Water Quenching or Spinning Disk Atomization





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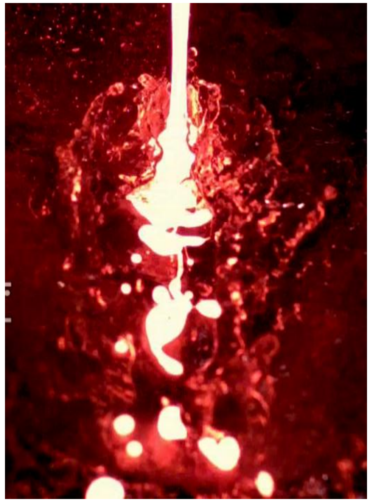
Carbothermal Treatment and Cooling of Metallurgical Residues

- Materials & Methods
  - Wet Quenching (WQ)
    - \+ State-of-the-art
    - \+ Process Stability: Slag Impact and Flow
    - – Wastewater
    - – Formation of Hydrogen Sulphide and Water Vapour
  - Spinning Disc Atomization (SDA)
    - \+ Possibility of Heat Recovery
    - \+ No Necessity of Fresh Water Consumption and Drying
    - – Higher Efforts in Process Engineering needed
    - – More sensitive to Material Properties



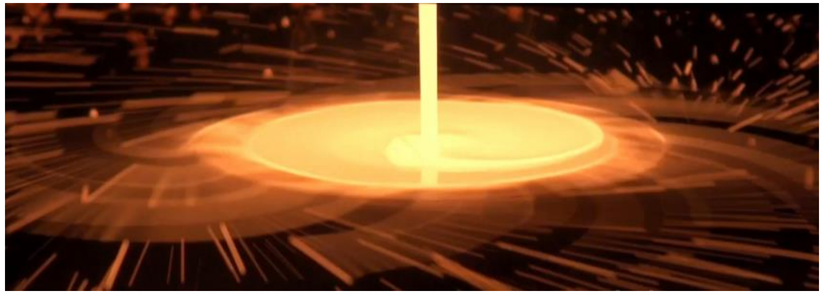
Why granulation?

→ Necessity of an amorphous structure for a reactive binder component

→ Glassy solidification achieved with rapid cooling

→ Less effort is required for crushing

→ Easier separation of the metallic fraction



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Heat recovery from slags

about 400 Mio. tons of blast furnace slags per year worldwide

tapping temperature: around 1500 °C

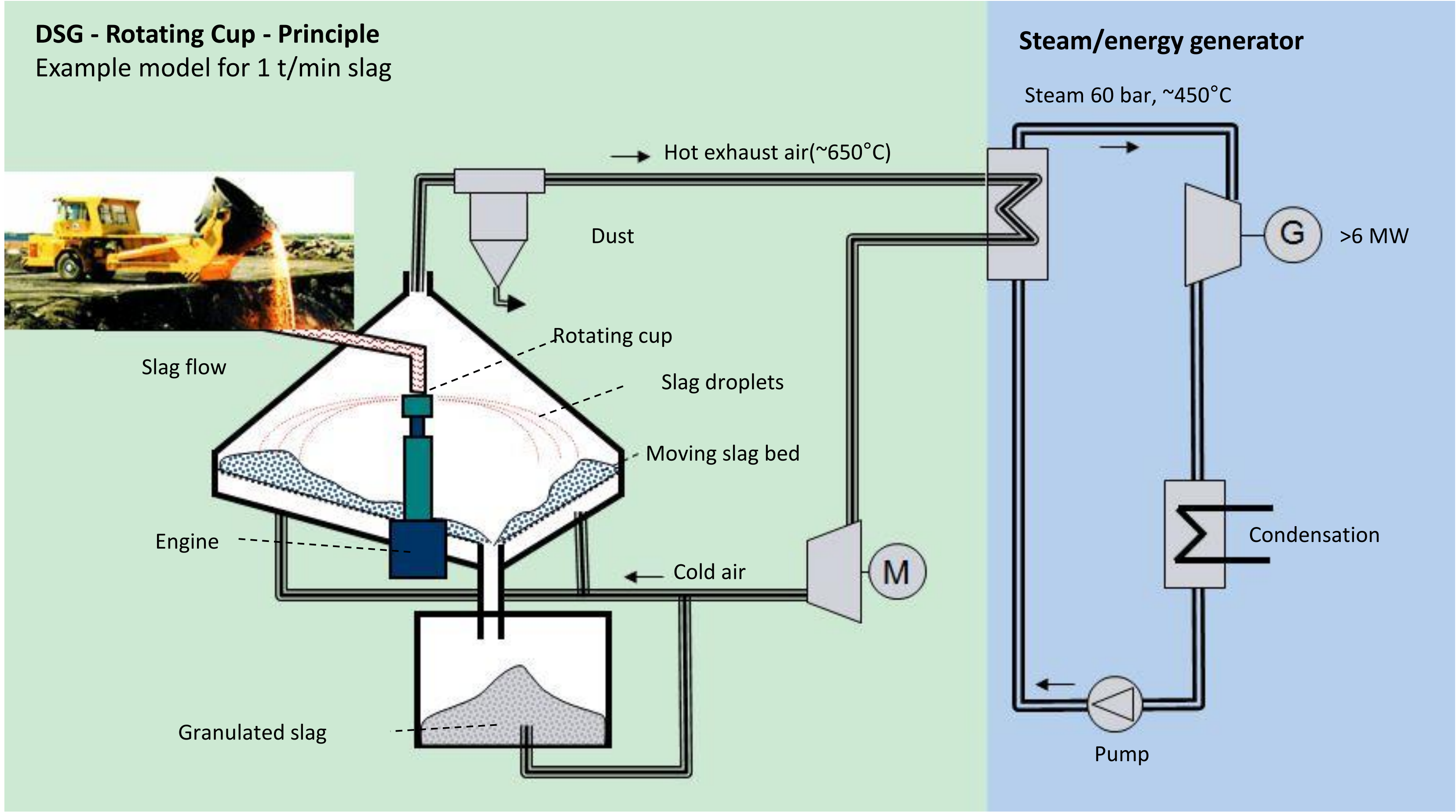
best available technology: wet granulation

cooling still done without heat recovery (1,5 GJ/t unused)

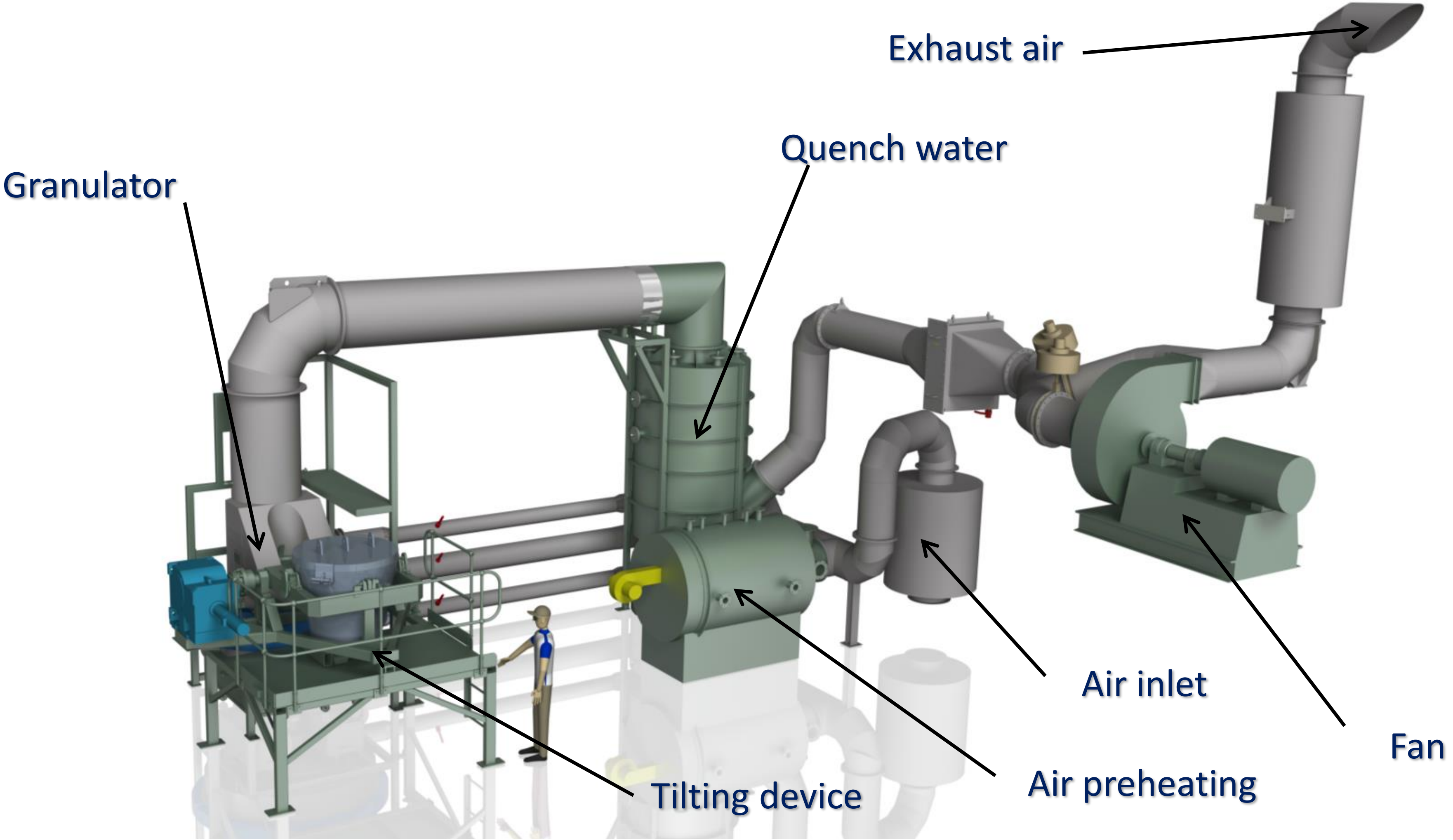
growing interest in energy efficiency in the iron and steel industry

Wet slag granulation at Mopani, Mufurila (Zambia)

Dry Slag Granulation - DSG



TPT pilot plant DSG



Carbothermal Treatment and Cooling of Metallurgical Residues

- Materials & Methods
  - Output Characterisation
    - Granulation is followed by (Drying,) Crushing, Sieving and Magnetic Separation into:

Mineral Fraction (SCM)

- Chemical Composition (XRF)
- Glass Content and Phase Composition (XRD)
- Rapid Reliable Relevant (R^3) testing procedure [Li et al., 2018]
  - Hydration Heat Release after 7 days (Isothermal Calorimetry)

Metal Fraction (SRM)

- Chemical Composition (ICP)
- Reduction Rate
  - Calculated by Mass Balance

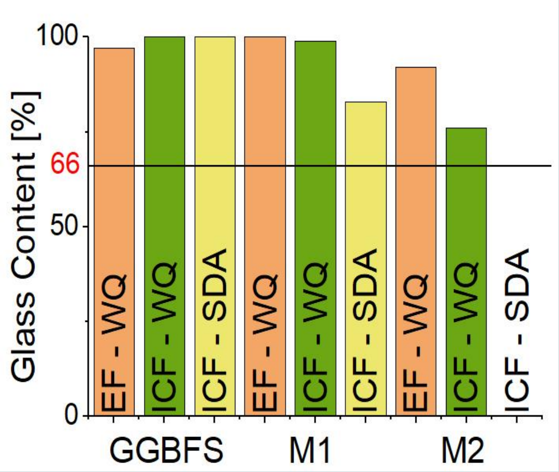
Li X, Snellings R, Antoni M, et al. (2018) Reactivity tests for supplementary cementitious materials: RILEM TC 267-TRM phase 1. Materials and Structures 51: 151.

Carbothermal Treatment and Cooling of Metallurgical Residues

Limiting value acc. to EN 15167-1

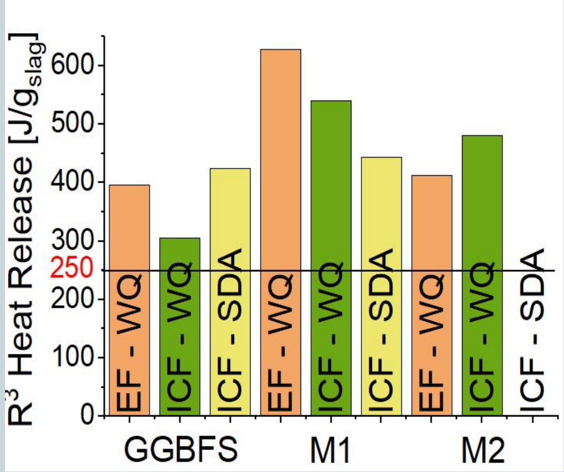
Characteristic of a rapid cooling

Required for latent-hydraulic properties



R^3 test method: mixture of SCM, $Ca(OH)_2$, KOH and K_2SO_4

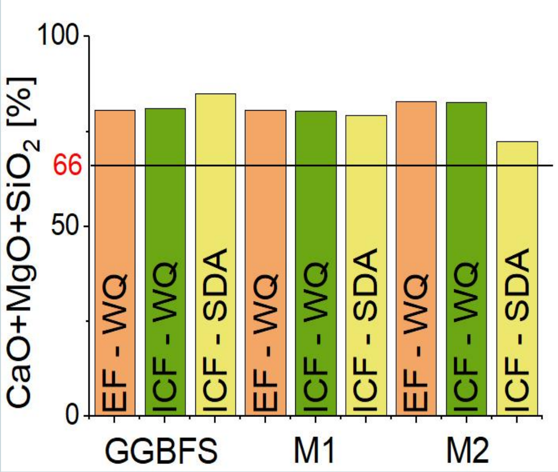
cumulative released heat after 7 days as indication of binder reactivity (hydration reaction)

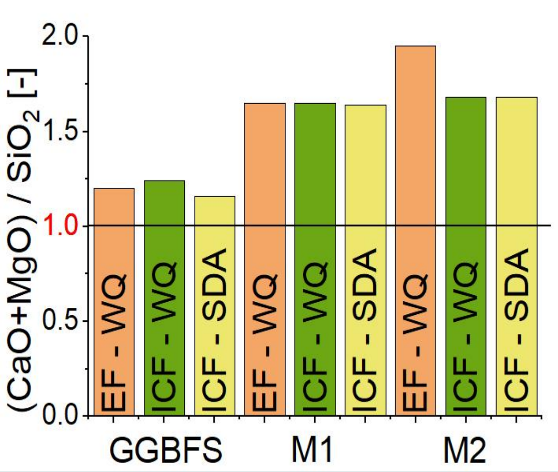


Mineral Fraction (SCM) – selected results

Chemical parameters as a verification of the mixture calculation

compliance with EN 15167-1





EF – Resistance Elevator Furnace; ICF – Inductively Heated Crucible Furnace; WQ – Water Quenching; SDA – Spinning Disk Atomization

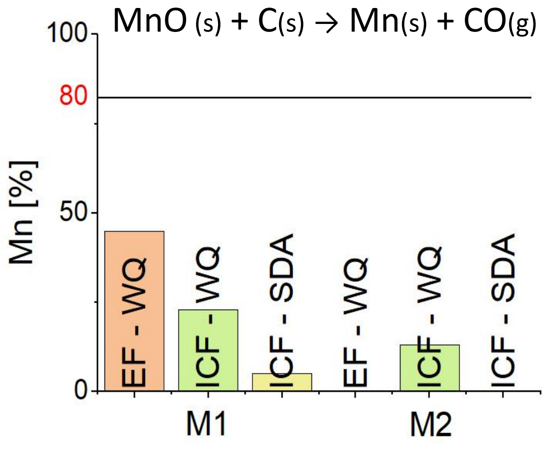
Doschek-Held, K, Krammer, A, Doschek-Held, K, Steindl, FR, Gatschlhofer, C, Wohlmuth, D & Sorger C, (in press.2024), Thermochemical treatment of iron-, calcium- or silica-rich residues from the iron and steel industry: recovery of valuable metals and alternative binder components. in Proceedings of the 6th EMCEI. Euro-Mediterranean Conference for Environmental Integration, Marrakesh, Marokko, 15/05/24.

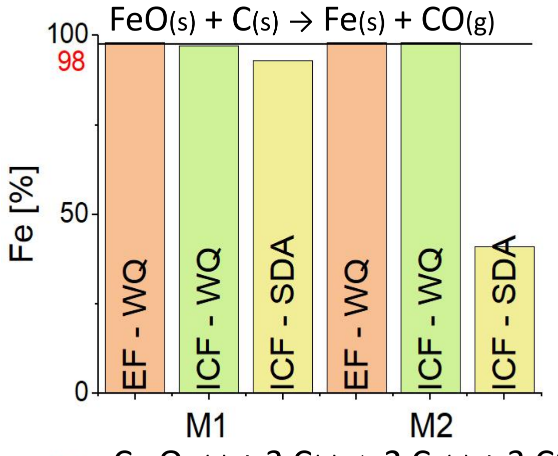
Carbothermal Treatment and Cooling of Metallurgical Residues

Metal Fraction (SRM) - selected results

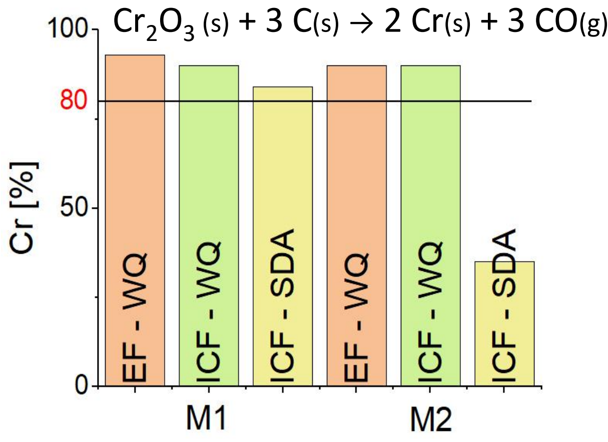
Redution Rates

- The metal reduction also influences the chemical composition of the mineral fraction, resulting in deviations from the calculated result.
- A very high reduction of iron and chromium was achieved regardless of the input material, furnace type and cooling variants selected. The ICF-SDA test for mixture M2 showed poorer results, which can be attributed to a disturbance in the energy supply.
- The reduction of manganese was significantly below the expected value.





EF – Resistance Elevator Furnace
ICF – Inductively Heated Crucible Furnace
WQ – Water Quenching
SDA – Spinning Disk Atomization



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Carbothermal Treatment and Cooling of Metallurgical Residues

- Conclusions

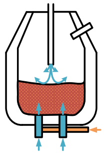
Mineral Fraction (SCM)

- Desired Chemical Composition
- Achievement of Rapid Cooling (Glass Content > 66%)
- R³ Hydration Heat Release → Suitability for Use as SCM

Metal Fraction (SRM) – Reduction Rates

- Separation from Mineral Fraction is Possible
- Efficient Recovery of Fe and Mn
- High Iron Content in Recovered Metal Alloy → Suitability for Use as SRM

SCM – Supplementary Cementitious Material ✓



SRM – Secondary Raw Material ✓

Doschek-Held, K, Krammer, A, Doschek-Held, K, Steindl, FR, Gatschlhofer, C, Wohlmuth, D & Sorger C, (in press.2024), Thermochemical treatment of iron-, calcium- or silica-rich residues from the iron and steel industry: recovery of valuable metals and alternative binder components. in Proceedings of the 6th EMCEI. Euro-Mediterranean Conference for Environmental Integration, Marrakesh, Marokko, 15/05/24.

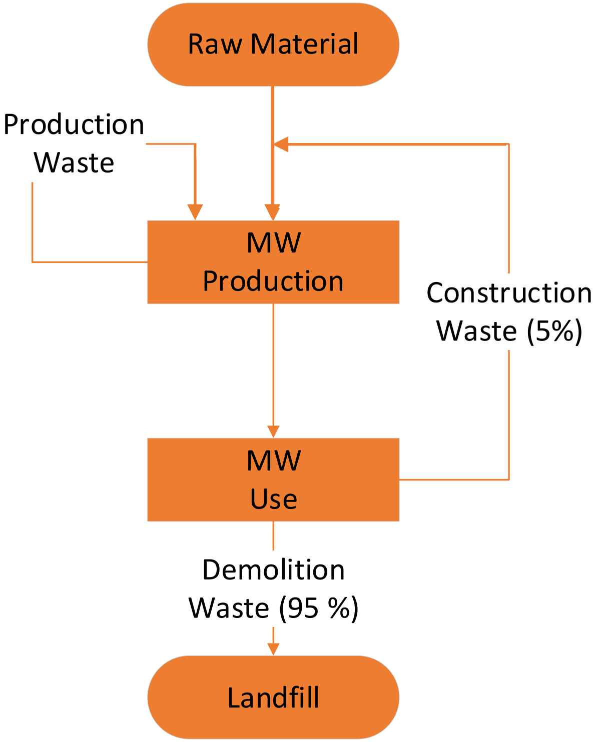
Carbothermal Treatment and Cooling of Metallurgical Residues

OUTLOOK

- **Improvement of metal recovery**: Investigation of Mn recovery
- **Alternative treatment processes and cooling methods** including upscaling
- Implementation of **Machine Learning**: Development of a prediction model to estimate the reactivity based on the chemical composition
- Further characterization of the properties of slags deposited to date and new slag types: **Determination of viscosity and melting ranges**
- Further enhancement of the MS Excel Solver into a **holistic prediction tool** for all resulting fractions and their properties

Mineral Wool Waste Recycling

▪ Introduction



Raw Materials

Stone Wool - **Volcanic rock (e.g. Basalt)** is melted together with limestone and/or dolomite at temperatures of up to 1500 °C in coal-fired furnaces before being fed into a defibring machine.

Glass Wool - The components **quartz sand, soda and limestone** and up to 80 m.-% **waste glass** as a secondary raw material are melted at around 1200°C in natural gas-fired glass furnaces and then defibred.

Production of Mineral Wool (MW) in 2020

- EU total: 266 mio. m³ → 10 mio. tons

Mineral Wool Waste (MWW) – Demolition Waste

- EU – MWW (2020): 2.5 mio. tons → 127 – 12.7 mio. m³
  - bulk density: 20 – 200 kg m^{-3}

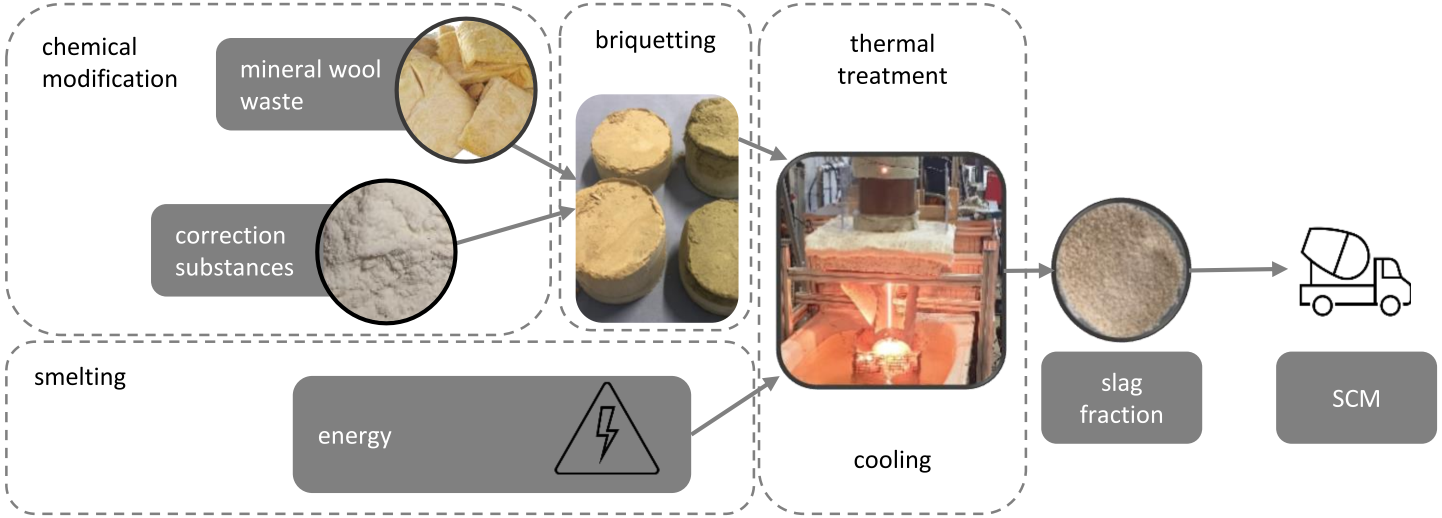
Recycling / Disposal

- **construction waste**: recycling is limited by chemical composition (EUCEB criteria)
- **demolition waste**: landfilling causes stability problems (2027 in AT - ban on deposition)

MÜLLER, Anette ; LEYDOLPH, Barbara ; STANELLE, Katja: Recycling mineral wool waste - technologies for the conservation of fiber structure. In: InterCeram: International Ceramic Review (2009), S. 378–381.; SCHULTZ-FALK, Vickie ; AGERSTED, Karsten ; JENSEN, Peter Arendt ; SOLVANG, Mette: Melting behaviour of raw materials and recycled stone wool waste. In: Journal of Non-Crystalline Solids 485 (2018), S. 34–41.

Mineral Wool Waste Recycling

- Motivation & Objectives
  - **Recycling of Mineral Wool Waste** (MWW) as a **Supplementary Cementitious Material** (SCM) comparable to Granulated Blast Furnace Slag



Increasing the recycling rate of construction and demolition waste

Avoidance of landfill disposal of mineral wool waste to promote a circular economy and to increase landfill stability

Doschek-Held, K., Krammer, A., Steindl, F. R., Sattler, T. M., & Juhart, J. (2023). *Mineral Wool Waste as Supplementary Cementitious Material - A Novel Thermochemical Treatment Approach*. 196-198. Paper presented at 3rd EURECA-PRO Conference 2023, Chania, Greece. https://doi.org/10.5281/zenodo.10468154

Mineral Wool Waste Recycling

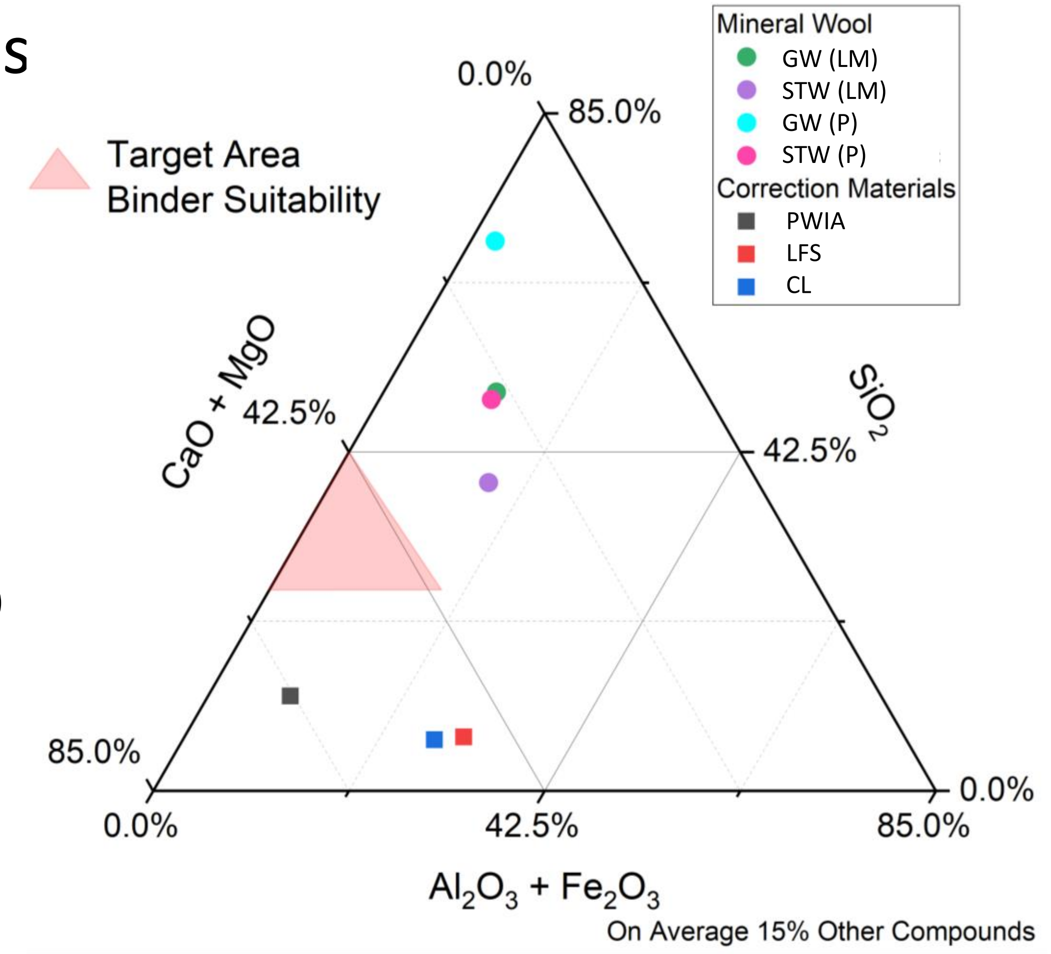
- Materials & Methods

Mineral Wool

- Glass Wool (GW)
- Stone Wool (STW)
  - Landfilled Material (LM)
  - Product (P)

Correction Materials

- Paper Waste Incineration Ash (PWIA)
- Ladle Furnace Slag (LFS)
- Coverter Lime (CL) - Sieving from LFS



Mineral Wool Waste Recycling

- **Results**
  - Production of a similar material **like granulated blast furnace slag**
  - Suitability as a **supplemetary cementitious material could be confirmed** in several test procedures
- **Conclusions** and **Outlook**
  - Possibility to **conserve natural and landfill resources** and to **increase the recycling rate** of construction and demolition waste
  - Further lab scale experiments to **identify influencing parameters** and **examine other correction materials** – like cement kiln dusts
  - **Pilot scale experiments** (100 kg/batch) to investigate the suitability as construction material

Doschek-Held, K., Krammer, A., Steindl, F. R., Sattler, T. M., & Juhart, J. (2023). *Mineral Wool Waste as Supplementary Cementitious Material - A Novel Thermochemical Treatment Approach*. 196-198. Paper presented at 3rd EURECA-PRO Conference 2023, Chania, Greece. https://doi.org/10.5281/zenodo.10468154

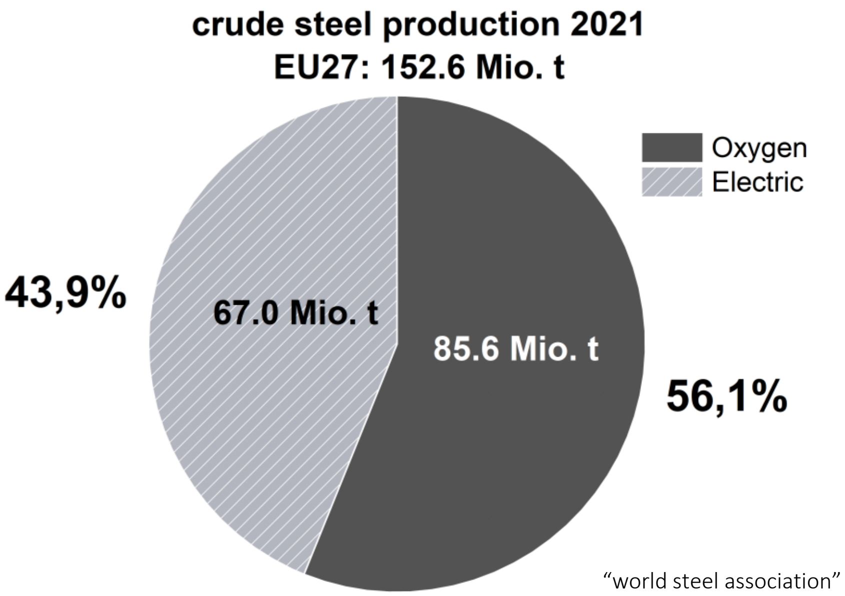
Basic Oxygen Furnace Slag Recycling

2021 – Crude steel production in EU27: **152.6 Mio. t**

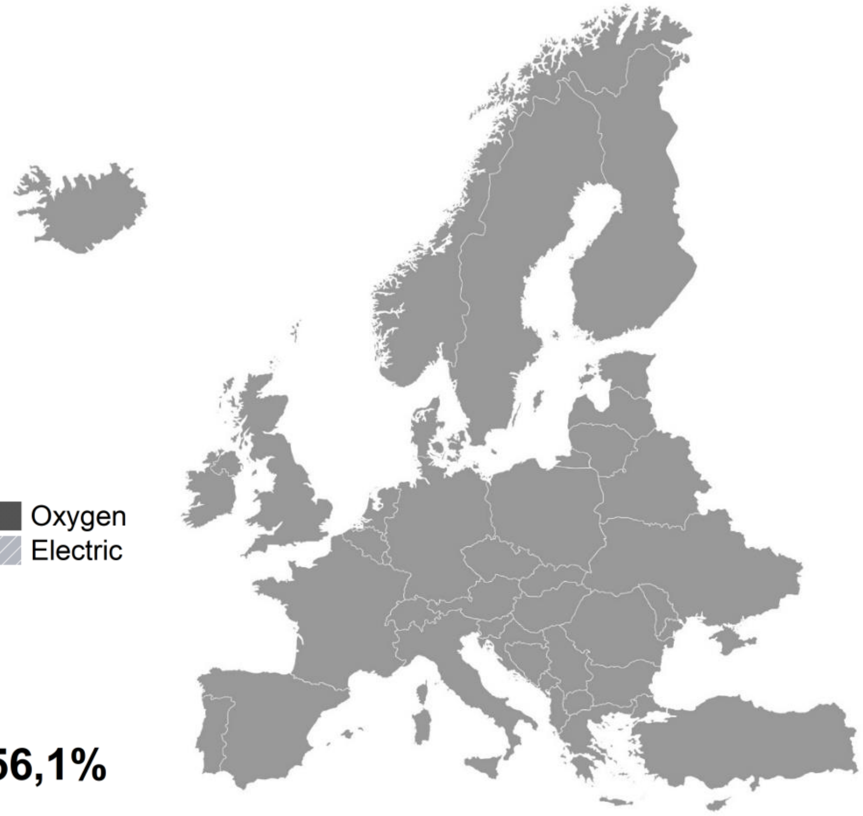
- Blast furnace/Basic oxygen furnace route: 85.6 Mio. t
- Electric arc furnace route: 67.0 Mio. t

Basic oxygen furnace slag:

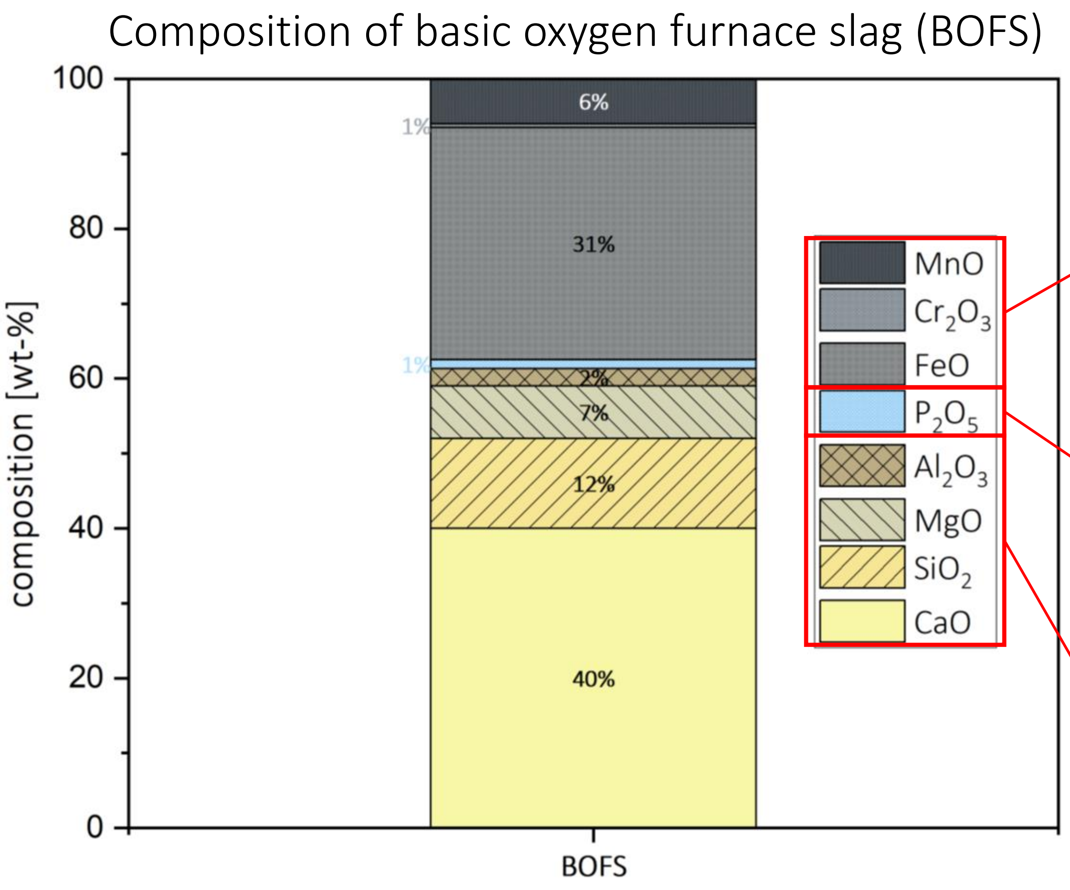
- Accumulation of 100 – 150 kg/t crude steel resulting in a annual amount of ≈ 10 Mio. t/year
- Representative transition metal content:
  - **Fe:** 20 – 25 wt-%
  - **Mn:** 3 – 6 wt-%
  - **Cr:** 0.2 – 0.4 wt-%



"world steel association"



Basic Oxygen Furnace Slag Recycling



"European Commission. Removal of Phosphorus from BOF-slag (PSP-BOF). Luxembourg; 2018."

Potential as a result of pyrometallurgical treatment (100 % yield):

Metallic alloy composing of:

- Iron (2 – 3 Mio. t/year)
- Manganese (0.3 – 0.6 Mio. t/year)
- Chromium (20 000 – 40 000 t/year)

Phosphorus:

- P_2O_5 (100 000 t/year)

Import EU:
5.0 - 5.5 Mio. t/year of rock phosphate (10 - 25 % P_2O_5)

"Tulsidas, Harikrishnan; Gabriel, Sophie; Kiegiel, Katarzyna; Haneklaus, Nils (2019): Uranium resources in EU phosphate rock imports. In: *Resources Policy* 61, S. 151–156. DOI: 10.1016/j.resourpol.2019.02.012."

Mineral product:

- Slag (6 Mio. t/year)

Basic Oxygen Furnace Slag Recycling

Possible separation technologies at a glance:

Mechanical processing

- Classical processing methods: comminution, classification, magnetic separation and flotation
- Problem with BOFS: intergrowth of iron and phosphorus in the slag phases

Hydrometallurgy

- *All metal recovery processes that utilise the material-specific solubility and different wettability of the elements and their compounds at lower temperatures - relative to pyrometallurgy – wet chemical processes*
- Bio-leaching: Biological wet-chemical processes (fungi, microorganism…)

Pyrometallurgy

- **Refers to the entirety of metal extraction and metal refining processes that require high temperatures and take place in the absence of oxygen**

Basic Oxygen Furnace Slag Recycling

Thermodynamics of pyrometallurgy – carbothermal reduction of basic oxygen furnace slag:

Measure of the driving force of a change of state in a system
→ maximum work performed by or on the system:

- V=const. : Free energy F
- p=const. : free enthalpy G (Gibbs energy)

$$dG = -S \cdot dT + V \cdot dp$$

… a system is in chemical equilibrium→ dG = 0

$$A + B \leftrightarrow C + D$$

$$\Delta_R G = \sum G_{Produkte} - \sum G_{Reaktanden}$$

$$\Delta_R G = G_C + G_D - (G_A + G_B) = H_C + H_D - (H_A + H_B) - T \cdot (S_C + S_D - (S_A + S_B)) = \Delta H - T\Delta S$$

$\boldsymbol{\Delta_R G < 0}$ the process (chem. reaction) takes place spontaneously
$\boldsymbol{\Delta_R G > 0}$ the process (chem. reaction) only takes place when energy is supplied

Basic Oxygen Furnace Slag Recycling

Thermodynamics of pyrometallurgy – carbothermal reduction of basic oxygen furnace slag:

Activity a_i: Measure of the chemical potency of a solute i (i.e. its ability or willingness to react chemically with other substances)

Factors influencing activity: p, T and the nature of the solution (type, structure and <u>composition of the solution</u>)

$$a_i = \gamma_i \cdot x_i$$

γ_i … Activity coefficient

$\gamma_i < 1$ → Tendency to segregate

$\gamma_i > 1$ → Tendency to connect

$\gamma_i = 1$ → Ideal state

… in the chem. equilibrium: $\Delta G^0 = -R \cdot T \cdot ln(K)$ … further applies: $\Delta G^0 = \Delta H_R - T \cdot \Delta S_R$

Essential reactions in the carbothermal treatment of slags are <u>oxidation or reduction reactions</u>:

$$x \cdot Me\ (s,l) + O_2 \leftrightarrow Me_xO_2(s,l)$$

$$K = \frac{a_{Me_xO_2}}{a_{Me}^x \cdot \frac{p_{O_2}}{p^0}}$$

Basic Oxygen Furnace Slag Recycling

Thermodynamics of pyrometallurgy – carbothermal reduction of basic oxygen furnace slag:

Essential reactions in the carbothermal treatment of slags are **oxidation or reduction reactions**:

$$x \cdot Me\,(s,l) + O_2 \leftrightarrow Me_xO_2(s,l) \qquad K = \frac{a_{Me_xO_2}}{a_{Me}^{x} \cdot \frac{p_{O_2}}{p^0}}$$

At a standard pressure of p^0 = 1 bar, or at an activity of metal and metal oxide = 1 (pure substances):

$$\Delta G^0 = -R \cdot T \cdot ln(K) = -R \cdot T \cdot ln\left(\frac{1}{p_{O_2}}\right) = R \cdot T \cdot ln(p_{O_2})$$ → **Oxygen potential**

$$R \cdot T \cdot ln(p_{O_2}) = \Delta H_R - T \cdot \Delta S_R$$

$2Fe + O_2 \leftrightarrow 2FeO$	$\Delta H_R < 0$: exothermic reaction, $\Delta S_R < 0$: Solid forms from one mole of gas
$2C + O_2 \leftrightarrow 2CO$	$\Delta H_R < 0$: exothermic reaction, $\Delta S_R > 0$: 2 moles of gas are formed from one mole of gas

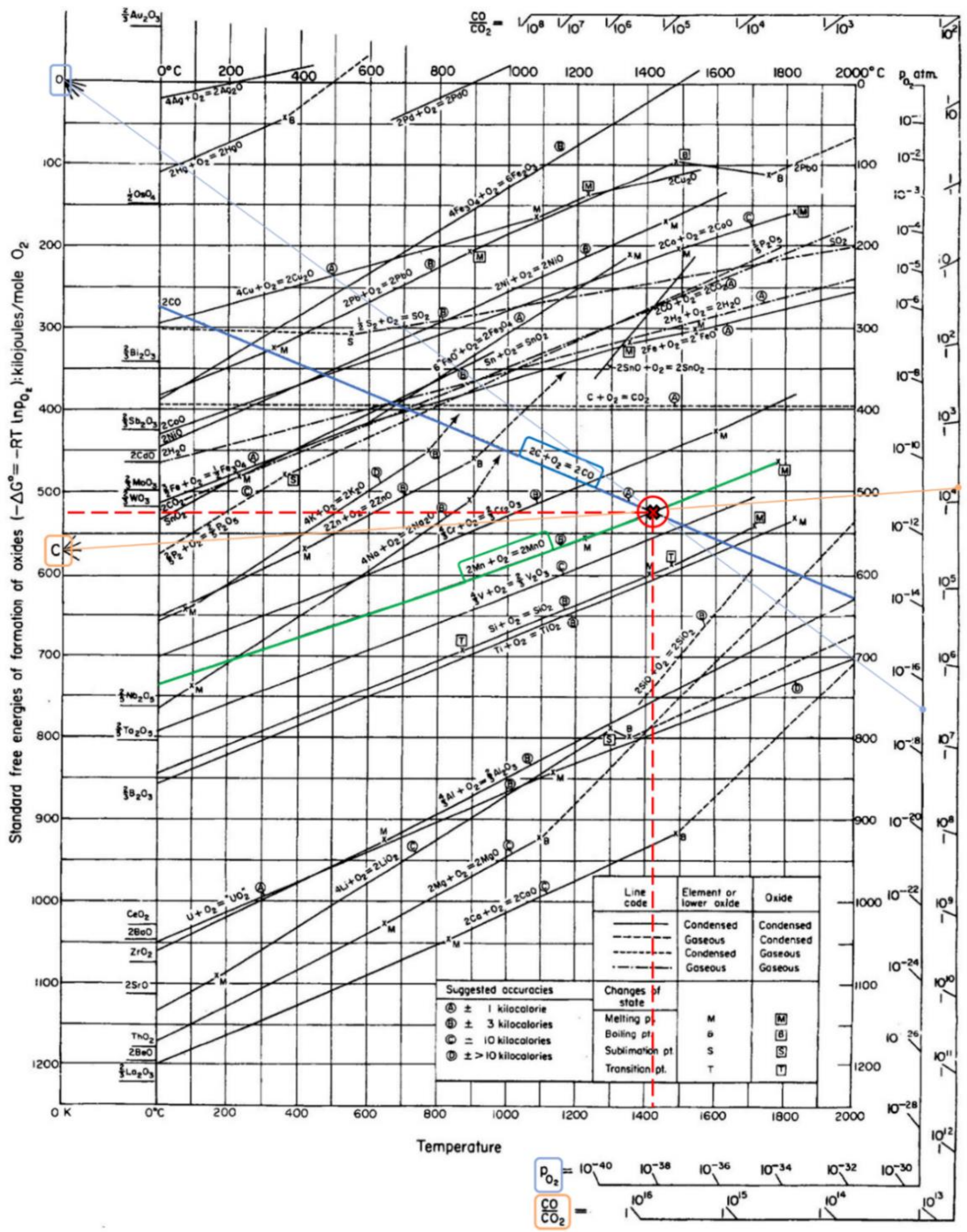
BOFS Recycling

Richardson Ellingham diagram:

- Plot of the Gibbs energy vs. temperature for oxidation reactions with one mole O_2
- Metals with lower potential reduce oxides of higher potential e.g., Al reduces FeO
- All oxidation reactions of metals show almost similar positive slopes (negative entropy change)
- The pressure dependent oxidation of carbon to CO show a negative slope (positive entropy change)
- Phase transformations → change in entropy (slope)

What can be read off from the diagram:

- Minimum reduction temperature with carbon or hydrogen as reductant
- Required CO/CO_2 ratio, H_2/H_2O ratio and oxygen partial pressure for the reduction



BOFS Recycling

Example for the reduction of MnO with carbon:

$$2MnO + 2C \leftrightarrow 2Mn + 2CO$$

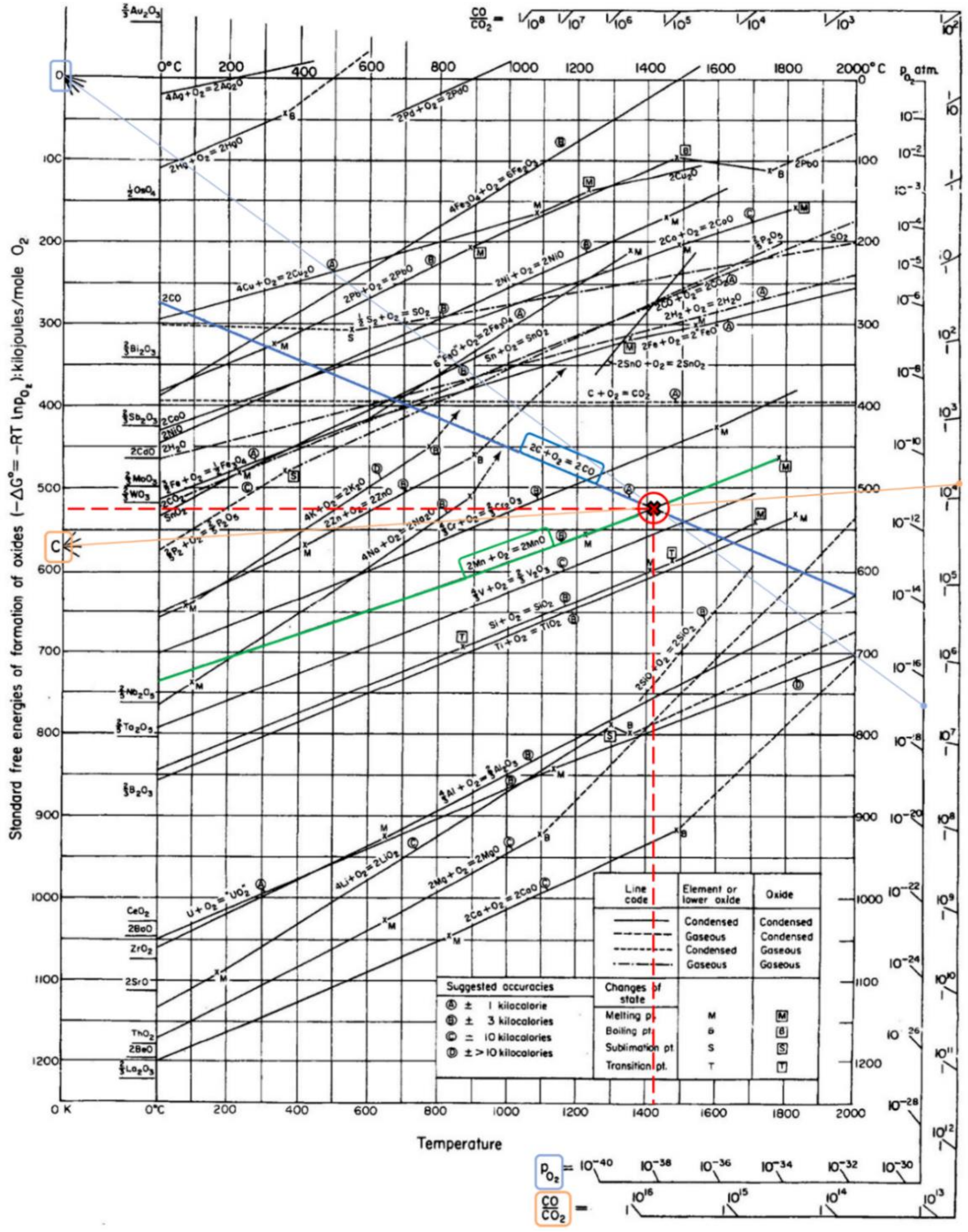
Richardson Ellingham diagram:

- Only valid for pure substances (a_{Me}, $aMe_xO_2 = 1$)

$$R \cdot T \cdot ln(p_{O_2}) = \Delta H_R - T \cdot \Delta S_R$$

Basic oxygen furnace slag is a multi-component system:

> "In addition to temperature and pressure, thermodynamic variables such as Gibbs energy or the chemical potential are also a function of composition (mutual influence of the components)"



BOFS Recycling

Conclusion from theoretical consideration of the pyrometallurgical treatment of BOFS:

- At process temperature (approximately 1873 K) FeO, MnO, Cr_2O_3 and P_2O_5 can be reduced with pyrometallurgical treatment by carbothermal reduction of BOFS due to thermodynamics:
  - FeO, MnO, and Cr_2O_3 forming a metal alloy:

$$2FeO + 2C \leftrightarrow 2Fe + 2CO$$
$$\frac{2}{3}Cr_2O_3 + 2C \leftrightarrow \frac{4}{3}Cr + 2CO$$
$$2MnO + 2C \leftrightarrow 2Mn + 2CO$$

  - P_2O_5 reduction form highly reactive phosphorus gas P_2 according to the high vapor pressure:

$$\frac{2}{5}P_2O_5 + 2C \leftrightarrow \frac{2}{5}P_2 + 2CO$$

  - Remaining metal oxides e.g., CaO, SiO_2, MgO, Al_2O_3 can only be reduced at higher temperatures, forming a slag

Basic Oxygen Furnace Slag Recycling

Objective: Production of **high-quality secondary raw materials** as a result of an **efficient pyrometallurgical recycling process**

Basic oxygen furnace slag

+ correction substances

Challenge:

Phosphorus recovery

Pyrometallurgical treatment

Gas fraction (CO, P_2)

Metal fraction

Mineral fraction

Metal fraction (Fe, Mn, Cr, C Phosphorus) as a secondary raw material in the steel industry

Mineral fraction (CaO, SiO_2, MgO, Al_2O_3) as a product similar to granulated blast furnace slag for use in the cement industry

Basic Oxygen Furnace Slag Recycling

Objective: Production of **high-quality secondary raw materials** as a result of an **efficient pyrometallurgical recycling process**

Challenge for phosphorus recovery from basic oxygen furnace slag:

- High affinity of gaseous phosphorus to the metal alloy → dissolution of phosphorus in a metal bath resulting in the formation of metal phosphides
    - Accumulation of phosphorus in the metal impairs its quality for reuse in the steel industry
    - The phosphorus is 'lost' in the metal and therefore cannot be recycled

Basic Oxygen Furnace Slag Recycling

Current research:

Phosphide formation

- Investigation of the affinity between phosphorus and iron, manganese, chromium

Phosphorus gasification

- Influencing the reduction of phosphorus through the chemical manipulation of BOFS

Phosphorus recovery

- Planning, conceptual design, and construction of an exhaust gas line for the recovery of gaseous phosphorus

Basic Oxygen Furnace Slag Recycling

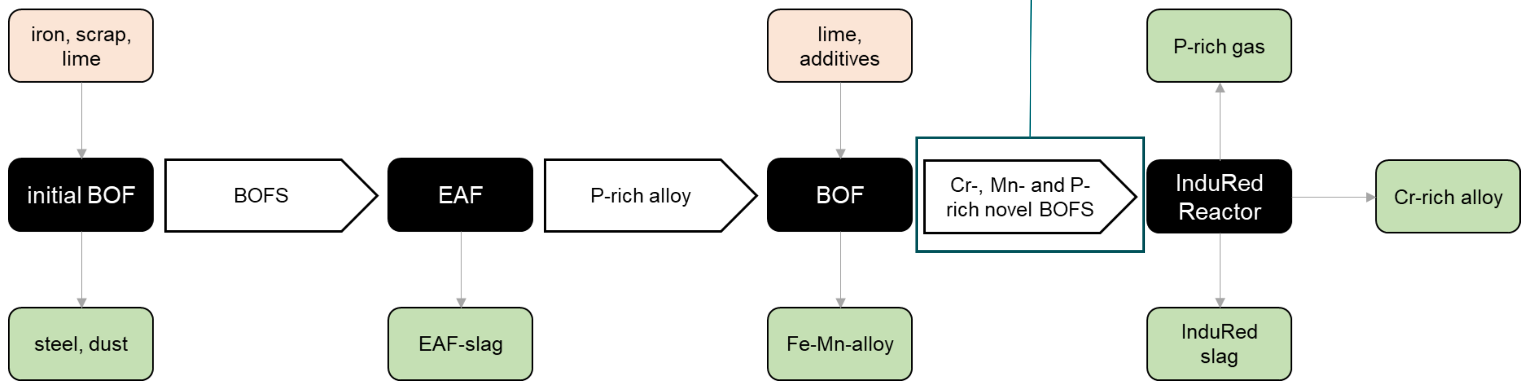
Current research – phosphide formation:

Preparation of the specimen
Totally 3 specimen: **BOFS-industry** **BOFS-synth.** **APR-synth.** used chemicals (purity >97%): $CaCO_3$, SiO_2, MgO, Al_2O_3, $Ca_3(PO_4)_2$, Fe_3O_4, Cr_2O_3, MnO_2

→ Production of the specimen → Obtaining the specimen → Carbothermal reduction → Separation into ME and MI → Analysis of ME and MI

Idea of a slag, which is:
- Depleted in Fe
- Enriched with P, Mn, and Cr

APR – Alternative Process Route



Basic Oxygen Furnace Slag Recycling

Current research – phosphide formation:

Theoretical consideration of transition metal phosphide species formation:

$$x \cdot [Me] + y \cdot \{P_2\} \leftrightarrows [Me_xP_{2y}] \qquad K = \frac{a_{Me_xP_{2y}}}{a_{Me}^x \cdot \left(\frac{p_{P_2}}{p^0}\right)^y}$$

$$\Delta G_R = -R \cdot T \cdot \ln\left(\frac{a_{Me_xP_{2y}}}{a_{Me}^x \cdot \left(\frac{p_{P_2}}{p^0}\right)^y}\right) = -R \cdot T \cdot \ln(K) \qquad \Delta G_R = \Delta H_R - T \cdot \Delta S_R$$

$3[Fe] + 0.5\{P_2\} \leftrightarrows [Fe_3P]$
$2[Fe] + 0.5\{P_2\} \leftrightarrows [Fe_2P]$
$[Fe_2P] + 0.5\{P_2\} \leftrightarrows 2[FeP]$
$[FeP] + 0.5\{P_2\} \leftrightarrows [FeP_2]$
$3[Cr] + 0.5\{P_2\} \leftrightarrows [Cr_3P]$
$\frac{8}{3}[Cr_3P] + \{P_2\} \leftrightarrows \frac{2}{3}[Cr_{12}P_7]$
$\frac{2}{5}[Cr_{12}P_7] + \{P_2\} \leftrightarrows \frac{24}{5}[CrP]$
$3\{Mn\} + 0.5\{P_2\} \leftrightarrows [Mn_3P]$
$4\{Mn\} + \{P_2\} \leftrightarrows 2[Mn_2P]$
$3\{Mn\} + \{P_2\} \leftrightarrows [Mn_3P_2]$
$\{Mn\} + 0.5\{P_2\} \leftrightarrows [MnP]$
$[MnP] + 0.5\{P_4\} \leftrightarrows [MnP_3]$

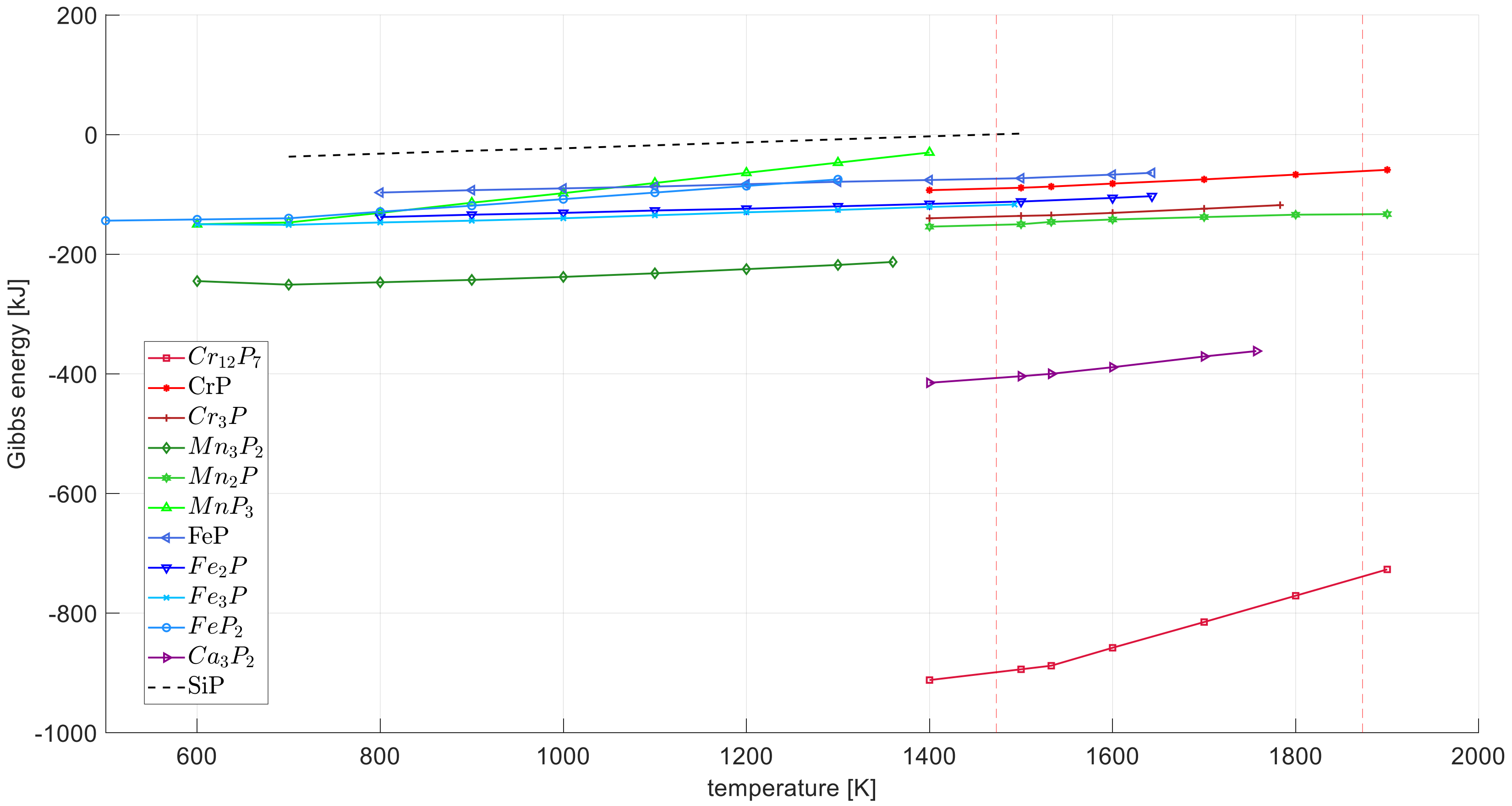
As for oxygen, a “Richardson Elingham” diagram can also be constructed for phosphorus using thermodynamic data of the phosphide formation reactions

Basic Oxygen Furnace Slag Recycling

Current research – phosphide formation:

From thermodynamic data from literature:

- Iron, Manganese, and chromium show all a high affinity to phosphorus
- Favored metal phosphides:
  - Iron: Fe_2P, Fe_3P
  - Manganese: Mn_3P_2
  - Chromium: Cr_3P



Christoph Gatschlhofer; Zlatko Raonic; Irmtraud Marschall; Anna Christine Krammer; Klaus Doschek-Held; Harald Raupenstrauch (2024): Investigation of the phosphide formation for transition metals during carbothermal reduction of industrial and synthetic slags. Manuscript submitted for publication. In: *Circular Economy and Sustainability*.

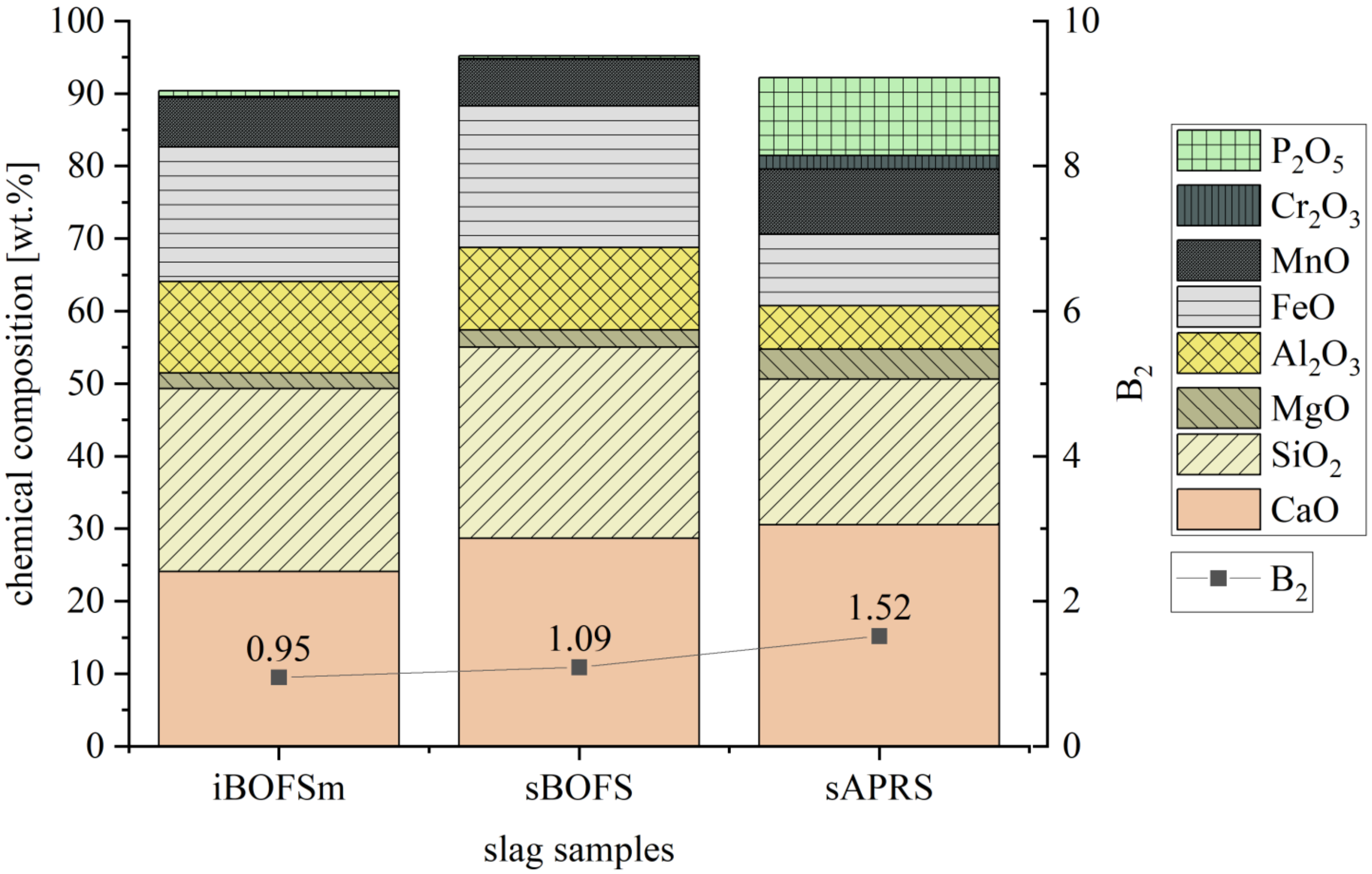
Basic Oxygen Furnace Slag Recycling

Current research – phosphide formation:

Preparation of the slag samples:

- iBOFS: Industrial basic oxygen furnace slag modified with pure quarts sand
- sBOFS: Synthetic replica of the modified industrial basic oxygen furnace slag
- sAPRS: Synthetic replica of the slag from the alternative process route

iBOFS, sBOFS, and sAPRS are prepared by a melting step in an Al_2O_3-crucible at 1550 °C (using high purity chemicals)



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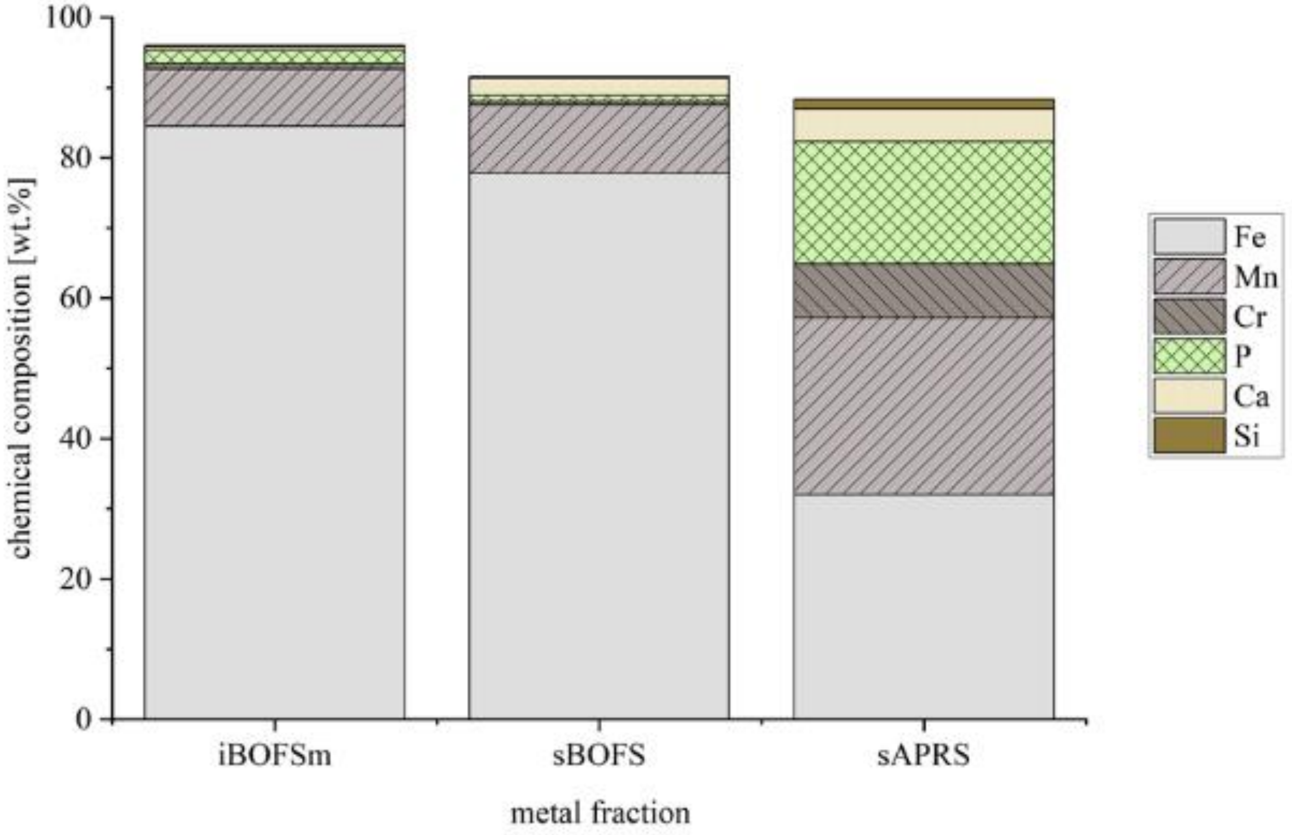
Basic Oxygen Furnace Slag Recycling

Current research – phosphide formation:

Carbothermal treatment in a graphite crucible at 1600 °C of:

- iBOFS: Industrial basic oxygen furnace slag modified with pure quarts sand
- sBOFS: Synthetic replica of the modified industrial basic oxygen furnace slag
- sAPRS: Synthetic replica of the slag from the alternative process route

Rapid cooling with inert gas → Separation of metal- and mineral fraction



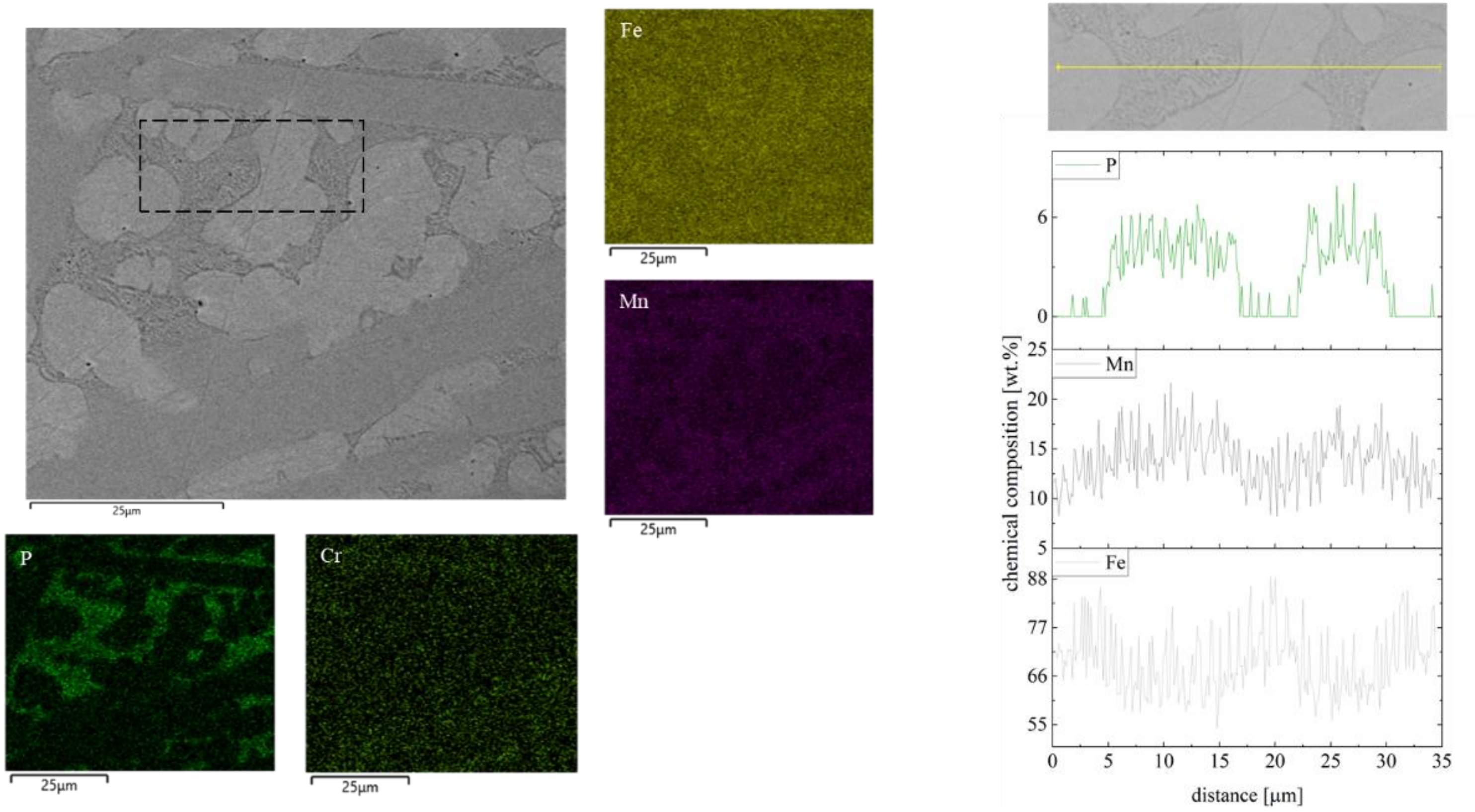
Christoph Gatschlhofer; Zlatko Raonic; Irmtraud Marschall; Anna Christine Krammer; Klaus Doschek-Held; Harald Raupenstrauch (2024): Investigation of the phosphide formation for transition metals during carbothermal reduction of industrial and synthetic slags. Manuscript submitted for publication. In: *Circular Economy and Sustainability*.

Basic Oxygen Furnace Slag Recycling

Current research – phosphide formation:

SEM-analysis results from carbothermally treated iBOFS:

- >95 % of phosphorus dissolves in the metal phase
- Ferromagnetic properties
- Partial solidification of phosphide compounds between metallic phases
- Phosphide phases are rich in manganese and slightly amounts of chromium are detectable



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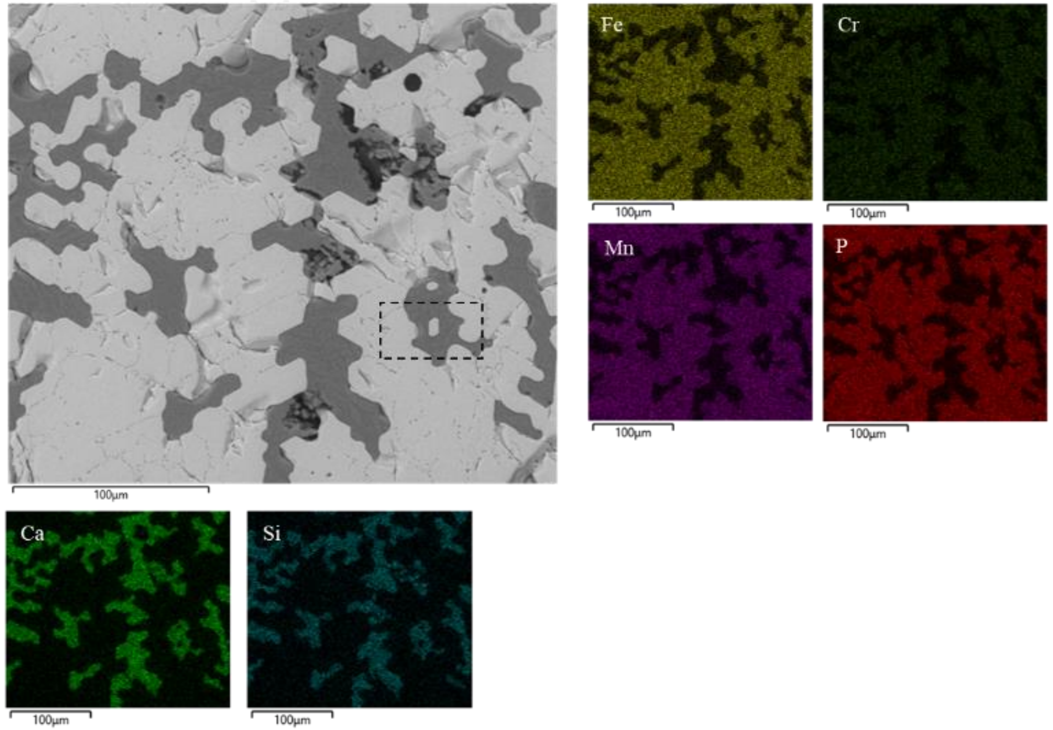
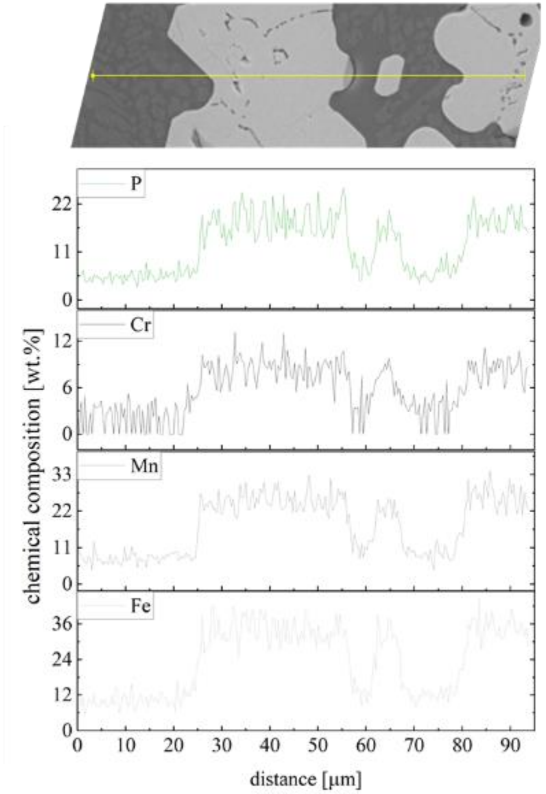
Basic Oxygen Furnace Slag Recycling

Current research – phosphide formation:

SEM-analysis results from carbothermally treated sAPRS:

- Pure non-magnetic phosphide species is formed
- No ferromagnetic properties
- Phosphorus content in the phosphide phase up to 20 wt-%
- Phosphide phases are a mixed iron-, manganese- and chromium-phosphide
- Phosphorus show a high affinity to all reduceable transition metal species present in BOFS





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Phosphorus recovery from sewage sludge ash

Background:

- **Sewage sludge** and **animal waste** contain significant amounts of phosphorus - continuous source
- **Sewage sludge accumulates in the sewage treatment plant →** after biogas is produced, the sludge is dewatered and dried
- **Utilization options** for dried sewage sludge:
  - Direct spreading on the field
  - Composting
  - Landfilling
  - **Thermal utilisation**
    - **Mono-incineration**
    - Co-incineration (Phosphorus in the ash is diluted to uneconomical levels for its recovery)
    - **Pyrolysis (Carbon remains in the material)**

} Unwanted components such as hormones, drug residues and heavy metals remain in the material

Phosphorus recovery from sewage sludge ash

Background:

- **Mono-incineration** of sewage sludge in **Stationary fluidised bed:**
  - Fluidisation of a bed material (sand)
  - High heat transfer rate at 850 - 950°C
  - No NOx formation
  - λ = 1.25 – 1.50
  - Start-up: Support burner insert (gas or oil burner)
  - Independent combustion from 4.5 MJ/kg
  - Ash discharge → exhaust gas flow and sand extraction
- **Pyrolysis** of sewage sludge:
  - thermal decomposition under oxygen exclusion or low-oxygen conditions
  - Wide temperature range (300 – 1000 °C)
  - Product streams from pyrolysis process:
    - ***Bio-oil***
    - ***Biochar*** (predominant proportion of phosphorus bound)
    - ***Pyrolysis*** gas

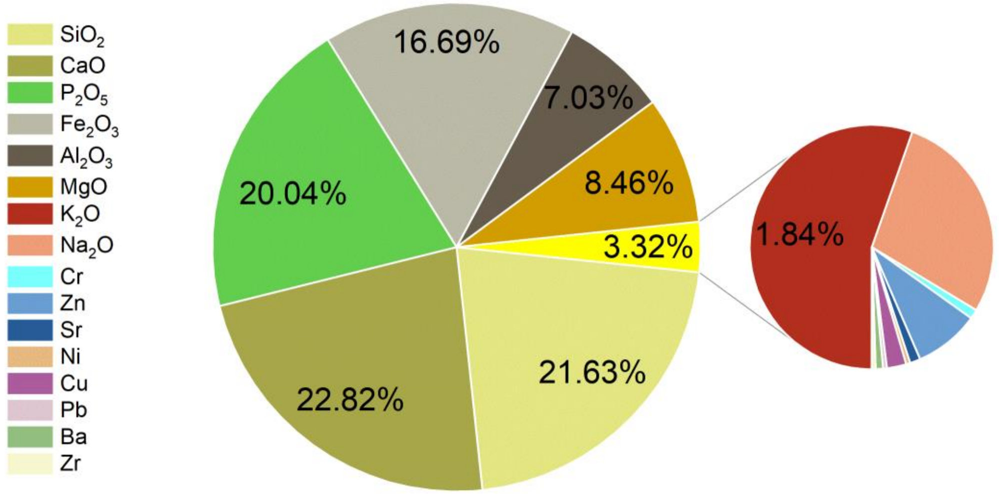
Calorific value of *dried sewage sludge*:

- Raw sludge: approx. *19 MJ/kg*
- Digested sludge: approx. *11 MJ/kg*

Phosphorus recovery from sewage sludge ash

<u>***Characterization of sewage sludge ash:***</u>

- *Elemental composition:*
    - *96,7 % (CaO, SiO_2, P_2O_5, Fe_2O_3, MgO und Al_2O_3)*
    - *High proportion of impurities*
- *Phase analysis by XRD: complicated mixture of*
    - *Whitlockite + apatite as phosphate carrier*
    - *MgO, CaO, haematite, quartz, Ca-sulphate*
    - *Feldspars, Ca-silicates, perhaps tridymite*



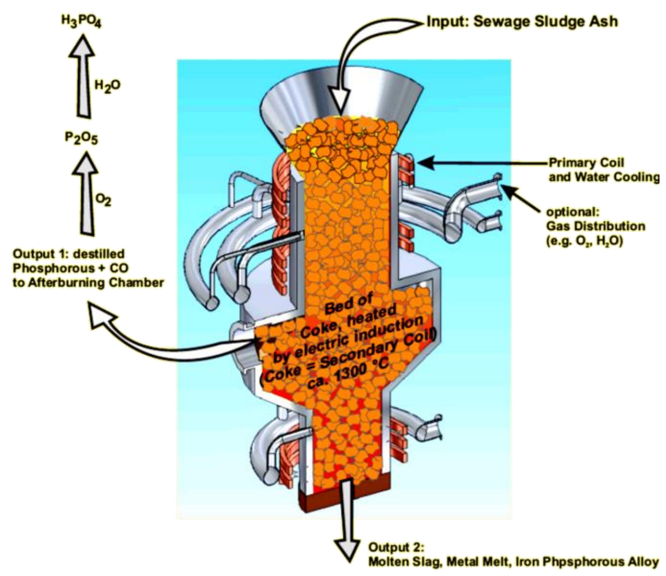
Briquetted sewage sludge ash

Phosphorus is bound in the sewage sludge by microorganism or predominantly by aluminum- or iron-precipitation salts → Incineration leads to phosphorus concentration in the ash

Phosphorus Recovery - RecoPhos

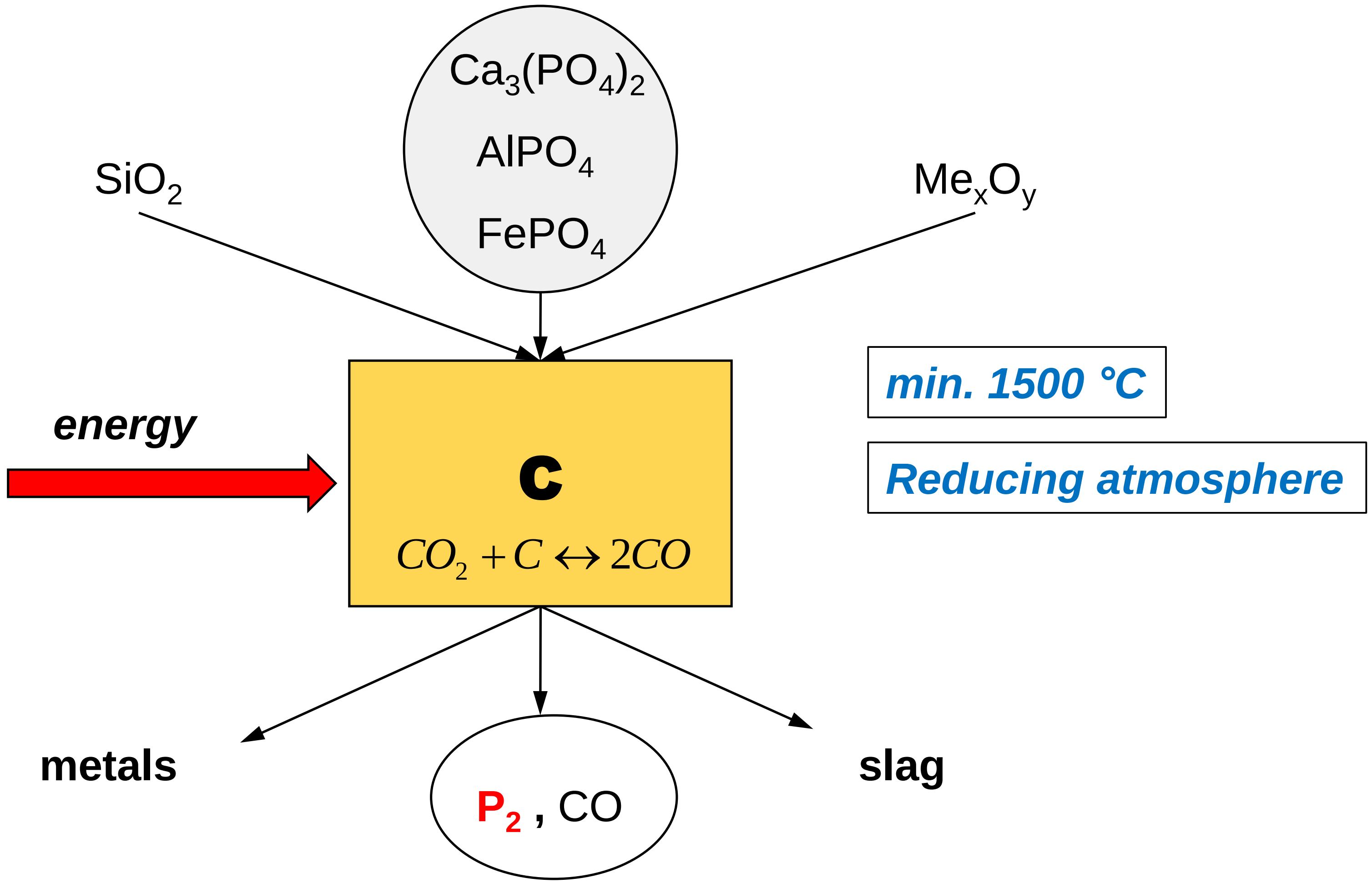
Recovery of Phosphorus from Sewage Sludge and Sewage Sludge Ashes with the Thermo-Reductive RecoPhos Process

Duration:	36 months (March 2012 – February 2015)
Instrument:	Eco-Innovation/FP7
Project Reference:	FP7-Environment; Project Number: 282856-2
Budget:	4.5 Mio. €
EC Contribution:	3.2 Mio. €
Contract Type:	Collaborative Project/Eco-Innovation
Project Coordinator:	Montanuniversität Leoben



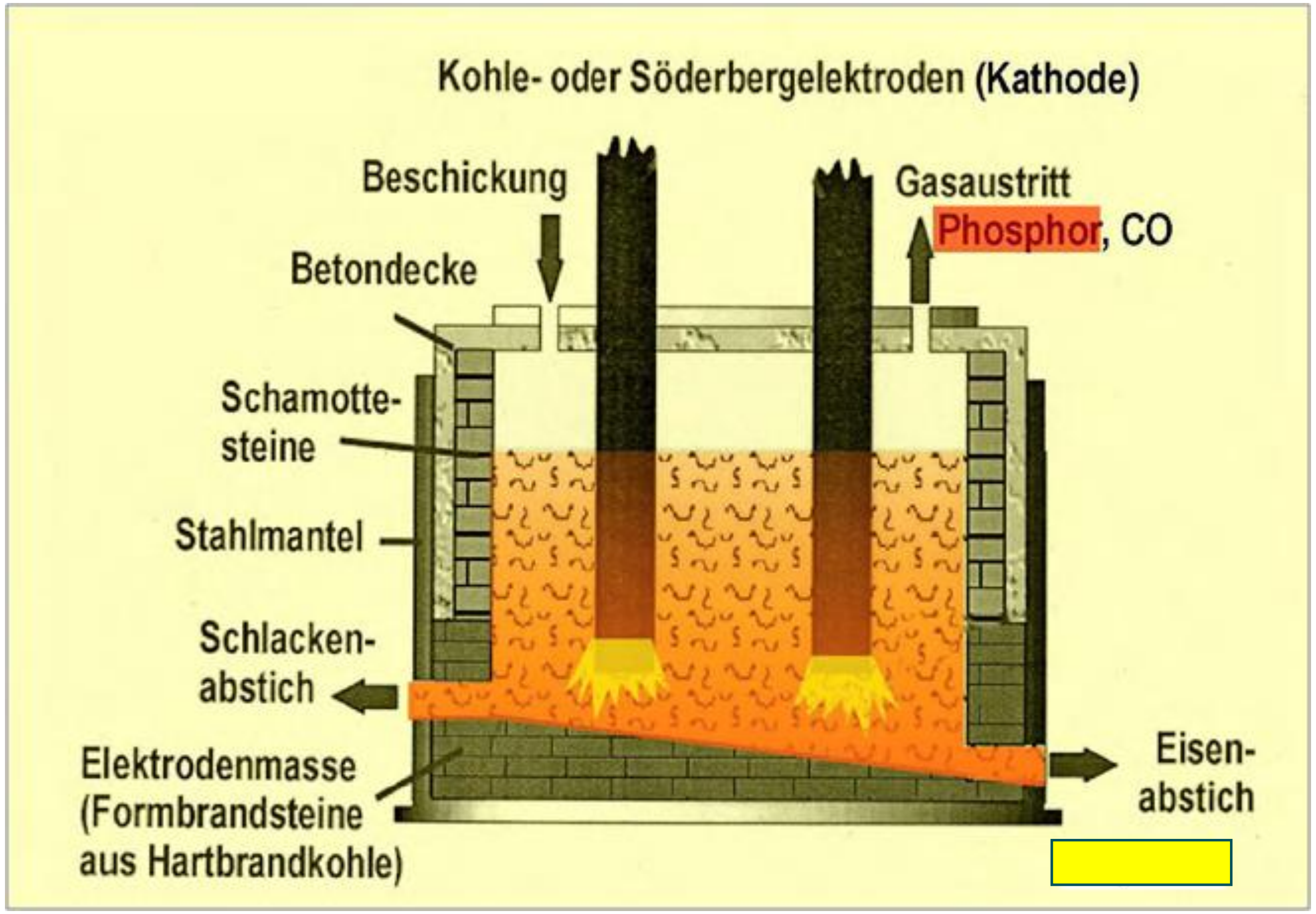
www.recophos.org

RecoPhos – Chemical Reactions



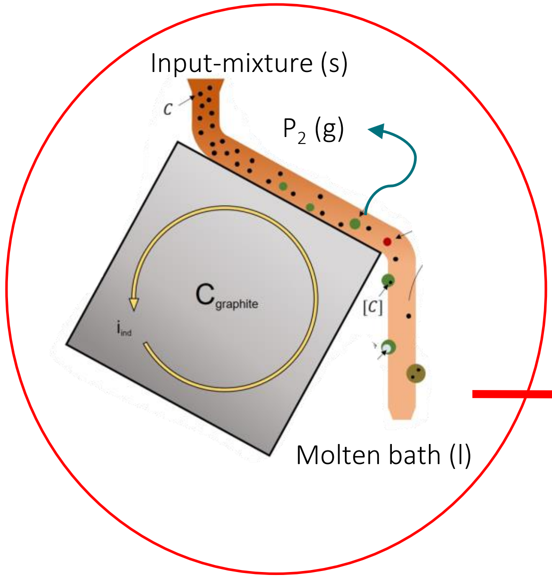
$$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C \rightarrow 3\,CaSiO_3 + 5\,CO + P_2$$

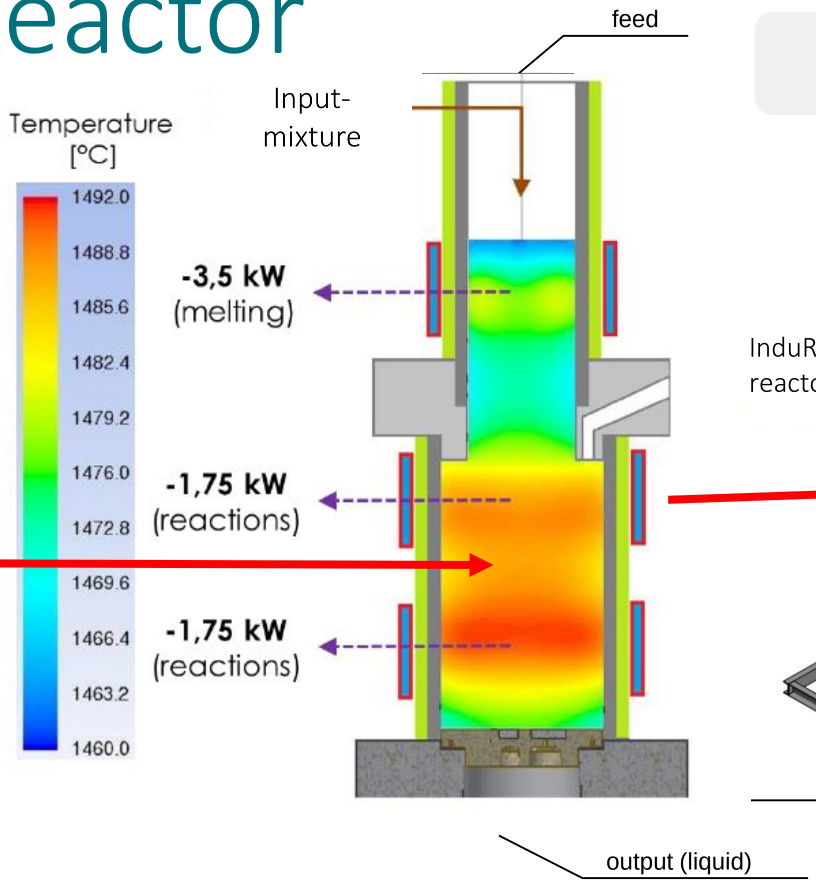
Production of Phosphorus
State of the art: Wöhler Process



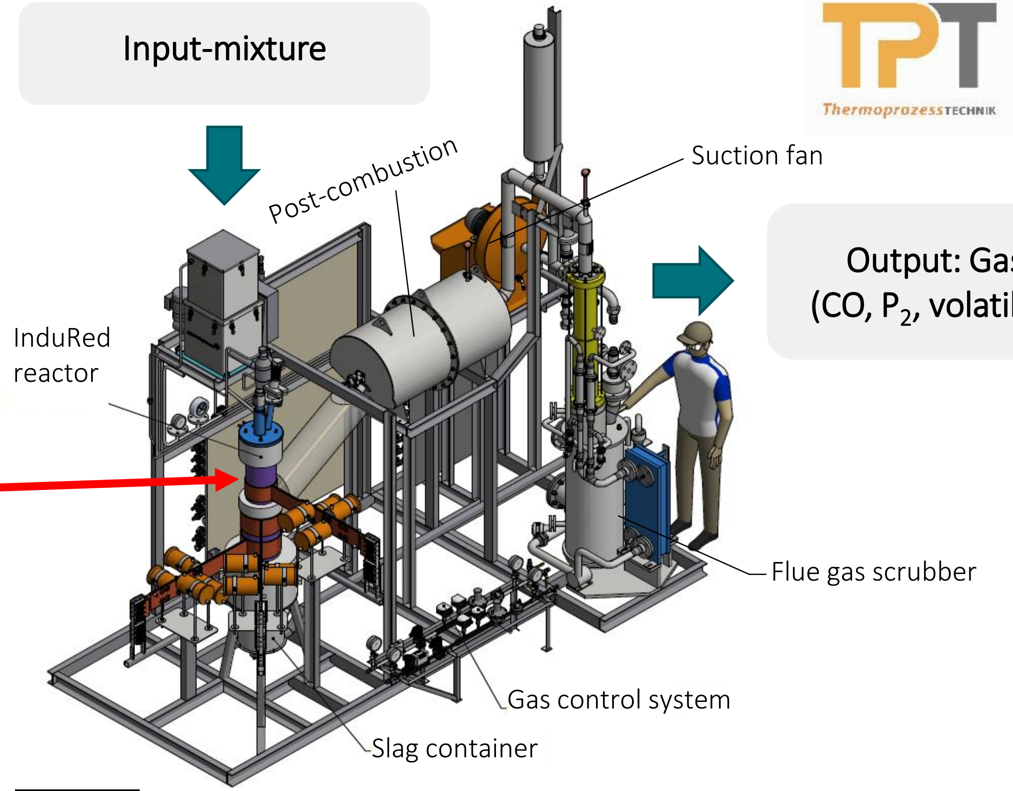
$$Ca_3(PO_4)_2 + 3\ SiO_2 + 5\ C \rightarrow 3\ CaSiO_3 + 5\ CO + P_2$$

InduRed Reactor





Input-mixture



Output: Gas (CO, P_2, volatiles)

Output: molten bath

Mineral fraction (CaO, SiO_2, MgO, Al_2O_3...) (Cement industry)

Metal fraction (Fe, C, P) if FeO enters the reactor (Steel industry)

[1] Raupenstrauch et al.: Apparatus and process for thermal treatment of raw material containing lithium compounds and phsophorous compounds, method of recovering lithium and/or phsophorous from residual material of lithium-ion batteries'. WO 2021/175703 A1

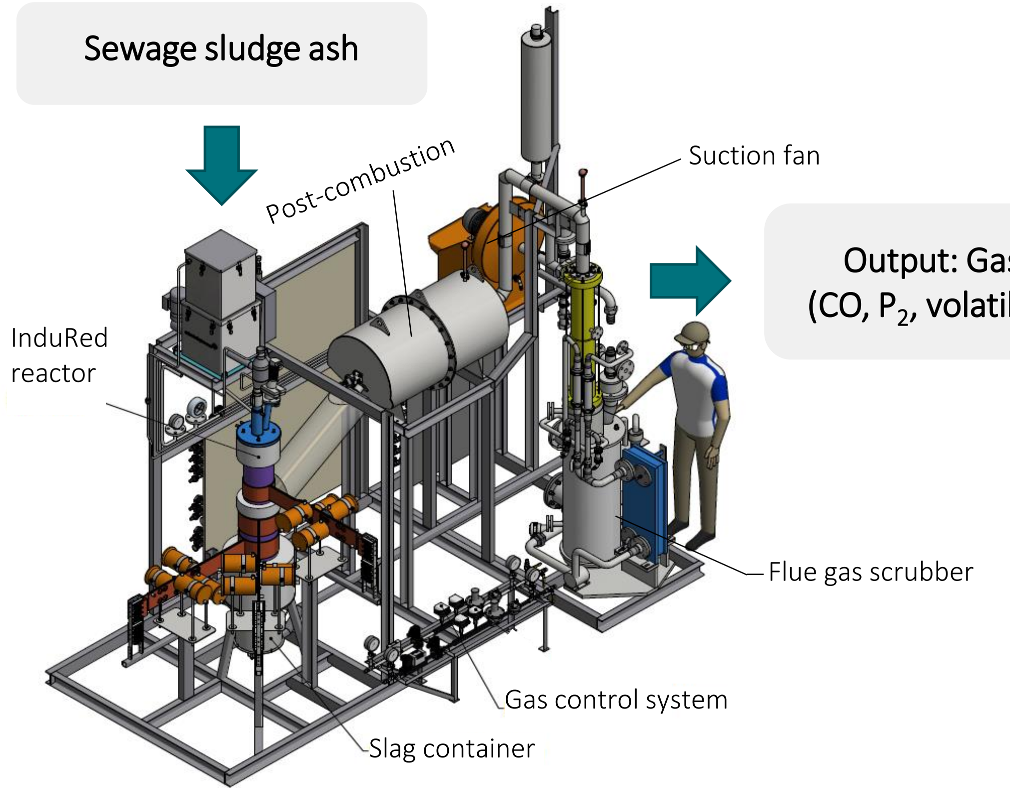
https://patents.google.com/patent/WO2021175406A1/en

Phosphorus recovery from sewage sludge ash

Methodological approach:

- Thermochemical digestion of sewage sludge ash using the RecoPhos process
- The following fractions can be recovered from chemically modified sewage sludge ash:
  - Phosphorus as phosphoric acid
  - Mineral fraction
  - Metal fraction

Sewage sludge ash



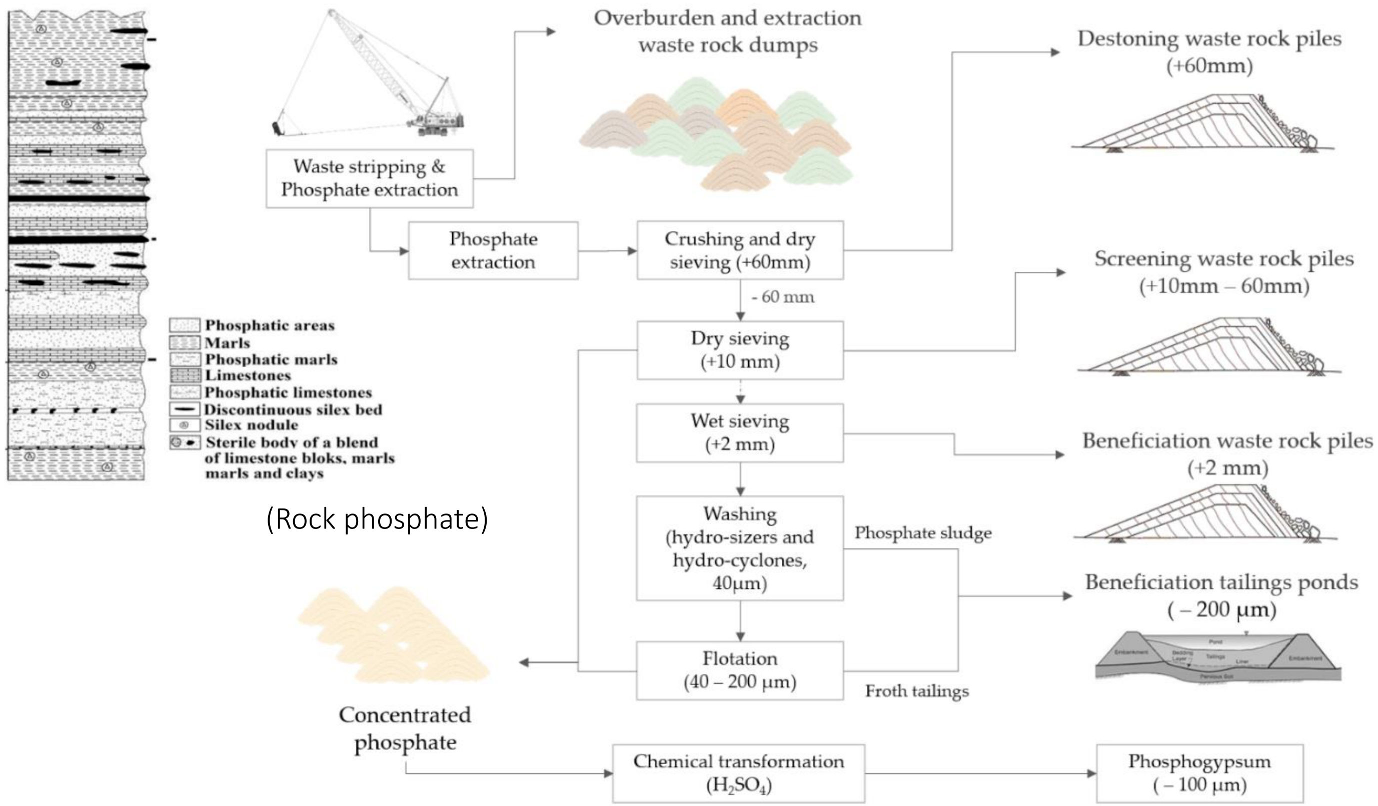
Output: Gas
(CO, P_2, volatiles)

Output: molten bath
Mineral fraction (Cement industry)
Metal fraction (Steel industry)

Thermochemical treatment of chemically modified Moroccan rock phosphate

Status quo:

- **Primary production** of rock phosphate leads to very large quantities of material going to landfill → **ecological problems**
- Rock phosphate is either processed locally into **phosphoric acid** or exported as a **raw material for mineral fertiliser** production

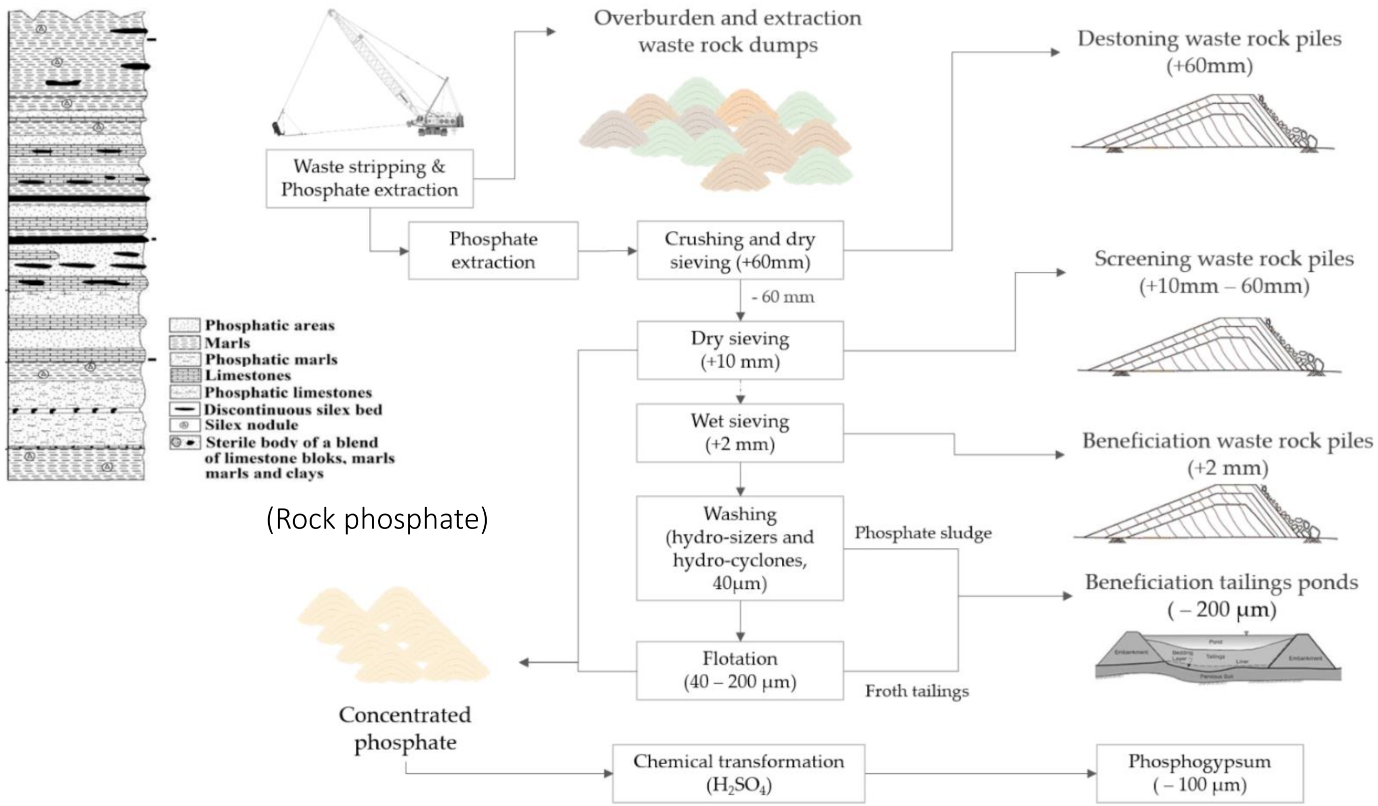


Source: Y. Taha, A. Elghali, R. Hakkou, and M. Benzaazoua, "Towards Zero Solid Waste in the Sedimentary Phosphate Industry: Challenges and Opportunities," *Minerals*, vol. 11, no. 11, p. 1250, 2021, doi: 10.3390/min11111250.

Thermochemical treatment of chemically modified Moroccan rock phosphate

Path from **phosphate ore** to **rock phosphate** (The example of Morocco):

- Extraction of phosphate rich mineral layers (removal of overburden und waste rock)
- Crushing and dry sieving (+60 mm)
- Dry sieving (+10 mm)
- Wet sieving (+2 mm)
- Washing (hydro-sizers and hydro-cyclones, 40 µm)
- Flotation (40 – 200 µm)
- Concentrated phosphate (**rock phosphate**)
- Production of phosphoric acid wet chemically with H_2SO_4



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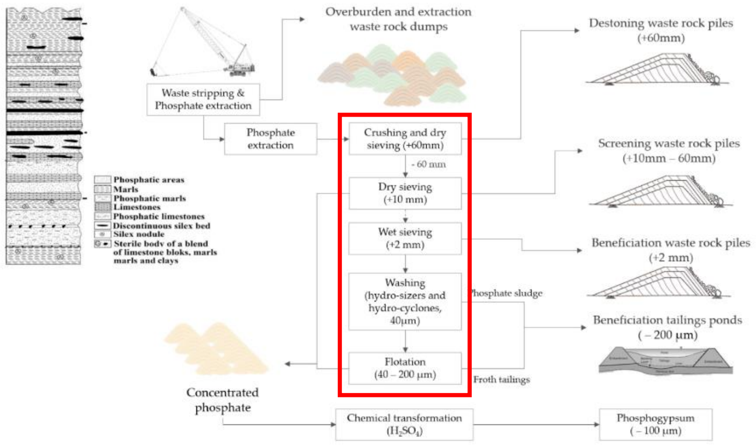
Thermochemical treatment of chemically modified Moroccan rock phosphate

Rock phosphate from Morocco:

- <u>**Mechanical treatment**</u>
  - Increased phosphorus content in certain grain sizes in sedimentary phosphate rock.
  - Obtain the so-called ‘**sweet-size fraction**’, which can have a P_2O_5 content > 30 wt.%, using even the simplest classification processes.
  - **Magmatic phosphate ore** has a significantly lower phosphate content than sedimentary phosphate ore. In the only European deposit in Finland, the phosphate ore has a phosphorus content of around 5 wt.%, while in Russia it is around 15 wt.%.
  - **Magmatic phosphate ore:** It is not possible to increase the P_2O_5 content using simple sieving processes. As a result, the processing of rock phosphate with a high phosphorus content is much more complex than with sedimentary phosphate ores. Typical treatment processes are mechanical crushing, screen classification and flotation, whereby in this case, unlike with sedimentary phosphate ore, several treatment processes must be used.

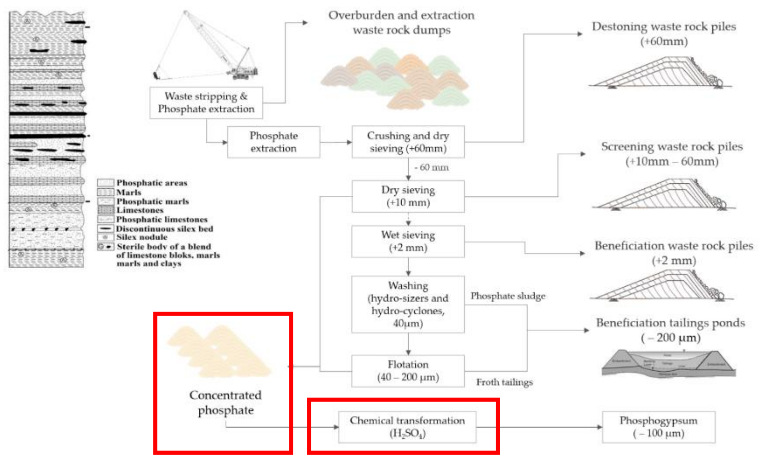


Fabian Kraus, Malte Zamzow, Lea Conzelmann, Christian Remy, Anne, Ökobilanzieller Vergleich der P-Rückgewinnung aus dem Abwasserstrom mit der Düngemittelproduktion aus Rohphosphaten unter Einbeziehung von Umweltfolgeschäden und deren Vermeidung. Dessau-Roßlau.

Thermochemical treatment of chemically modified Moroccan rock phosphate

Rock phosphate from Morocco:

- **<u>Wet-chemical treatment</u>**
  - Some of the mechanically processed rock phosphate from Morocco is then dried and transported to Europe. This product can be used directly as a fertiliser. However, the greater proportion of the rock phosphate produced is processed directly on site into phosphoric acid (H_3PO_4). Sulphuric acid (H_2SO_4) is usually used for the production of phosphoric acid. Around **<u>50 %</u>** of the global demand for sulphuric acid is used for the production of phosphoric acid and phosphate fertilisers.
  - The following processes are mainly used:
    - **Dihydrate process**
    - **Hemihydrate process**
  - Around 96 % of the phosphoric acid produced worldwide is manufactured using either the dihydrate process or the hemihydrate process.



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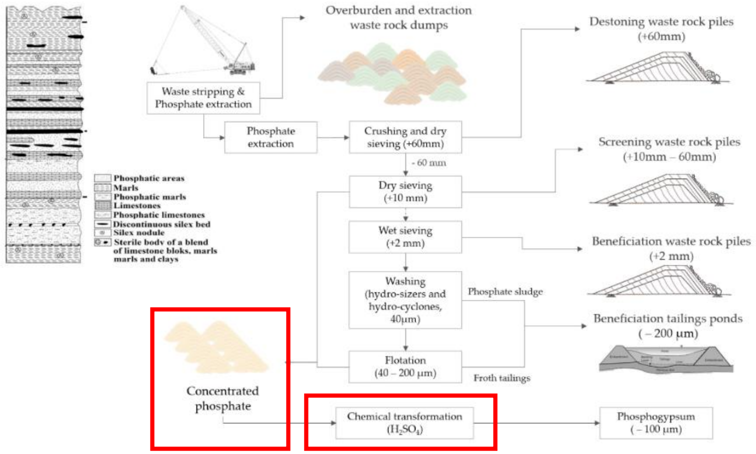
Thermochemical treatment of chemically modified Moroccan rock phosphate

Rock phosphate from Morocco:

- <u>Wet-chemical treatment</u>
- **Dihydrate process:** Around 80 % of the phosphoric acid produced using wet chemical processes is produced using the dihydrate process. This process involves three reaction steps:
  - Exothermic reaction of rock phosphate with sulphuric acid.
  - Separation of phosphoric acid and gypsum at constant temperatures of 70 to 80 °C by means of filtration. This produces a phosphoric acid with an H_3PO_4 content of around 40 %.
  - Concentration of the weak phosphoric acid using a vacuum evaporator.



$$Ca_{10}F_2(PO_4)_6 + 10\,H_2SO_4 + 20\,H_2O \rightarrow 6\,H_3PO_4 + 10\,[CaSO_4 \cdot 2\,H_2O] + 2\,HF \quad -\Delta H$$

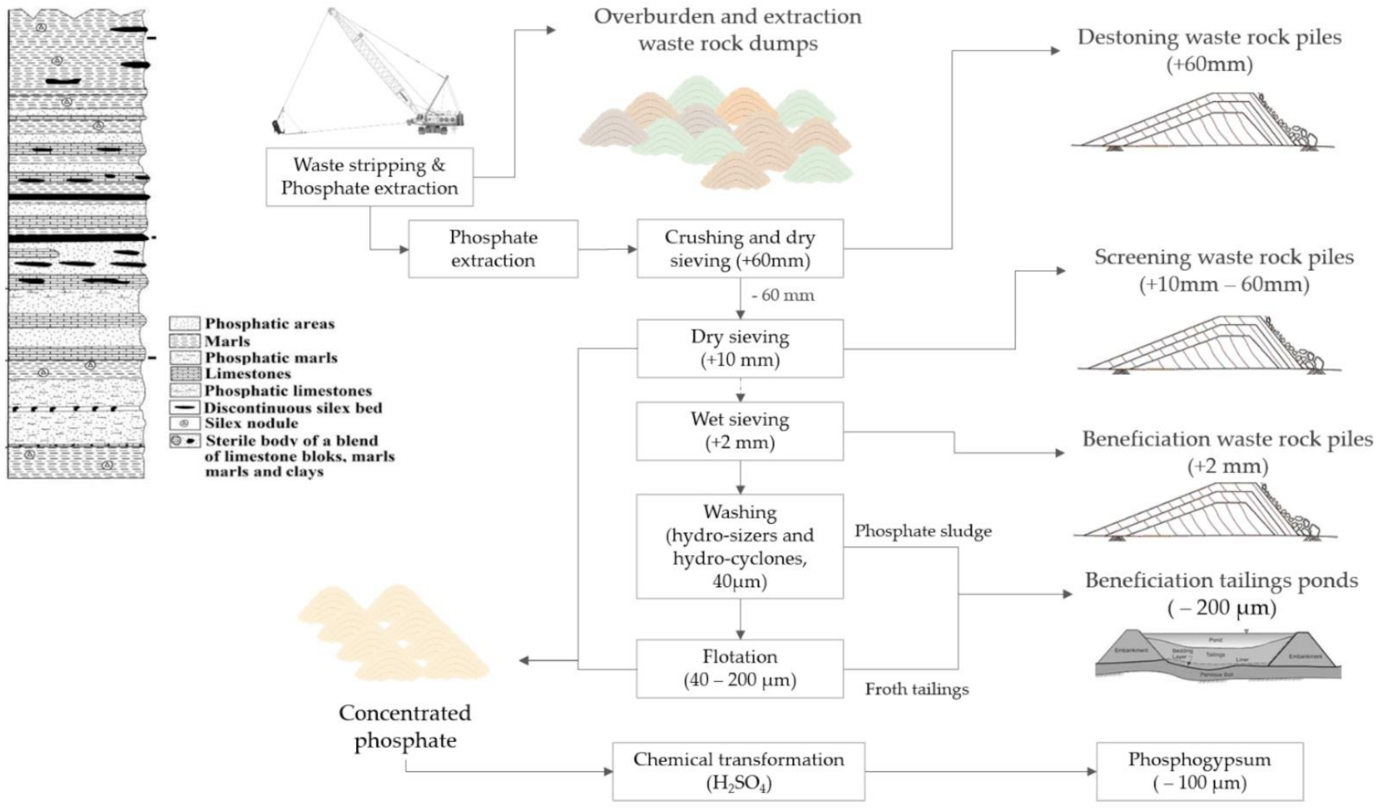
Fabian Kraus, Malte Zamzow, Lea Conzelmann, Christian Remy, Anne, Ökobilanzieller Vergleich der P-Rückgewinnung aus dem Abwasserstrom mit der Düngemittelproduktion aus Rohphosphaten unter Einbeziehung von Umweltfolgeschäden und deren Vermeidung. Dessau-Roßlau.

- The dihydrate process is characterised above all by high operational stability and a high recovery rate of approx. 94 - 96 % P_2O_5. An additional feature of this process is that both dry and wet rock phosphate of varying quality can be processed.

Thermochemical treatment of chemically modified Moroccan rock phosphate

Originating residues from **phosphate ore** to **rock phosphate** (The example of Morocco):

- Waste rock (overburden and intermediate layers)
- Residues from crushing and subsequent dry sieving (> 60 mm)
- Residues from dry sieving (> 10 mm)
- Residues from wet sieving
- Phosphate **sludge** from flotation and the hydro-cyclone
- Foam residues from flotation
- Phosphogypsum from phosphoric acid production of rock phosphate



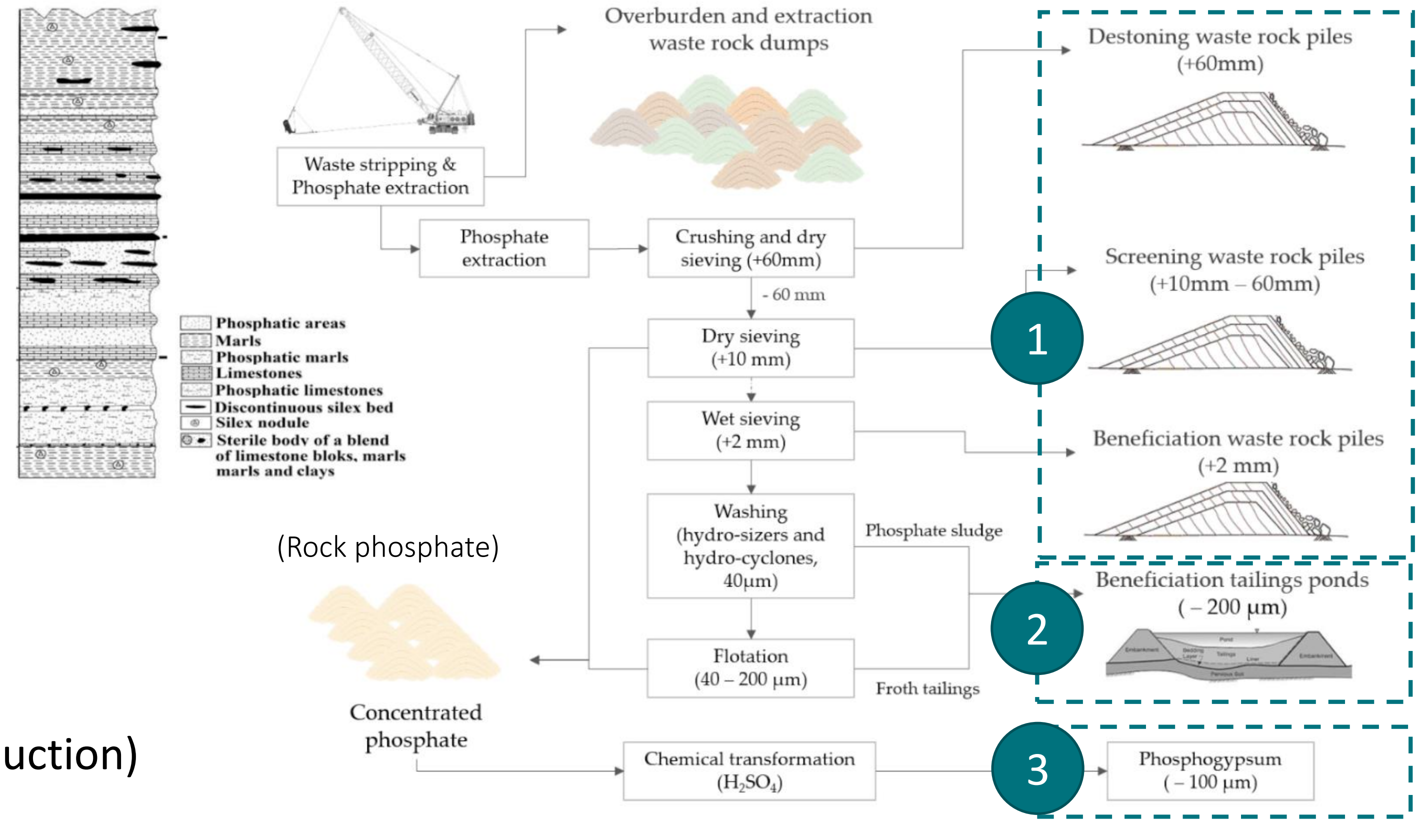
Y. Taha, A. Elghali, R. Hakkou, and M. Benzaazoua, "Towards Zero Solid Waste in the Sedimentary Phosphate Industry: Challenges and Opportunities," *Minerals*, vol. 11, no. 11, p. 1250, 2021, doi: 10.3390/min11111250.

Thermochemical treatment of chemically modified Moroccan rock phosphate

Beneficiation of ***phosphate ore*** to ***rock phosphate*** leads to high amounts of unutilised, mostly landfilled by-products

By-products can be divided into:

- **(1) Waste rock** (dry and wet sieving)
- **(2) Tailings** (hydro sizers and flotation)
- **(3) Phosphogypsum** (phosphoric acid production)



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Thermochemical treatment of chemically modified Moroccan rock phosphate

Some deposited material flows show high potential in terms of phosphorus content

- **(1) Waste rock** (dry and wet sieving)
- **(2) Tailings** (hydro sizers and flotation)
- **(3) Phosphogypsum** (phosphoric acid production)

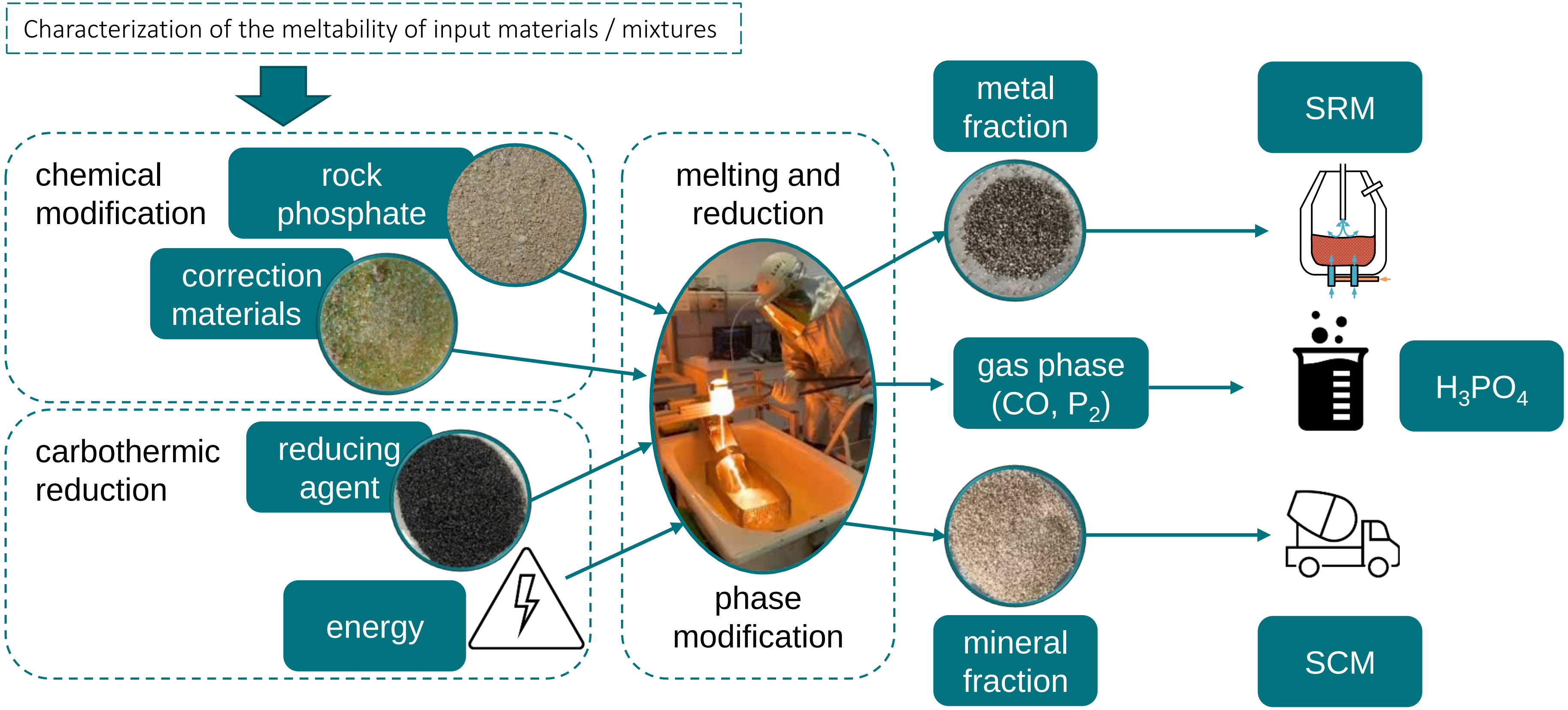
Main component	Rock phosphate [wt.%]	(1) Waste rock [wt.%]	(2) Tailings [wt.%]
P_2O_5	**33,2**	**16,9**	**14,0**
CaO	53,4	43,0	34,2
SiO_2	3,6	11,6	22,8
MgO	0,3	4,1	3,3
Al_2O_3	0,2	2,5	0,9
Fe_2O_3	0,3	0,4	2,5
F	2,3	1,7	-
Sum	93,3	80,2	77,7

Component	(3) Phosphogypsum **[kg / kg H_3PO_4]**
Water	0,77
Sulfate as SO_4^{2-}	1,75
Calcium as Ca^{2+}	0,88
Phosphate as PO_4^{3-}	**0,04**
F, as F^-	0.009
Total	3,67

Own representation, data from:
„ R. Hakkou, M. Benzaazoua, and B. Bussière, “Valorization of Phosphate Waste Rocks and Sludge from the Moroccan Phosphate Mines: Challenges and Perspectives,” Procedia Engineering, vol. 138, pp. 110–118, 2016, doi: 10.1016/j.proeng.2016.02.068.“
“Althaus H.-J., Chudacoff M., Hischier R., Jungbluth N., Osses M. and Primas A., Life Cycle Inventories of Chemicals: Final report ecoinvent data v2.0 No8.”

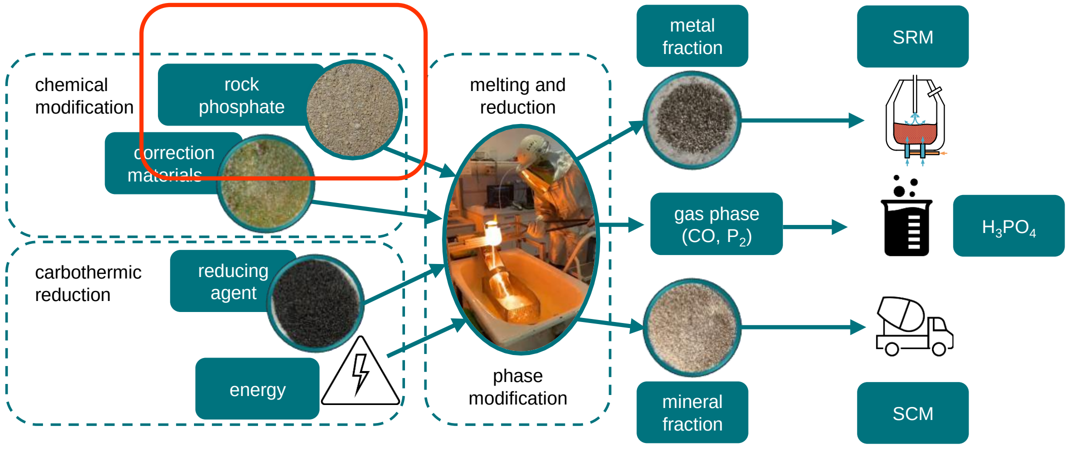
Thermochemical treatment of chemically modified Moroccan rock phosphate

<u>*Scheme of the thermochemical treatment trials:*</u>



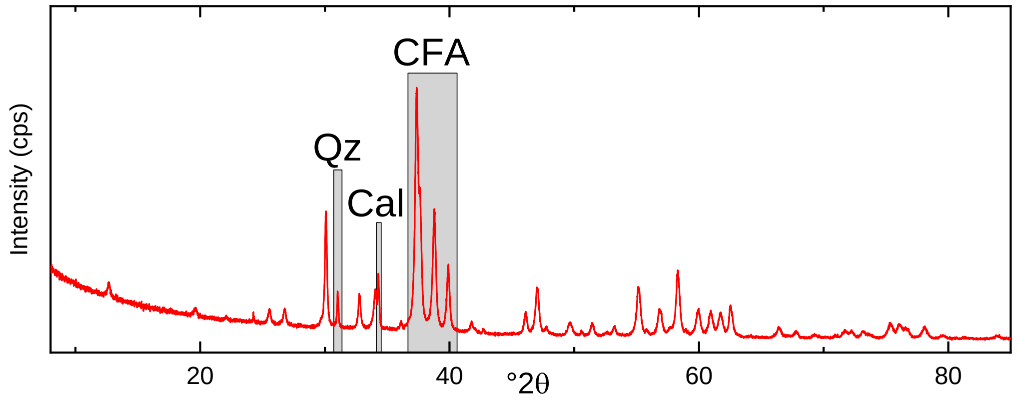
Thermal treatment of rock phosphate: P-recovery and production of an alternative binder component; Gatschlhofer, C., Krammer, A., Doschek-Held, K., Steindl, F. R., Grengg, C. & Raupenstrauch, H., 30 Juni 2024, (Accepted/In print) *Proceedings of the 6th EMCEI.*

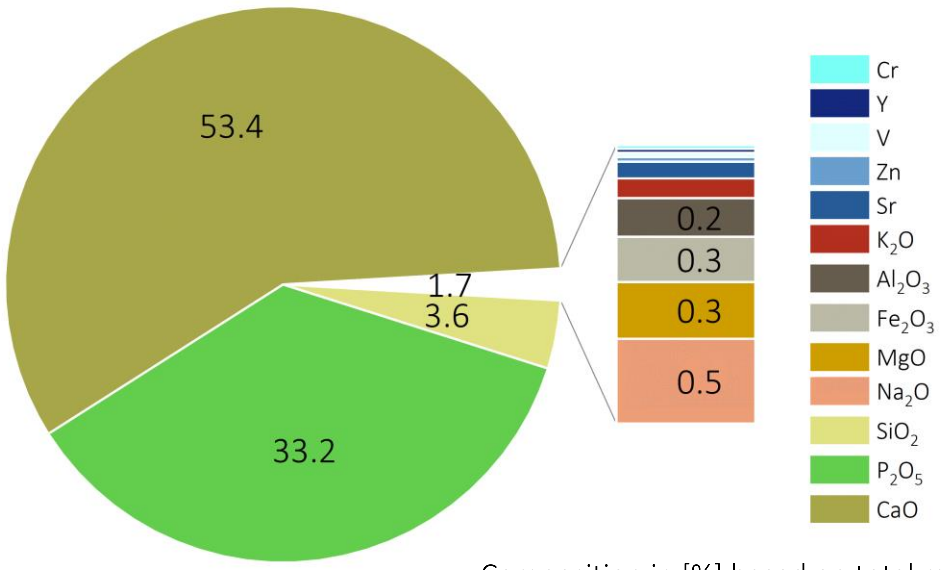
Thermochemical treatment of chemically modified Moroccan rock phosphate



Characterization of pure rock phosphate:

- *Chemical composition by XRF:*
  - *Approx. 90 % (CaO, P_2O_5 and SiO_2)*
- *XRD-results:*
  - *Mostly carbonate fluorapatite (88.5 %)*
  - *Amorphous structures (5.84 %)*
  - *Traces of quartz (1.72 %), calcite (3.3 %), and dolomite (0.63 %)*





Composition in [%] based on total mass

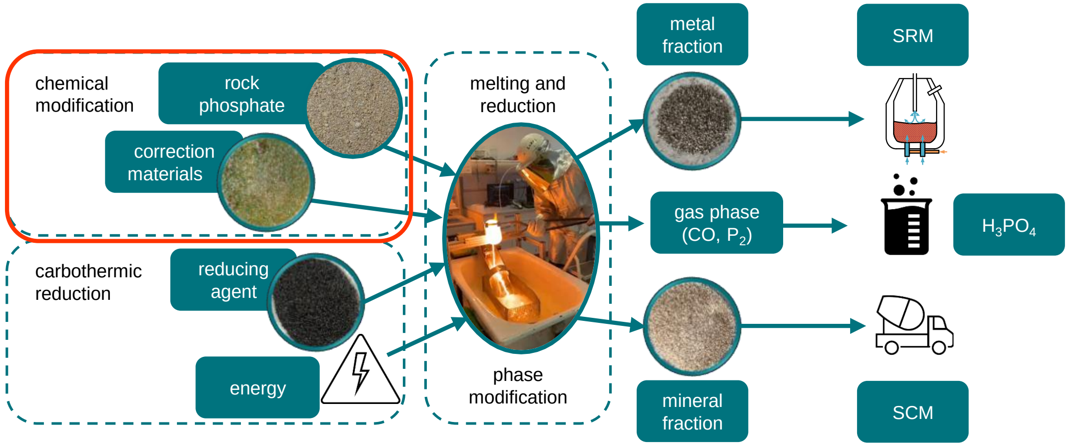
LOI and trace elements:

LOI [%]	Ba [ppm]	Cr [ppm]	Sr [ppm]	V [ppm]	Y [ppm]	Zn [ppm]
6.6	83	315	1141	372	283	304

LOI = Loss of ignition

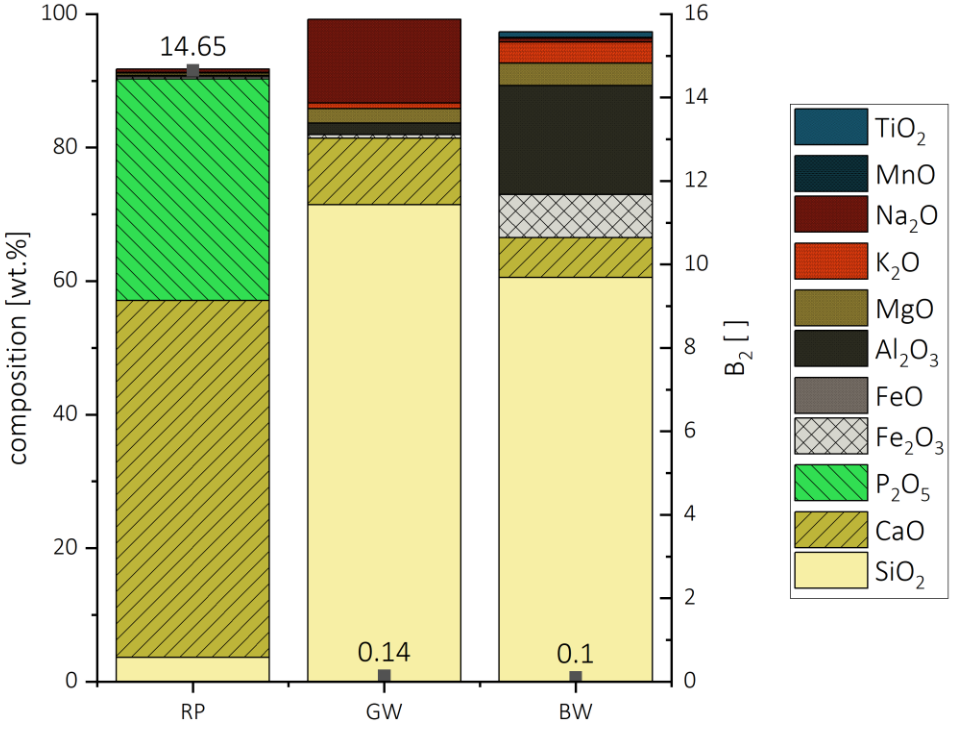
Thermal treatment of rock phosphate: P-recovery and production of an alternative binder component; Gatschlhofer, C., Krammer, A., Doschek-Held, K., Steindl, F. R., Grengg, C. & Raupenstrauch, H., 30 Juni 2024, (Accepted/In print) *Proceedings of the 6th EMCEI.*

Thermochemical treatment of chemically modified Moroccan rock phosphate



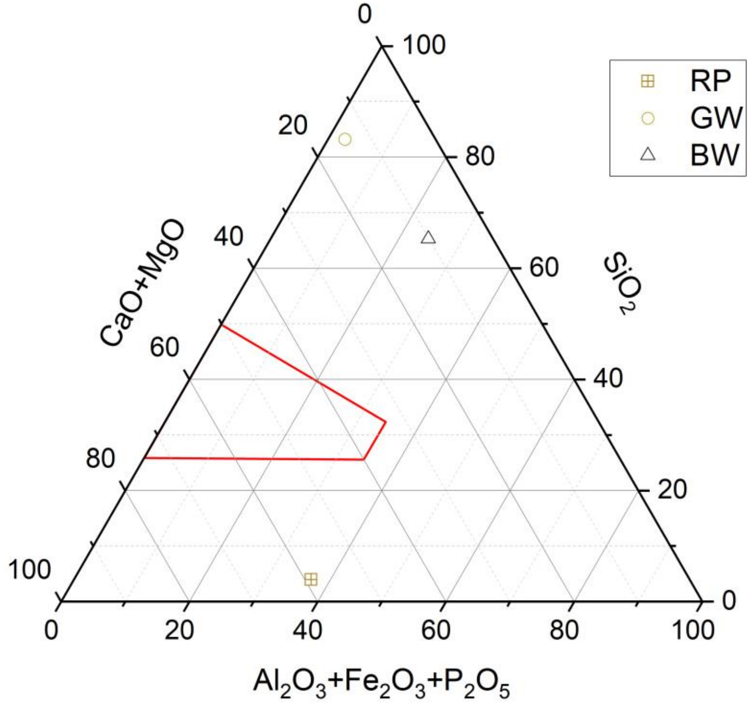
Used input-materials:

Input material



RP (Rock phosphate)
GW (Glass waste – consists of no iron oxide)
BW (Brick waste – consists of iron oxide)

$$B_2 = \frac{wt.\%\ (CaO)}{wt.\%\ (SiO_2)}$$



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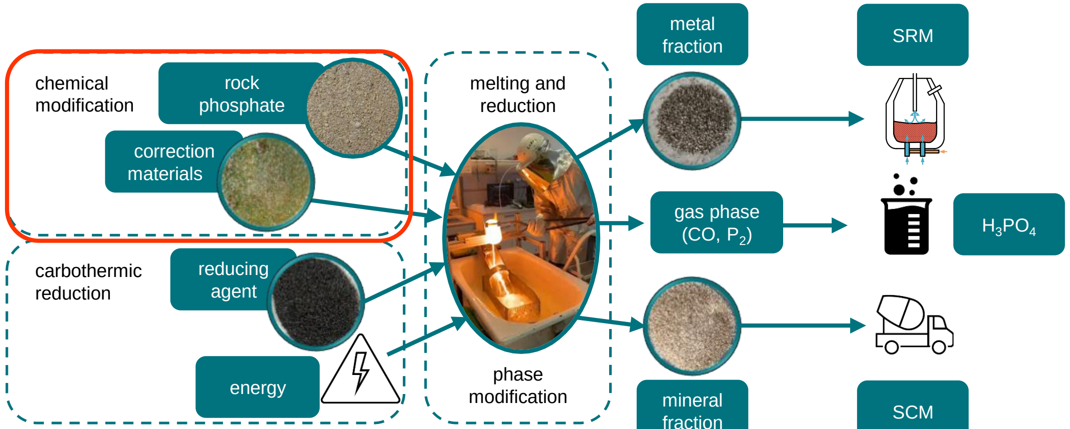
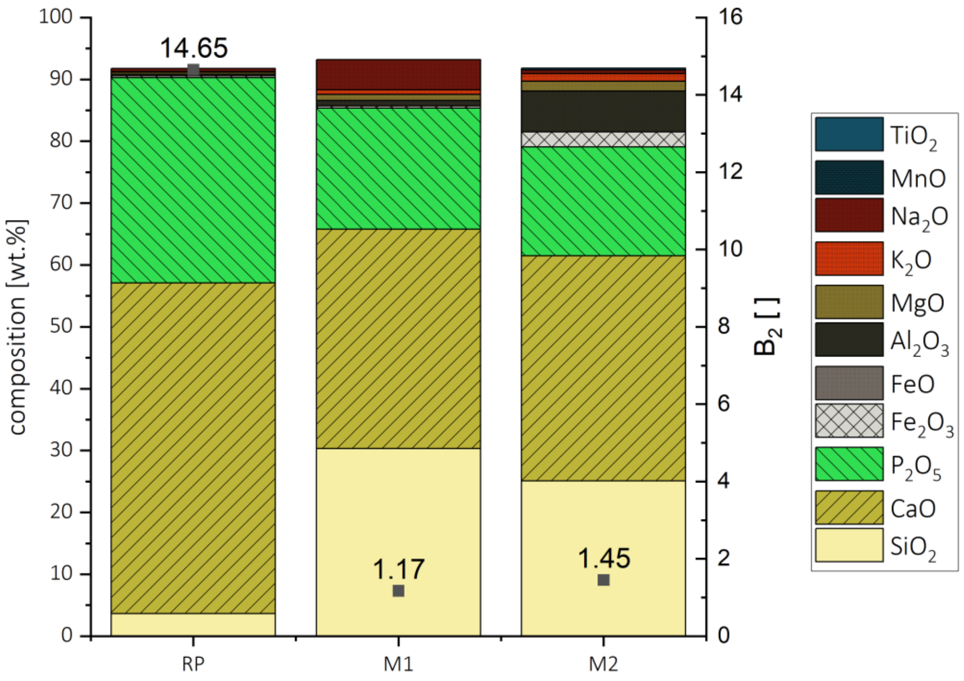
Thermochemical treatment of chemically modified Moroccan rock phosphate

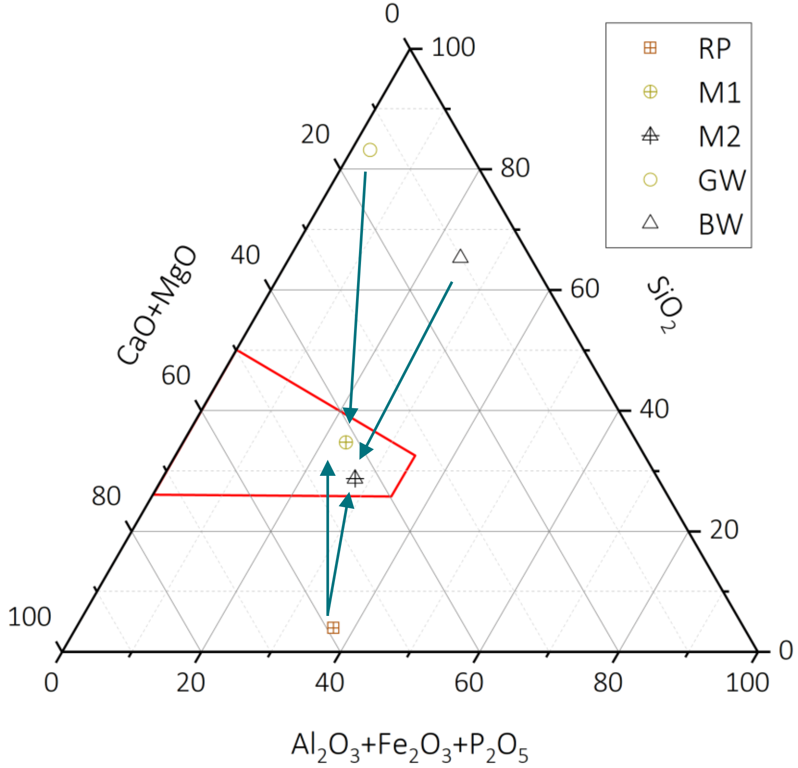


Chemical modification:

Input mixture



RP (Rock phosphate)
M1 (Mixture rock phosphate + glass waste – without iron)
M2 (Mixture rock phosphate + brick waste – with iron)



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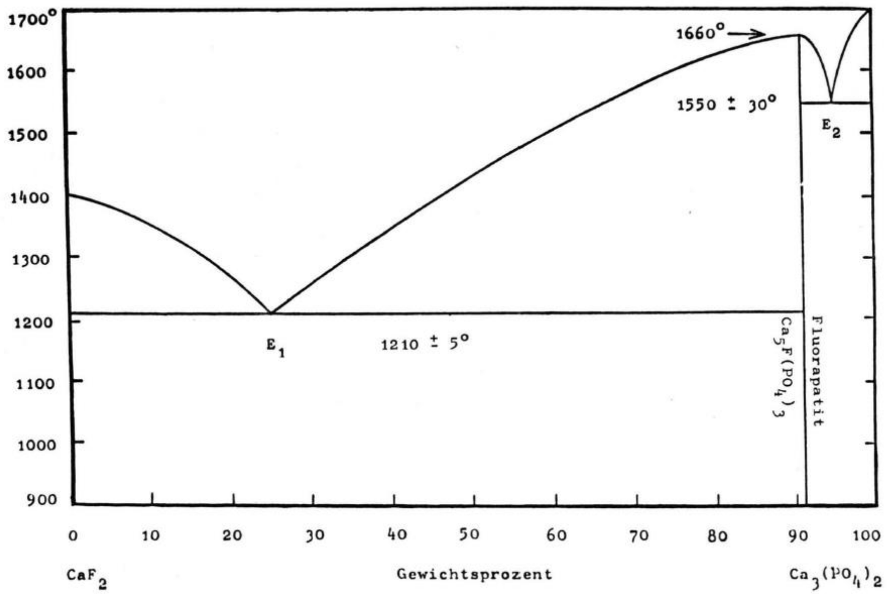
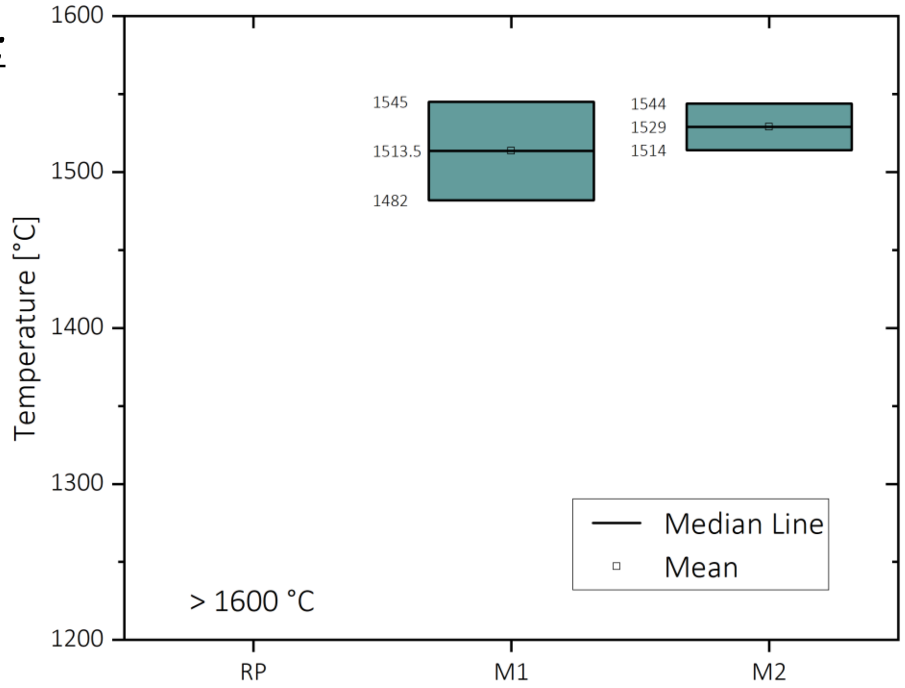
Thermochemical treatment of chemically modified Moroccan rock phosphate

Investigation of the melting behavior (thermo-optical):

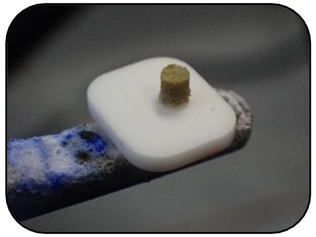
Temperature [°C]	Heating rate [°C/min]	Holding time [min]
0 - 1350	80	-
1350 -1450	50	-
1450 - 1700	10	-
1700	-	5



E-D. Franz (1983): Fluorapatite - A Model for the Synthesis of Dental Enamel in the System CaF2-Ca3(P04)2. In: *Zeitschrift für Naturforschung*, S. 1037–1040.



After addition of carbon:
RP: 1541 – 1567 °C
M1: 1373 – 1446 °C
M2: 1382 – 1446 °C



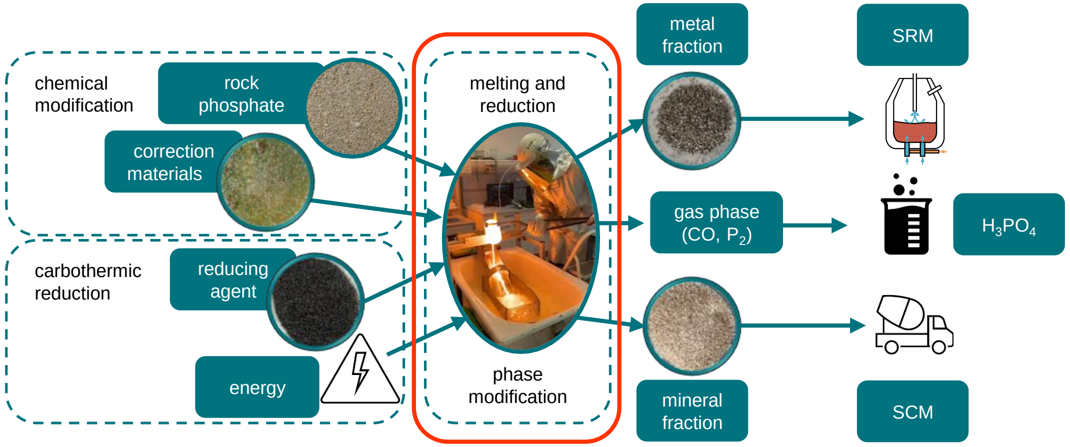
Pure rock phosphate (RP)

Mixture without iron (M1)

Mixture with iron (M2)

Thermal treatment of rock phosphate: P-recovery and production of an alternative binder component; Gatschlhofer, C., Krammer, A., Doschek-Held, K., Steindl, F. R., Grengg, C. & Raupenstrauch, H., 30 Juni 2024, (Accepted/In print) *Proceedings of the 6th EMCEI.*

Thermochemical treatment of chemically modified Moroccan rock phosphate



Thermochemical treatment:

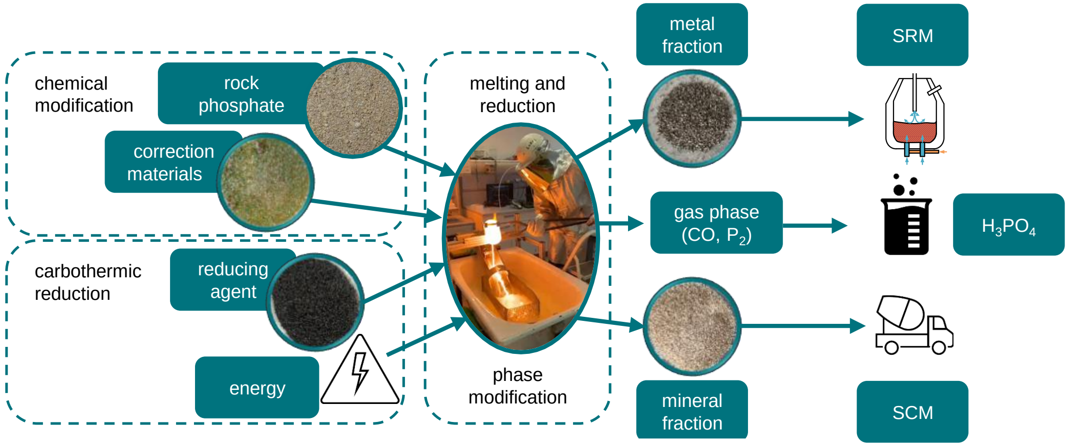
- 200 g input material of
  - **Pure rock phosphate** without any correction material
  - Mixture M1: **Rock phosphate + glass waste – without iron**
  - Mixture M2: **Rock phosphate + brick waste – with iron**
- Treatment temperature: 1500 °C and 1600 °C
- Treatment time: 30 min
- Treatment container: Graphite crucible
- Reductant: Carbon powder
- Resistance furnace: Thermconcept ELHT 16/18
- Post treatment of the melt: Wet-granulation in a dynamic water bath

Research focus:

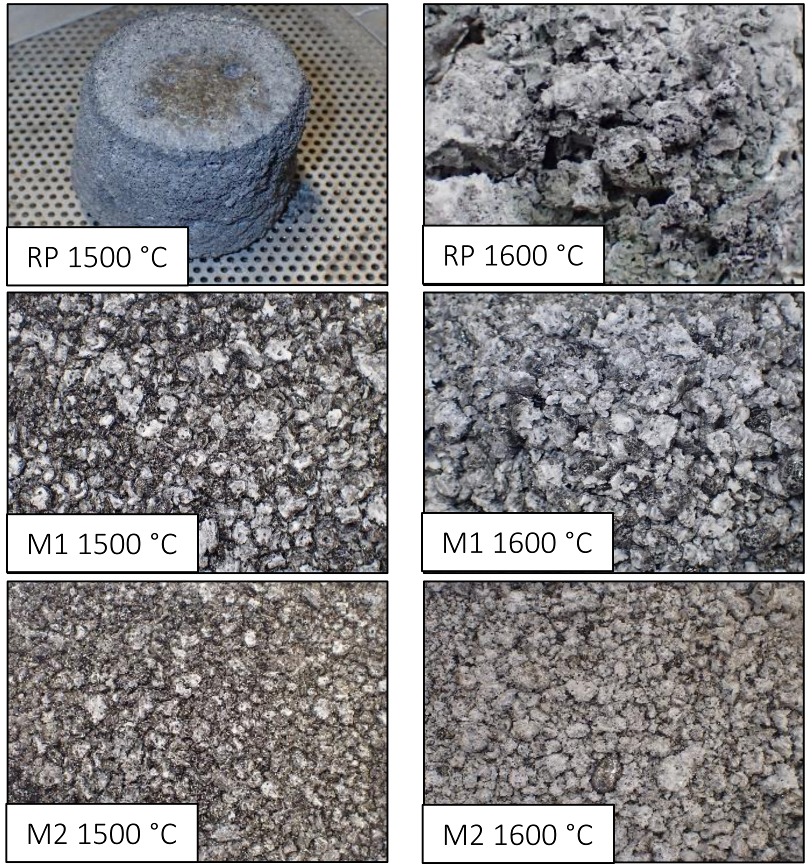
- **Removal rate of phosphorus via the gas phase**
- **Quality** of the produced **mineral fraction**
- **Quality** of the produced **metal fraction**

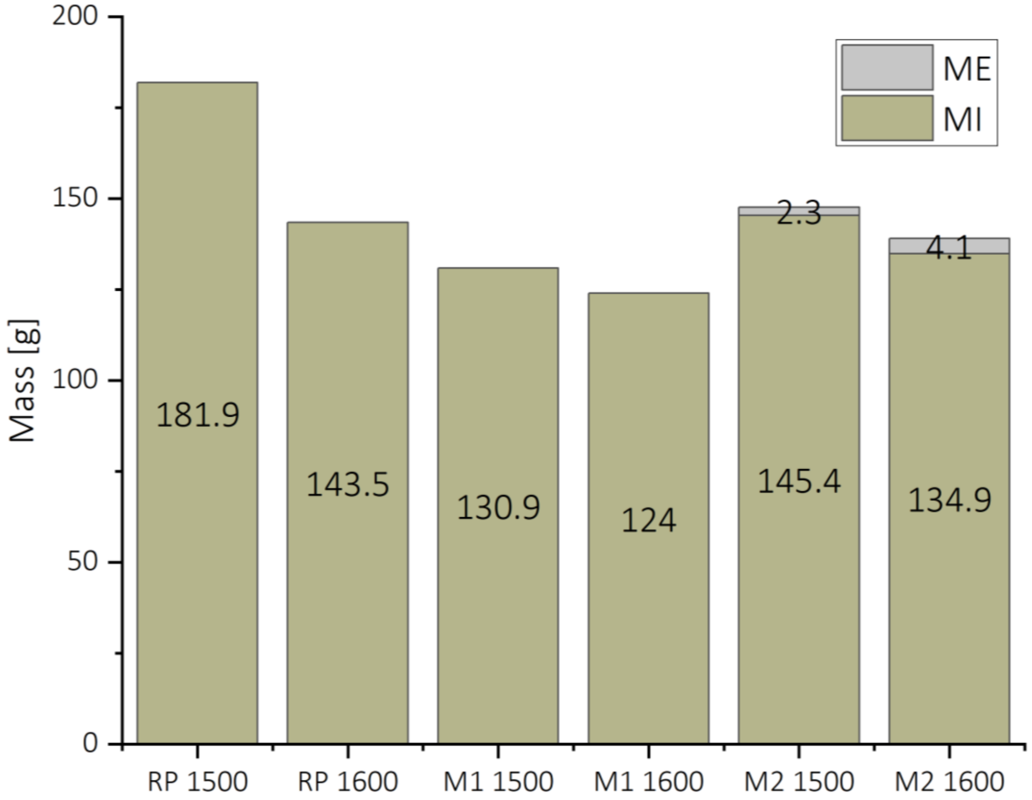
Thermal treatment of rock phosphate: P-recovery and production of an alternative binder component; Gatschlhofer, C., Krammer, A., Doschek-Held, K., Steindl, F. R., Grengg, C. & Raupenstrauch, H., 30 Juni 2024, (Accepted/In print) *Proceedings of the 6th EMCEI.*

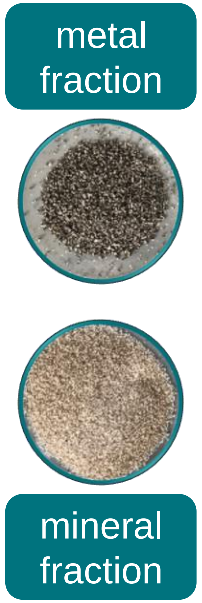
Thermochemical treatment of chemically modified Moroccan rock phosphate



Thermochemical treatment - results:

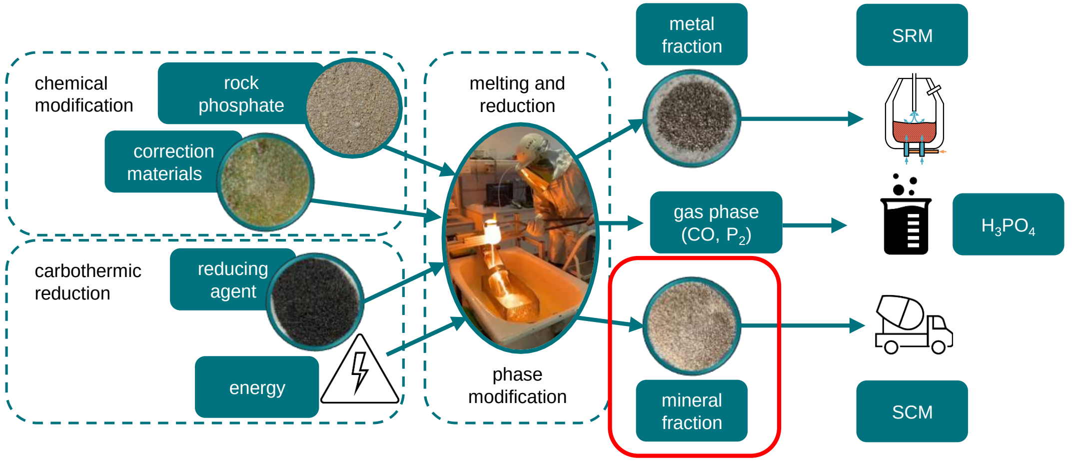






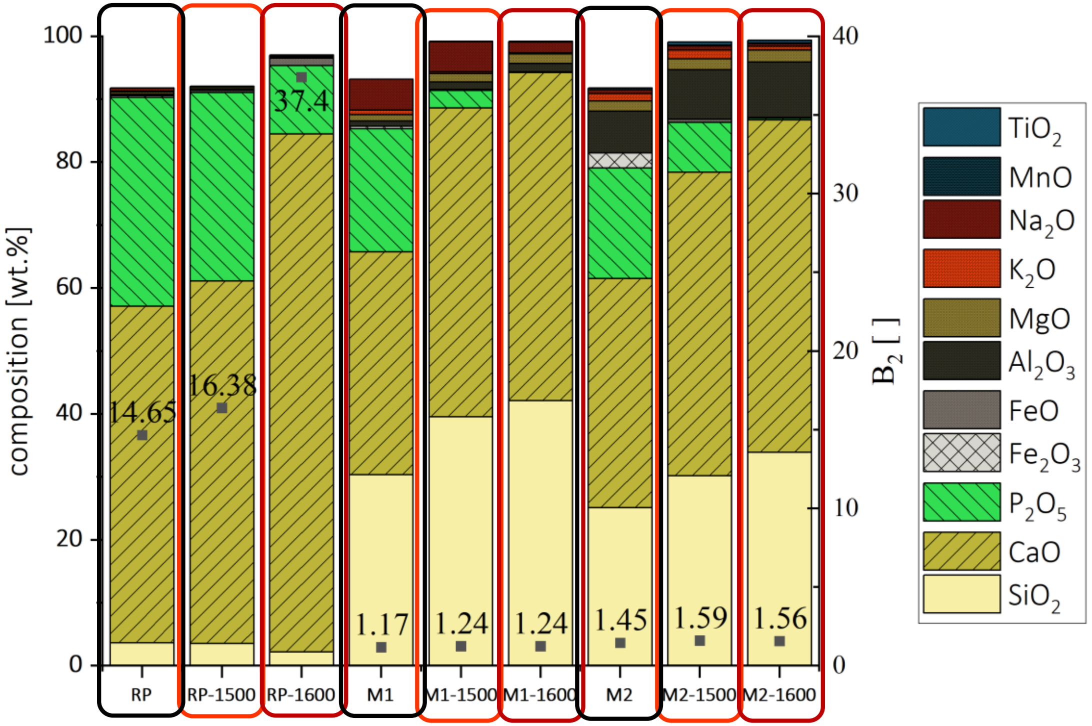
Thermal treatment of rock phosphate: P-recovery and production of an alternative binder component; Gatschlhofer, C., Krammer, A., Doschek-Held, K., Steindl, F. R., Grengg, C. & Raupenstrauch, H., 30 Juni 2024, (Accepted/In print) *Proceedings of the 6th EMCEI.*

Thermochemical treatment of chemically modified Moroccan rock phosphate



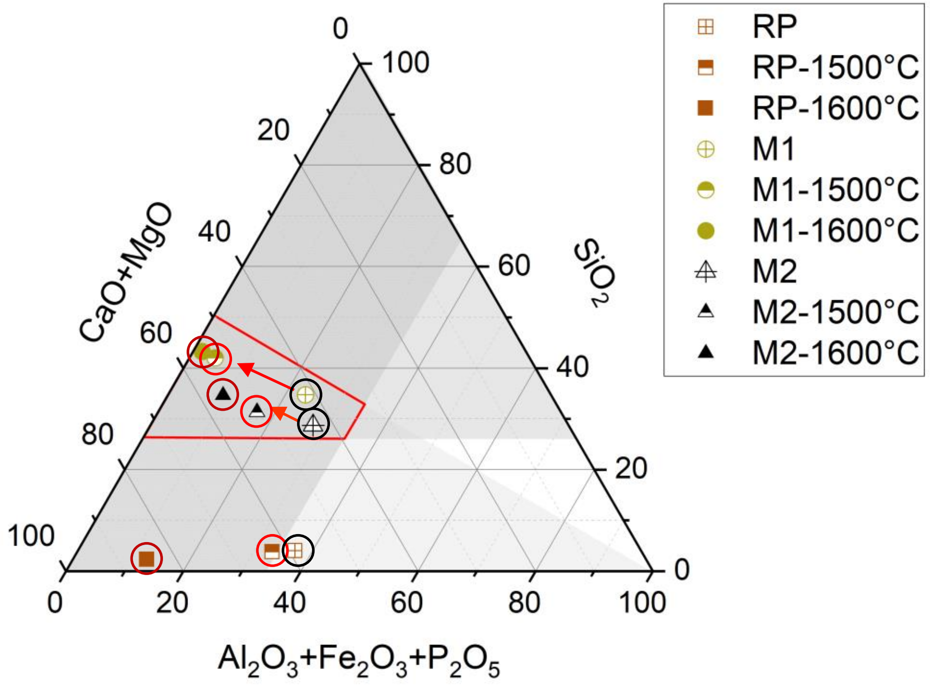
Thermochemical treatment - results:

mineral fraction

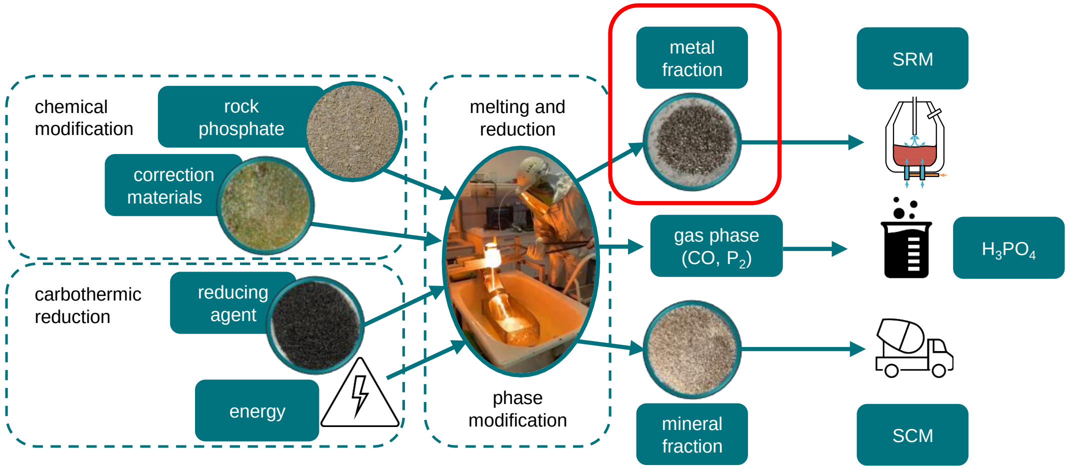


RP (Rock phosphate)
M1 (Mixture without iron)
M2 (Mixture with iron)

$$B_2 = \frac{wt.\%\,(CaO)}{wt.\%\,(SiO_2)}$$



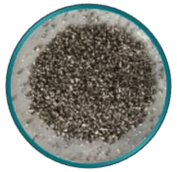
Thermal treatment of rock phosphate: P-recovery and production of an alternative binder component; Gatschlhofer, C., Krammer, A., Doschek-Held, K., Steindl, F. R., Grengg, C. & Raupenstrauch, H., 30 Juni 2024, (Accepted/In print) *Proceedings of the 6th EMCEI.*



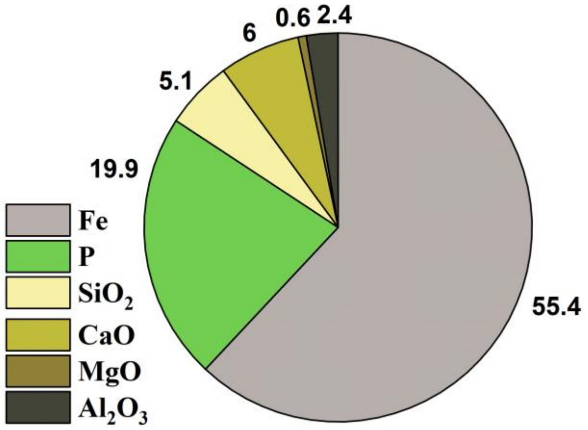
Thermochemical treatment of chemically modified Moroccan rock phosphate

Thermochemical treatment - results:

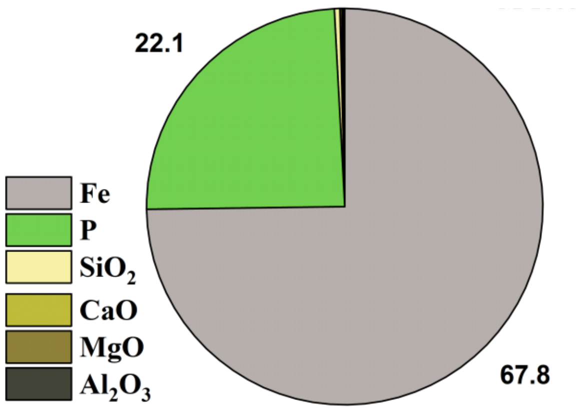
metal fraction



M2: Metal fraction (**2.3 g**) at **1500 °C**



M2: Metal fraction (**4.1 g**) at **1600 °C**



Metal fraction from M2:

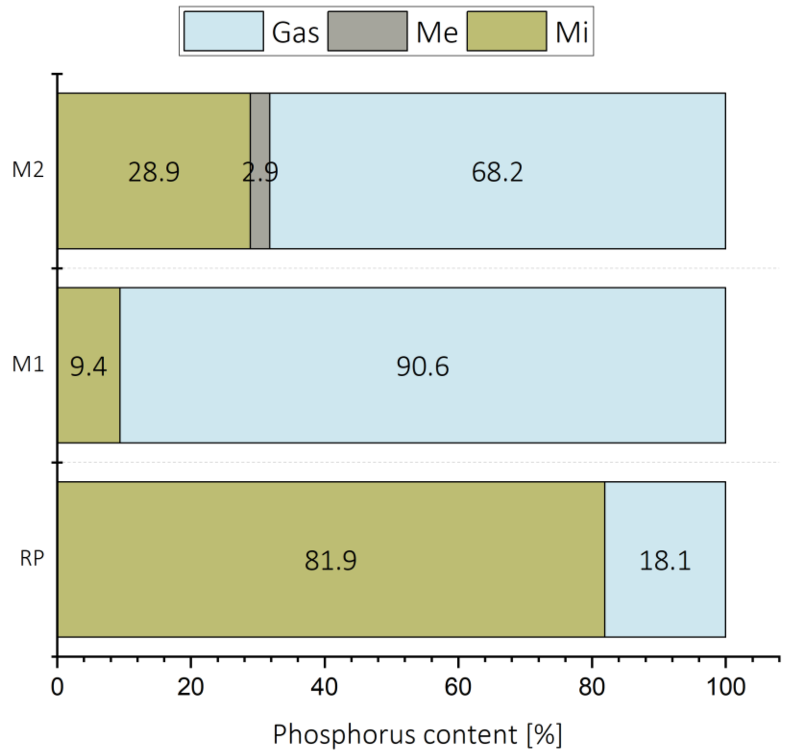
- Metallic fraction was non-magnetic
- Poor magnetic separation (Ca, Si, Mg and Al content originate from mineral impurities or non-metallic inclusions)
- Not actually a metal but a iron phosphide
  - Fe_2P or Fe_3P – Fe/P = 22 % or 16 %

Thermal treatment of rock phosphate: P-recovery and production of an alternative binder component; Gatschlhofer, C., Krammer, A., Doschek-Held, K., Steindl, F. R., Grengg, C. & Raupenstrauch, H., 30 Juni 2024, (Accepted/In print) *Proceedings of the 6th EMCEI.*

Thermochemical treatment of chemically modified Moroccan rock phosphate

Phosphorus balance – results:

Phosphorus balance at 1500 °C:



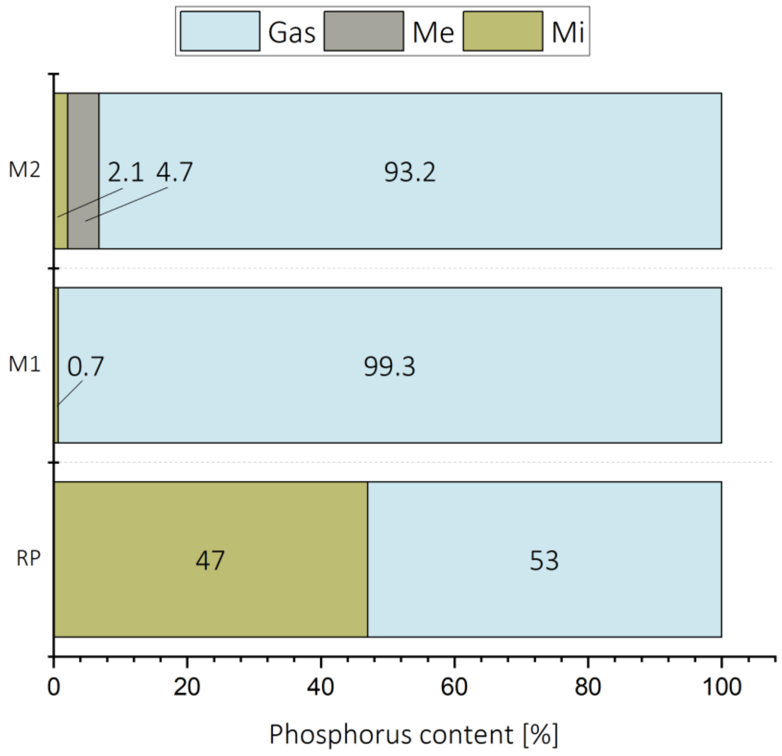
Phosphorus input (100 %):

M2: 17.5 g P

M1: 17.1 g P

RP: 29.0 g P

Phosphorus balance at 1600 °C:



WHERE RESEARCH MEETS THE FUTURE

Thermal treatment of rock phosphate: P-recovery and production of an alternative binder component; Gatschlhofer, C., Krammer, A., Doschek-Held, K., Steindl, F. R., Grengg, C. & Raupenstrauch, H., 30 Juni 2024, (Accepted/In print) *Proceedings of the 6th EMCEI.*

Thermochemical treatment of chemically modified Moroccan rock phosphate

Reactivity of upcycled phosphate materials – results:

Mineralogical composition

- Amorphous content → depending on input materials
- RP at 1500 and 1600 °C:
  incomplete reduction, Ca-phosphate, CaO, Ca-silicates,…
  → low amorphous content, low reactivity
- M1 and M2 and 1500 and 1600 °C:
  amorphous > 98 %, slag-like substances → high reactivity

Usage as supplementary cementitious material

- good substitute for Portland cement
- high strength in alkali-activated materials
  (higher than high-performance cement!)

→ similar to granulated blast-furnace slag!

Thermal treatment of rock phosphate: P-recovery and production of an alternative binder component; Gatschlhofer, C., Krammer, A., Doschek-Held, K., Steindl, F. R., Grengg, C. & Raupenstrauch, H., 30 Juni 2024, (Accepted/In print) *Proceedings of the 6th EMCEI.*

Thermochemical treatment of chemically modified Moroccan rock phosphate

Conclusions:

- By ***chemical modification*** of **rock phosphate**: Shift of the ***melting interval*** towards lower temperatures:
  - **T_M: > 1600 °C** of pure rock phosphate
  - **T_M: 1541 – 1567 °C** of pure rock phosphate and carbon
  - **T_M: 1370 – 1450 °C** by the addition of a silica source and carbon

- The ***removal rate of phosphorus*** via the ***gas phase*** depends on the following parameters:
  - **Temperature**: Higher temperatures favour the reduction of oxidic phosphorus compounds
  - **Chemical composition**: **SiO_2**, **Al_2O_3**, and **MgO** contents strongly influence the thermodynamic and kinetic properties with regard to the reducibility of fluorapatite in the order mentioned above
  - **Transition metal content: FeO** content form an alloy before oxidic phosphorus compounds are reduced, resulting in a saturation of phosphorus in the metal bath (phosphide formation)

- By thermochemical treatment of ***chemically modified rock phosphate:*** mineral fraction similar to ***granulated blast furnace slag*** according to ***EN 15167***

Thermal treatment of rock phosphate: P-recovery and production of an alternative binder component; Gatschlhofer, C., Krammer, A., Doschek-Held, K., Steindl, F. R., Grengg, C. & Raupenstrauch, H., 30 Juni 2024, (Accepted/In print) *Proceedings of the 6th EMCEI.*

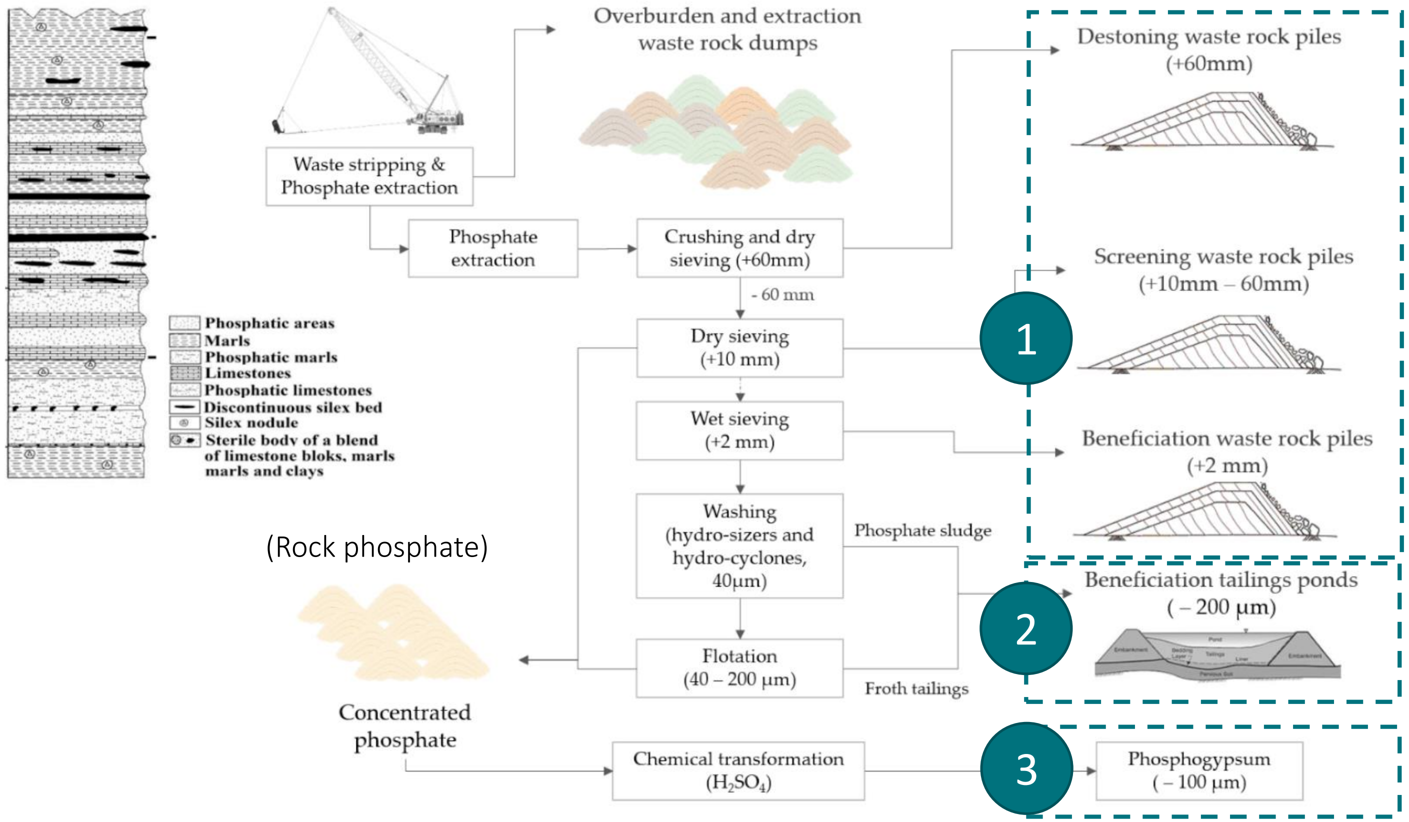
Thermochemical treatment of chemically modified Moroccan rock phosphate

Conclusion:

- Thermochemical treatment of rock phosphate: Transfer of over **99 % of the phosphorus into the gas phase** conceivable
  → Production of phosphoric acid
- **Avoidance** of the problematic **phosphorgypsum** accumulation by means of thermochemical treatment

Outlook:

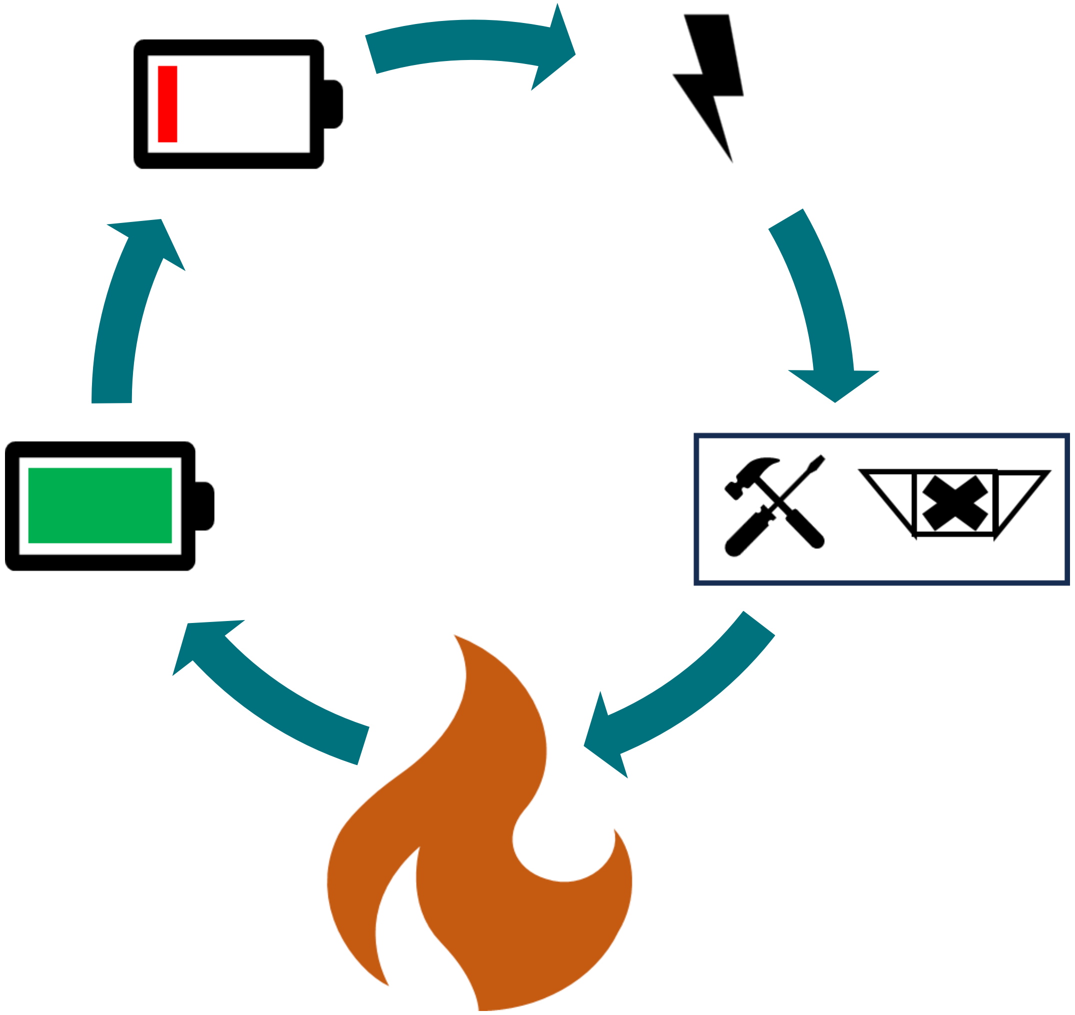
- Thermochemical treatment of phosphorus-rich waste streams (1) and (2)



Source: Y. Taha, A. Elghali, R. Hakkou, and M. Benzaazoua, "Towards Zero Solid Waste in the Sedimentary Phosphate Industry: Challenges and Opportunities," *Minerals*, vol. 11, no. 11, p. 1250, 2021, doi: 10.3390/min11111250.

Thermal treatment of rock phosphate: P-recovery and production of an alternative binder component; Gatschlhofer, C., Krammer, A., Doschek-Held, K., Steindl, F. R., Grengg, C. & Raupenstrauch, H., 30 Juni 2024, (Accepted/In print) *Proceedings of the 6th EMCEI.*

LIB Recycling



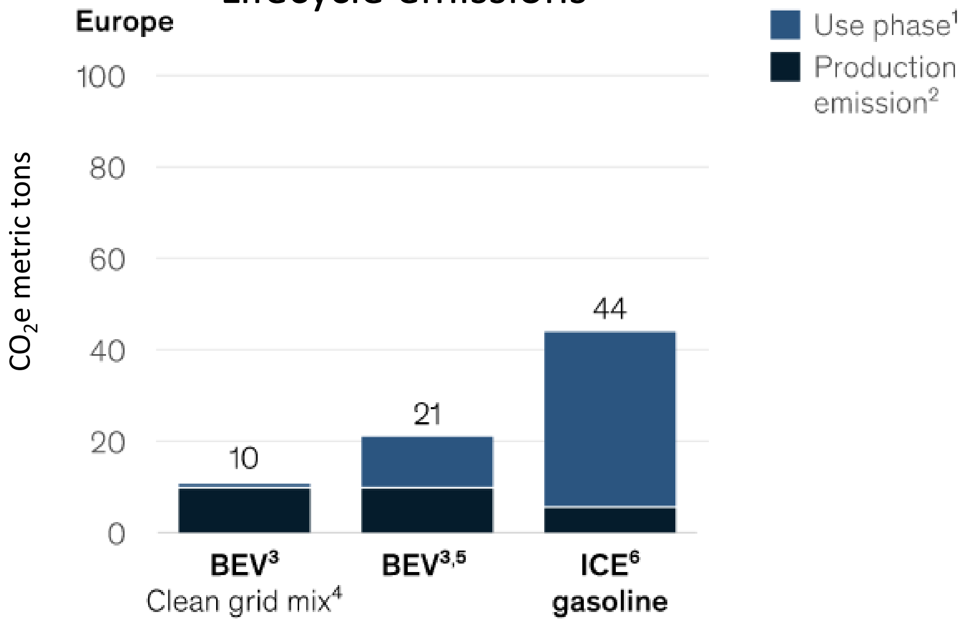
Motivation – Markt situation – Demand

Motivation: Global warming & reduction of CO_2 emissions

Electrification of energy-intensive sectors

Li-ion battery market forecast From 160 GWh in 2018 to > 4.7 TWh in 2030 (Global)

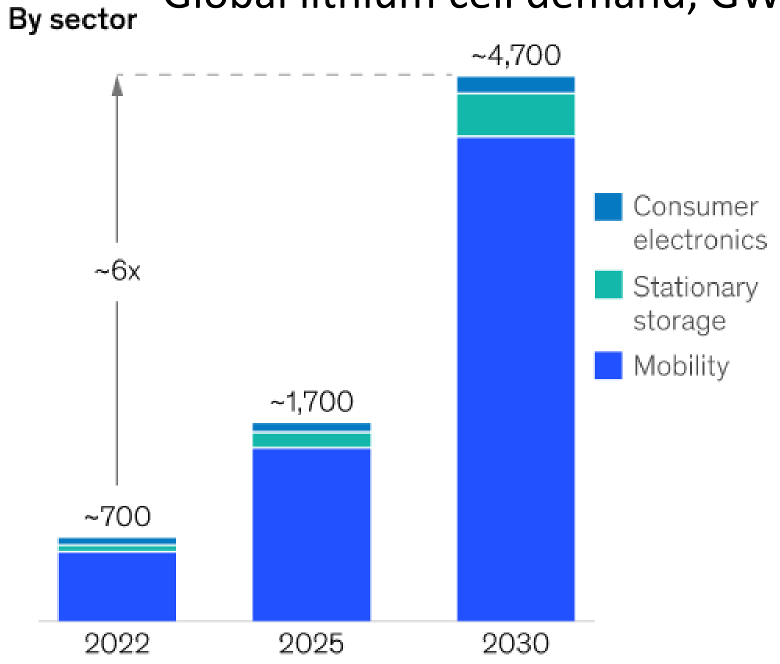
Lifecycle emissions



BEV Battery electric vehicles

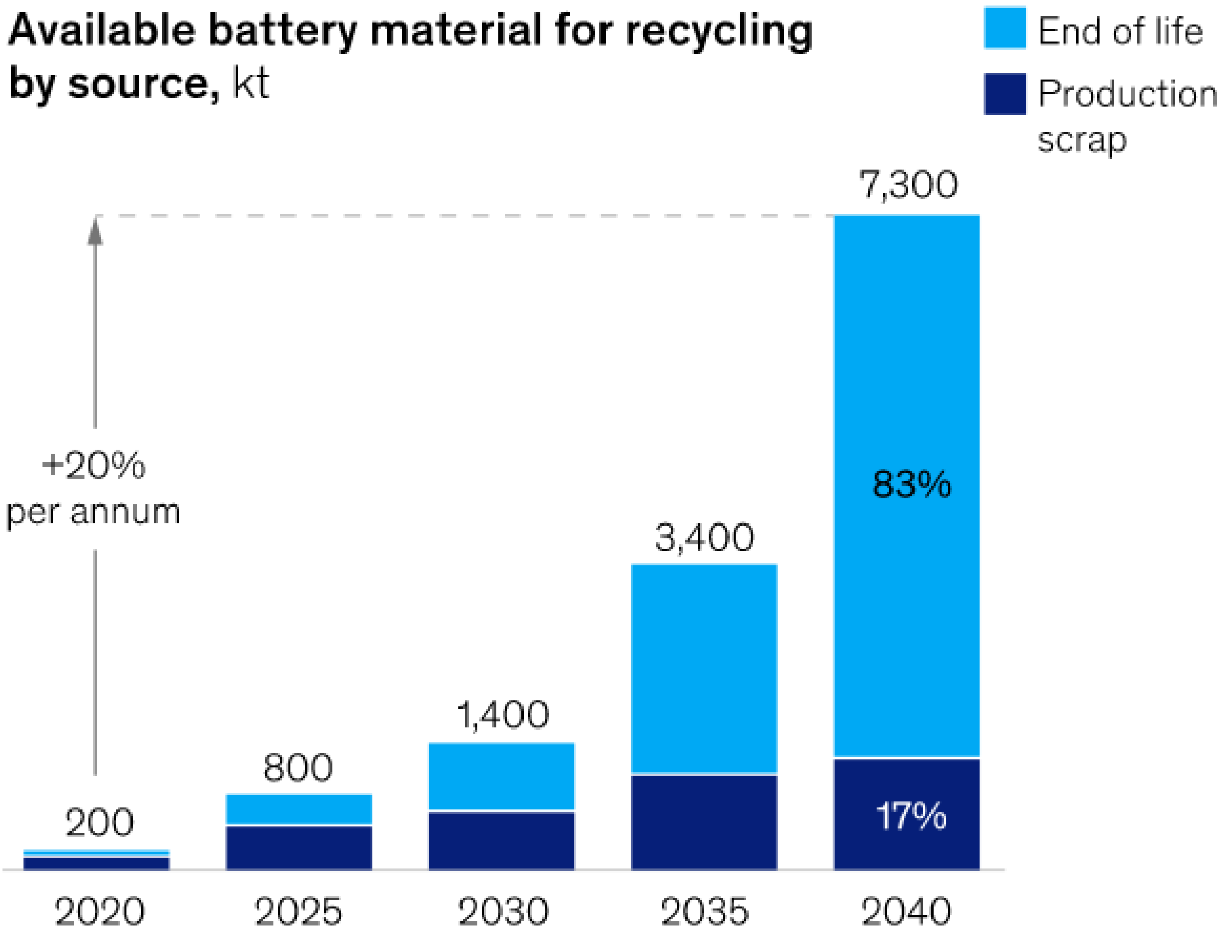
ICE Internal comb. engines

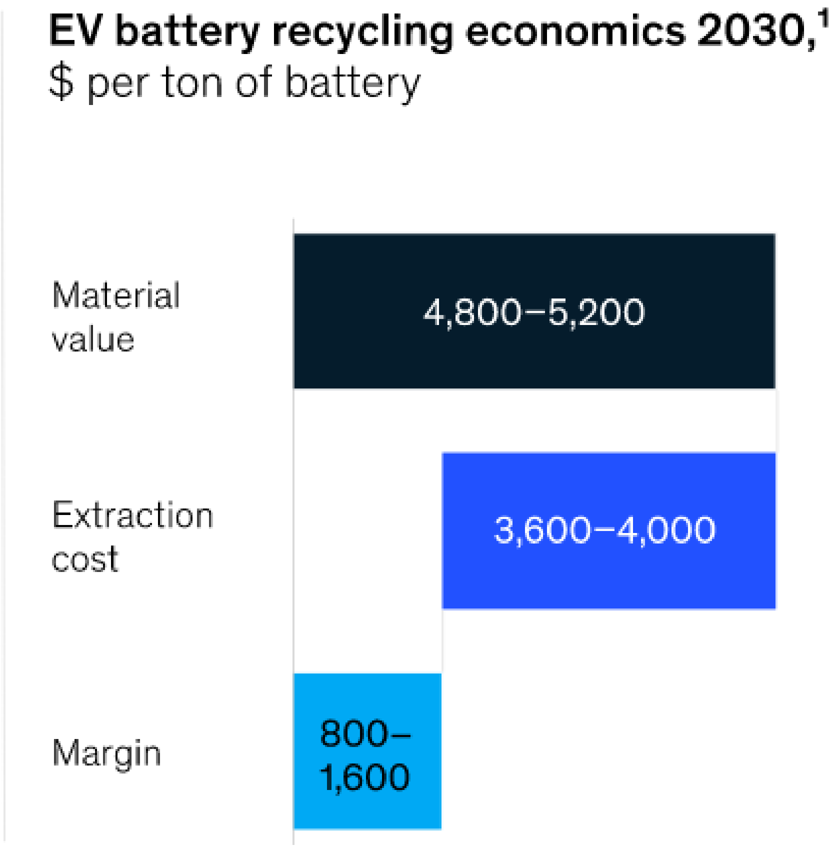
Global lithium cell demand, GWh



McKinsey: Battery 2030: Resilient, sustainable, and circular, accessible via : https://www.mckinsey.com/industries/automotive-and-assembly/our-insights/battery-2030-resilient-sustainable-and-circular

Recycling prognosis



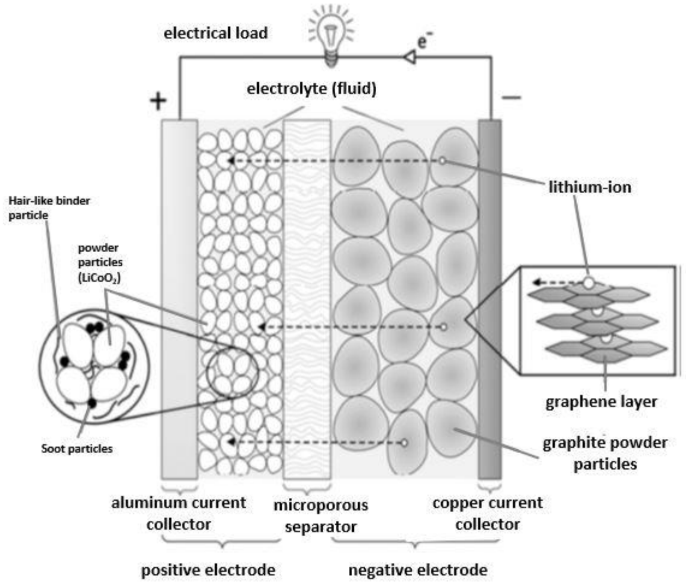


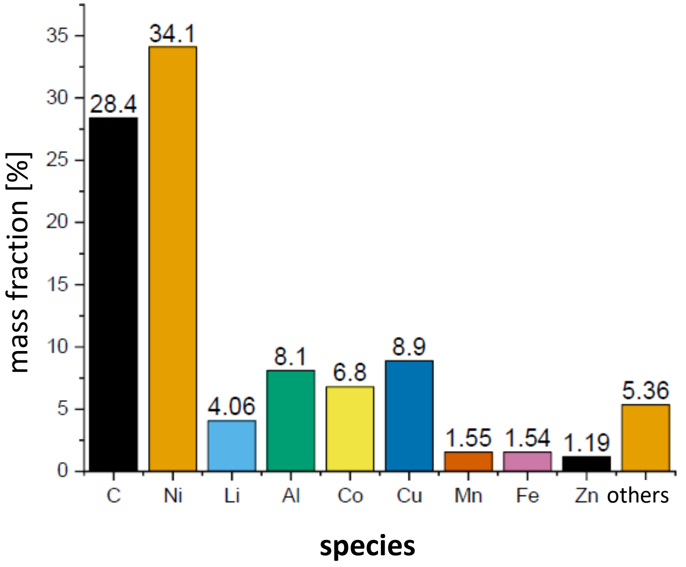
McKinsey: Battery 2030: Resilient, sustainable, and circular, accessible via: https://www.mckinsey.com/industries/automotive-and-assembly/our-insights/battery-2030-resilient-sustainable-and-circular

Recycling: Refinement

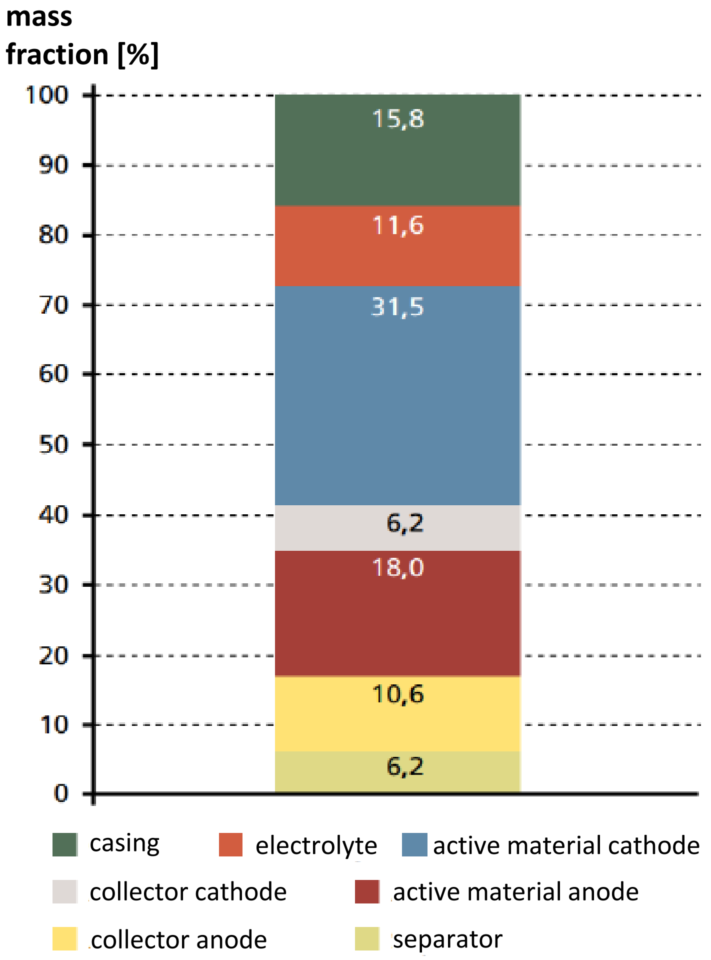
What is in the LIB?

- Not exclusively rare and valuable raw materials
- Individual cells as a stack with electronics in a housing (battery system)
- In each cell: arrester foils, cathode, anode, electrolyte, separator





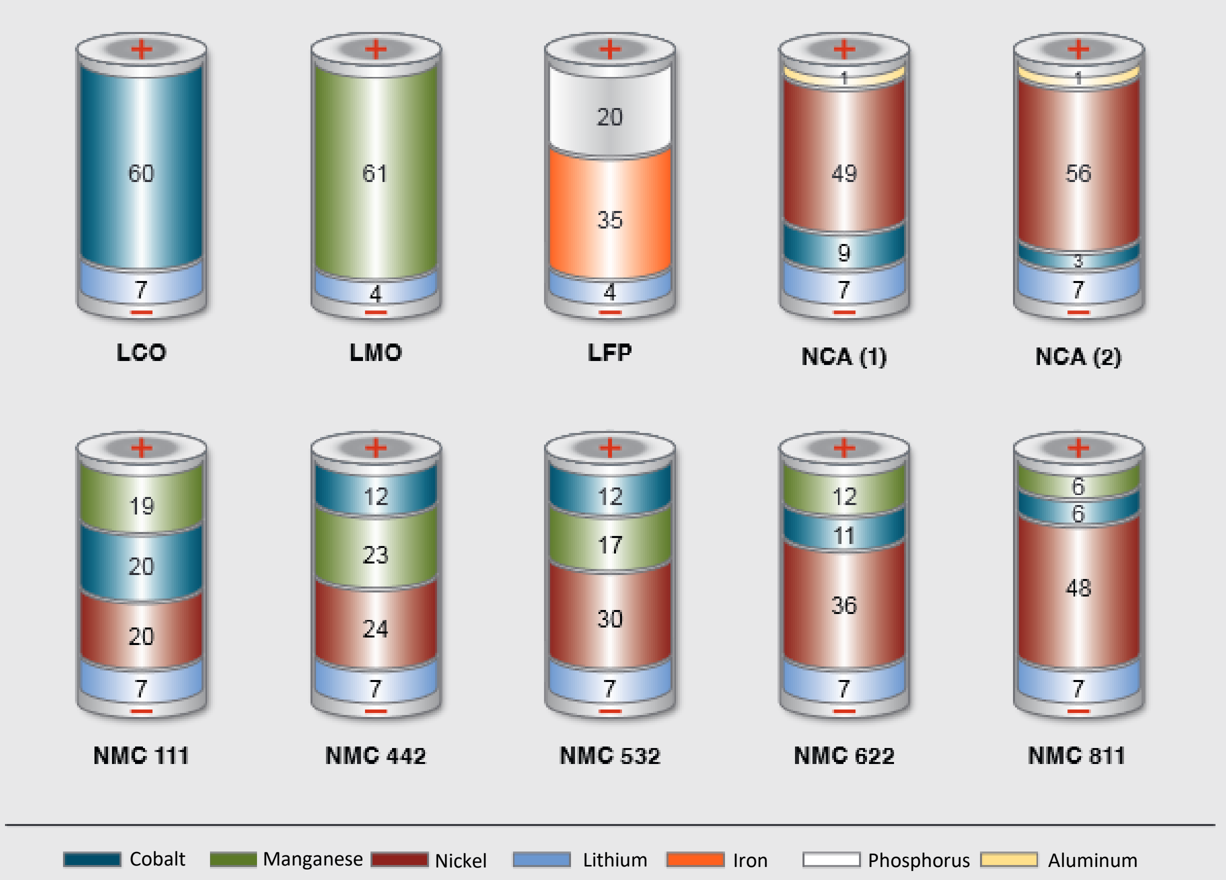
composition of the active material



composition of a LIB

goal of refinement: separation of the individual components

Recycling: Refinement

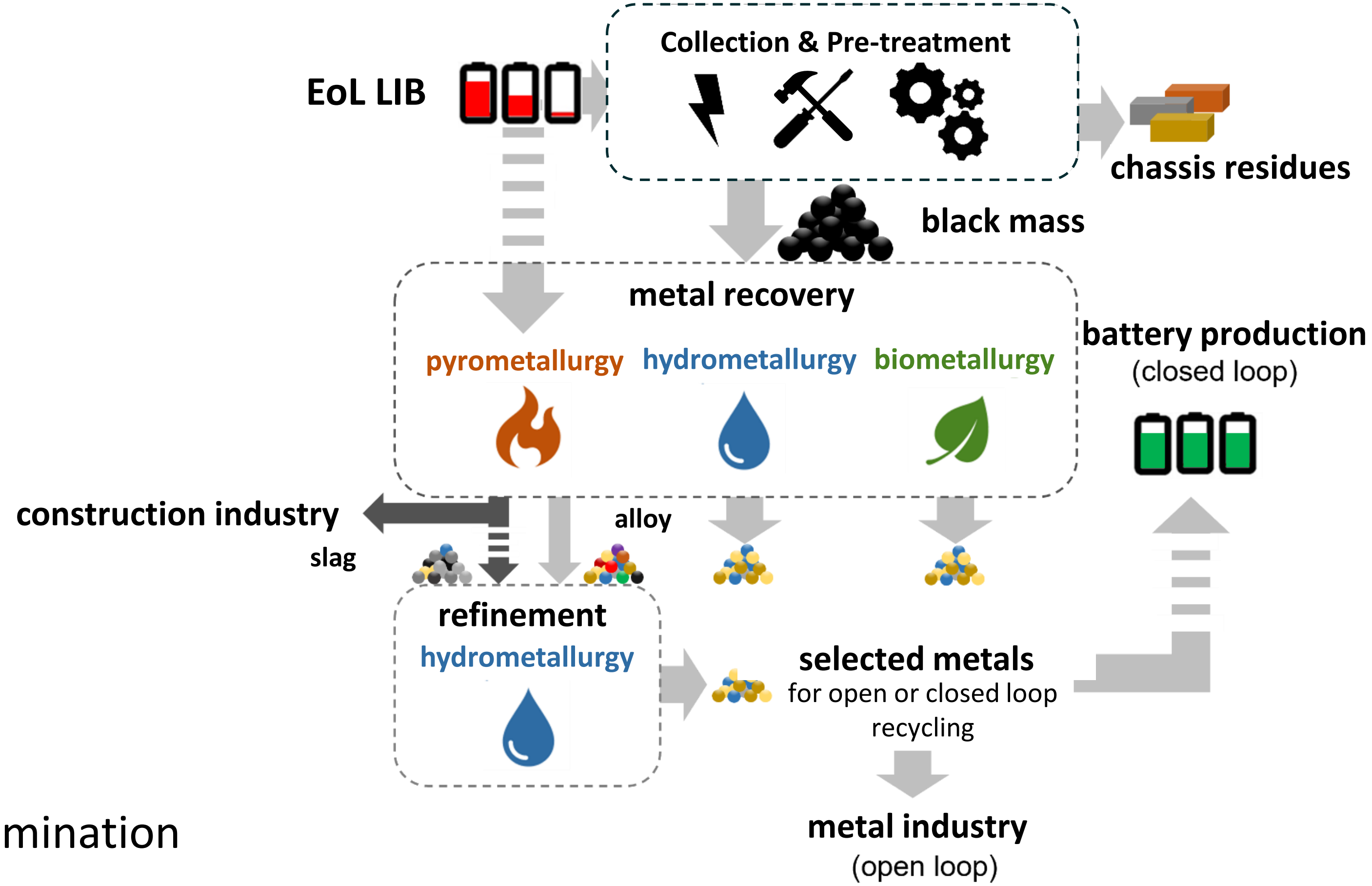


The figure shows metal contents (in % by weight) without oxygen content. Depending on the cathode active material, the oxygen content varies between 33 and 41% by weight

Source: https://www.deutsche-rohstoffagentur.de/DE/Gemeinsames/Produkte/Downloads/Commodity_Top_News/Rohstoffwirtschaft/67_Lithium-Ionen-Batterierecycling.pdf?__blob=publicationFile&v=5

LIB recycling routes

- **Pyrometallurgy**
  - Recovery of Ni, Co
  - Lithium – slagging
- **Hydrometallurgy**
  - High recycling rates
  - High use of chemicals and process stages
  - Susceptible to variable input flow
- **Biometallurgy**
  - Use of ecological leaching materials
  - Bacterial cultures susceptible to Cu contamination
  - Low throughput quantities



[3] Windisch-Kern et al., Recycling chains for lithium-ion batteries: A critical examination of current challenges, opportunities and process dependencies, Waste management (New York, N.Y.) 138 (2022), 125–139. DOI: 10.1016/j.wasman.2021.11.038

Recycling Challenges

- **Process steps**
- **Challenges / Disadvantages**

Process steps		Challenges / Disadvantages
transportation and collection	→	safety – damaged products
pre-treatment	→	LIB standardization problems – design
material recovery	→	variable chemical composition
material processing	→	fulfilment of purity levels

Pyrometallurgy

- **What is Pyrometallurgy?**

  High-temperature process to extract metals from ores or recycled materials.
  Involves smelting and refining at temperatures above 1000 °C.

- **Steps in Pyrometallurgical Battery Recycling:**

  - **Pre-Treatment:**
    Shredding of battery components.
    Removal of casings and separators.

  - **Smelting:**
    Batteries are fed into a high-temperature furnace.
    Metals are melted and separated as an alloy.

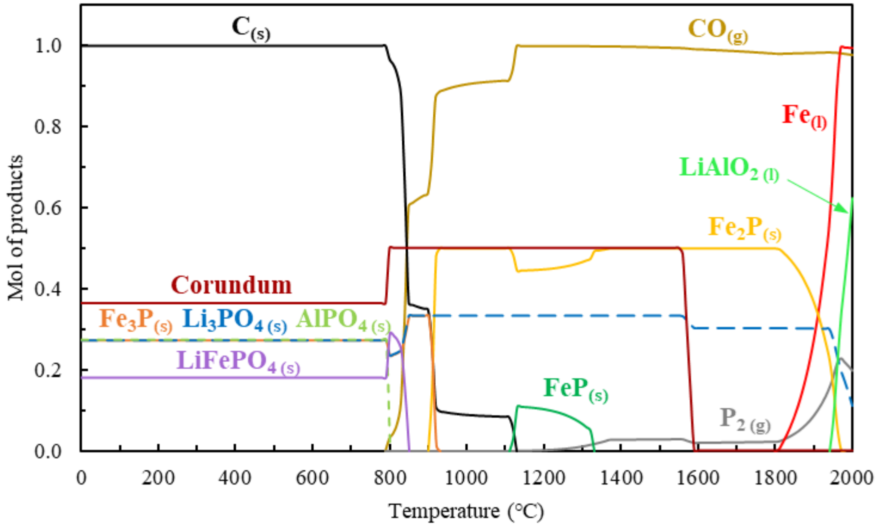
  - **Refining:**
    Removal of impurities to produce high-purity metal products.

Pyrometallurgy

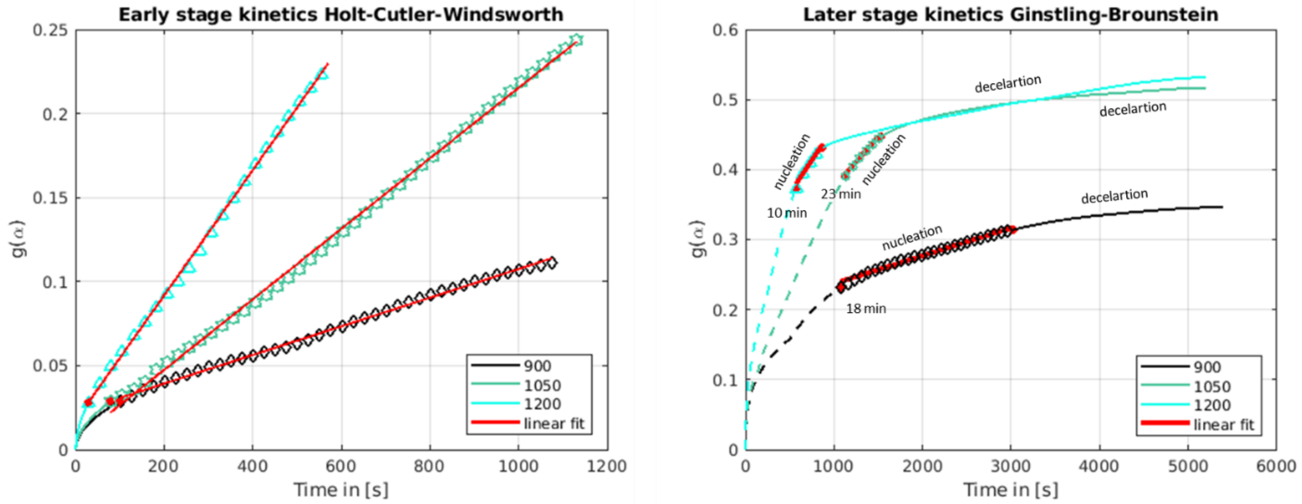
- **Advantages:**
  - Efficient recovery of valuable metals like **cobalt**, **nickel**, and **copper**.
  - Can handle a **variety of battery** chemistries and designs.
  - **Well-established** industrial process with existing infrastructure.
- **Disadvantages:**
  - **High energy consumption** and associated costs.
  - **Emission** of greenhouse gases and other pollutants.
  - Generation of **Li rich slag** and other **waste products**.
- **Innovative reactor concept:**
  - **Inductively heated** (electric energy) system
  - **Zero emission approach**
  - **Reuse** of **mineral fraction** and **alloy**, total **Li** (and **P**) **recovery**

Pyrometallurgy – Thermokinetics LiFePO4

- **Investigation of thermokinetic properties in carbothermal and aluminothermic reduction of synthesised $LiFePO_4$ black mass**



Equilibrium calculation results on carbothermic reduction of $LiFePO_4$

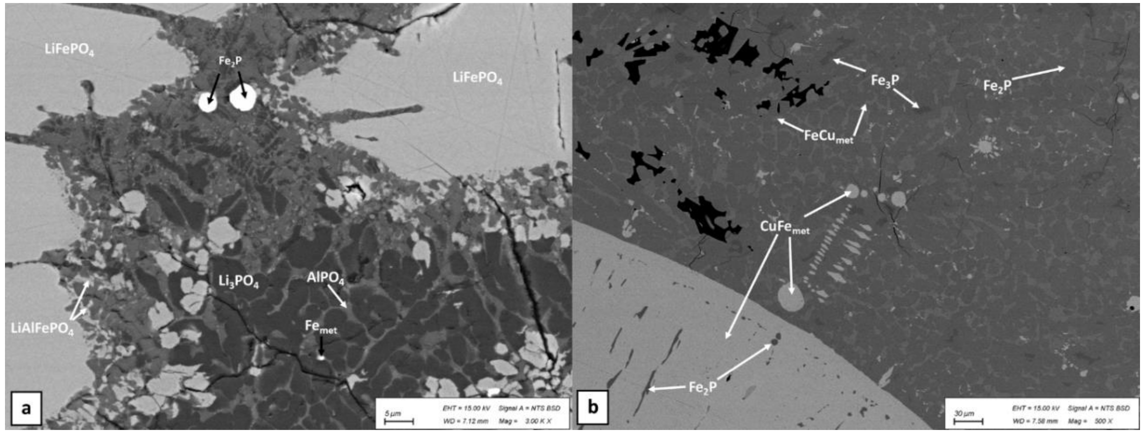


Early (left)and later stage kinetic (right) data fitted with a diffusion and nucleation-controlled model

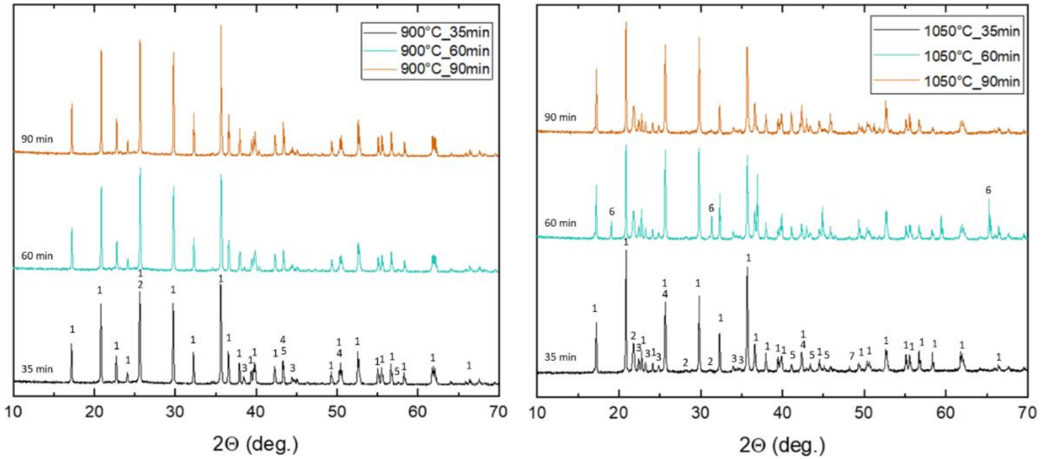
Lukas Wisniewzski; Zlatko Raonic; Bintang A. Nuraeni; Irmtraud Marschall; Bima Satritama; M. Akbar Rhamdhani; Stefan Riesel (2024):Investigation of thermokinetics in carbo- and aluminothermic reduction of synthezised $LiFePO_4$ black mass
Manuscript submitted for publication. In: Journal of Cleaner Production

Pyrometallurgy – thermokinetic LiFePO4

- **Investigation of thermokinetic properties in carbothermal and aluminothermic reduction of synthesised $LiFePO_4$ black mass**



Backscatter electron image of the $LiFePO_4$ mixture after carbothermal reduction at 1050°C and 90 minutes. a.) transition area between metal droplet and remaining carbon and $LiFePO_4$ crystals. b.) sintered structure of Li_3PO_4 with $AlPO_4$ between large elongated $LiFePO_4$ crystals



XRD analysis of the $LiFePO_4$ samples after carbothermal reduction for 35 minutes, 60 minutes and 90 minutes. a.) 900 °C (phases: 1: $LiFePO_4$, 2: C: 3: Al, 4: Cu, 5: Al_2O_3), b.) 1050°C (phases: 1: $LiFePO_4$, 2: $AlPO_4$, 3: Li_3PO_4, 4: C, 5: Fe_3P / Fe_2P, 6: $LiFe_{0.88}Al_{1.78}O_4$, 7: $LiCu_{0.15}Fe_{0.80}PO_4$)

Lukas Wisniewzski; Zlatko Raonic; Bintang A. Nuraeni; Irmtraud Marschall; Bima Satritama; M. Akbar Rhamdhani; Stefan Riesel (2024):Investigation of thermokinetics in carbo- and aluminothermic reduction of synthezised $LiFePO_4$ black mass Manuscript submitted for publication. In: Journal of Cleaner Production

Magnetohydrodynamics in reactive multiphase flow

Conservation Equations Multiphase System:

Mass: $$\frac{\partial \alpha_i}{\partial t} + \nabla \cdot (\boldsymbol{u}_i \alpha_i) = S_m$$

Momentum: $$\frac{\partial \alpha_i \boldsymbol{u}_i}{\partial t} + \nabla \cdot (\alpha_i \boldsymbol{u}_i \boldsymbol{u}_i) = \nabla \cdot \left(\frac{\alpha_i}{\rho_i} \boldsymbol{\tau}_i\right) + \alpha_i \mathbf{f}^{\mathbf{b}} + \frac{\alpha_l}{\rho_l} (\mathbf{v} \times \boldsymbol{B}) + S_i$$

Energy: $$\frac{\partial \alpha_i \rho_i \left(e_i + \frac{1}{2} \boldsymbol{u}_i^{2}\right)}{\partial t} + \nabla \cdot \left[\alpha_i \rho_i \boldsymbol{u}_i \left(e_i + \frac{1}{2} \boldsymbol{u}_i^{2}\right)\right] = \alpha_i \boldsymbol{u}_i \cdot \left[\nabla \cdot \boldsymbol{\tau}_i + \rho_i \mathbf{f}^{\mathbf{b}}\right] + \nabla \cdot \mathbf{q} + \alpha_l \frac{1}{\sigma} \mathbf{J}^2 + \mathrm{S_e}$$

Species: $$\frac{\partial (\rho Y_i)}{\partial t} + \nabla \cdot (\rho \boldsymbol{u} Y_i) = -\nabla \cdot \boldsymbol{J}_i + \mathrm{R_i} + \mathrm{S_i}$$

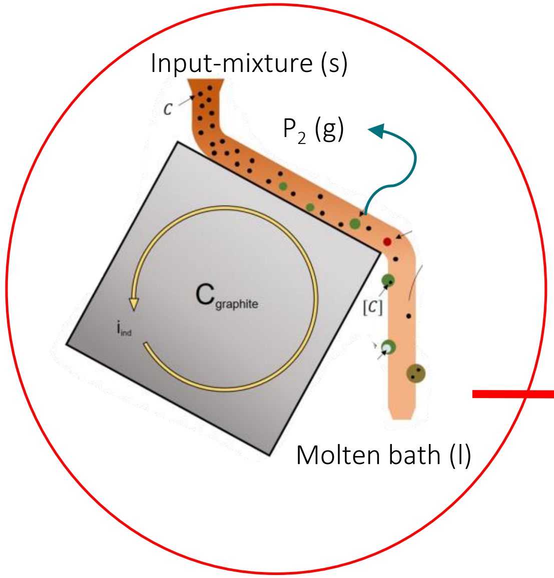
Maxwell equations A-Φ model ($\boldsymbol{B} = \nabla \times \mathbf{A}$):

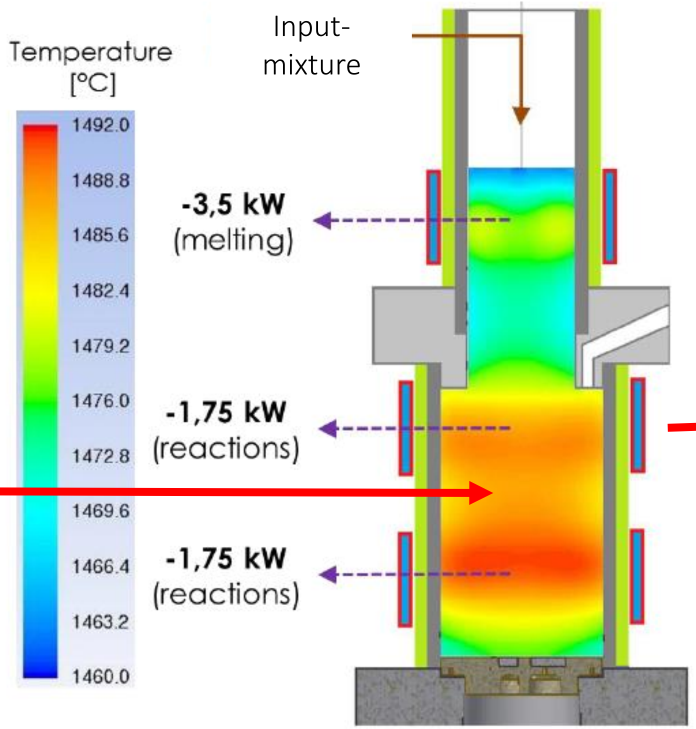
$$\sigma \mu_0 \frac{\partial \mathbf{A}}{\partial t} - \frac{1}{\mu_r} \Delta \mathbf{A} = \sigma \mu_0 (\mathbf{v} \times \nabla \times \mathbf{A}) - \left(\nabla \frac{1}{\mu_r}\right) \times \boldsymbol{B} - \nabla \Phi_{corr}$$

$$\Delta \Phi = \nabla \cdot (\mathbf{v} \times \boldsymbol{B})$$

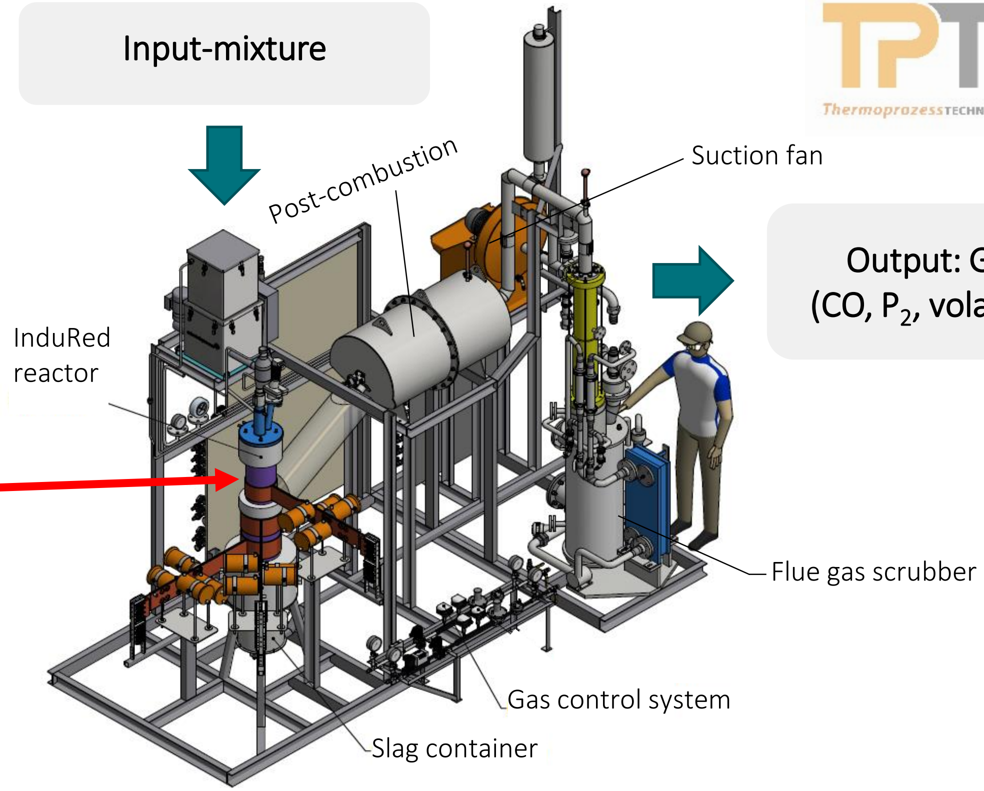
$$\mathbf{J} = \sigma\left(-\Delta \Phi - \frac{\partial \mathbf{A}}{\partial t} + \mathbf{v} \times \boldsymbol{B}\right)$$

InduRed reactor





Input-mixture



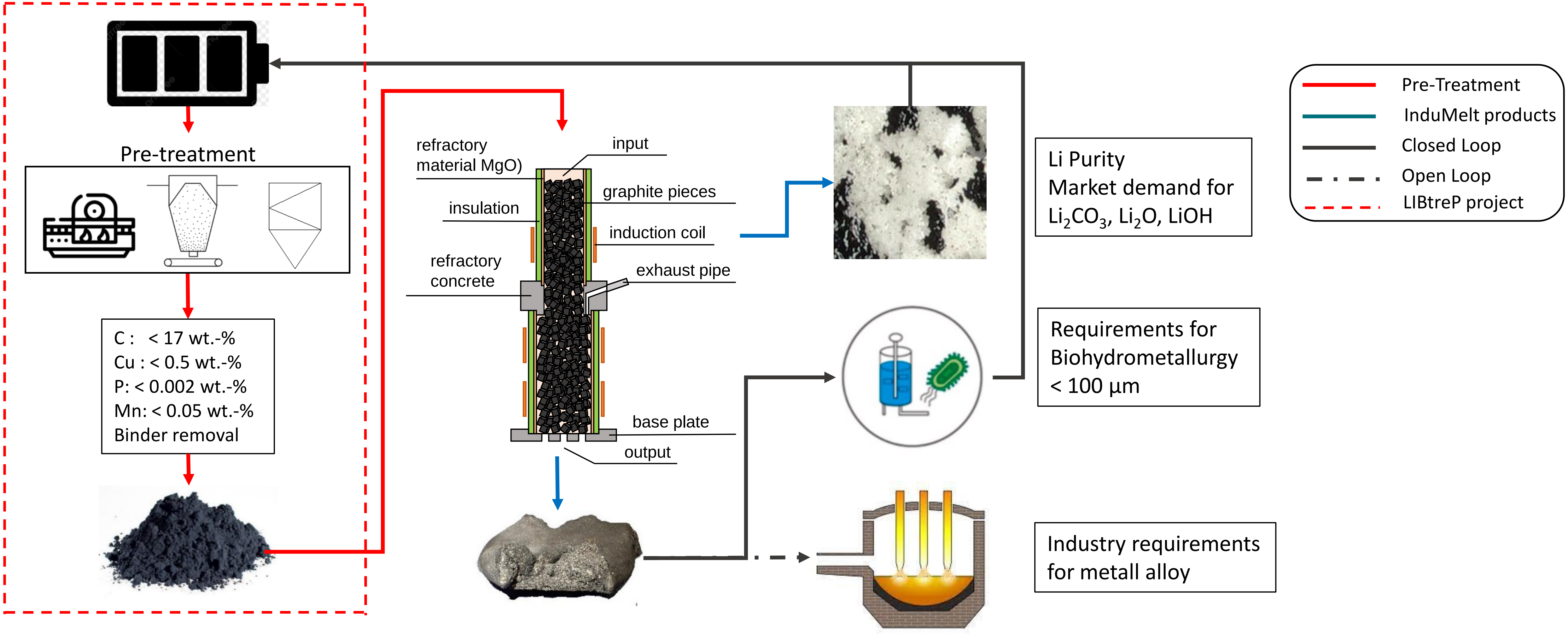
Output: Gas
(CO, P_2, volatiles)

Output: molten bath
Mineral fraction (CaO, SiO_2, MgO, Al_2O_3…)
Metal fraction (Fe, C, P) <u>if FeO enters the reactor</u>

[1] Raupenstrauch et al.: Apparatus and process for thermal treatment of raw material containing lithium compounds and phsophorous compounds, method of recovering lithium and/or phsophorous from residual material of lithium-ion batteries'. WO 2021/175703 A1

https://patents.google.com/patent/WO2021175406A1/en

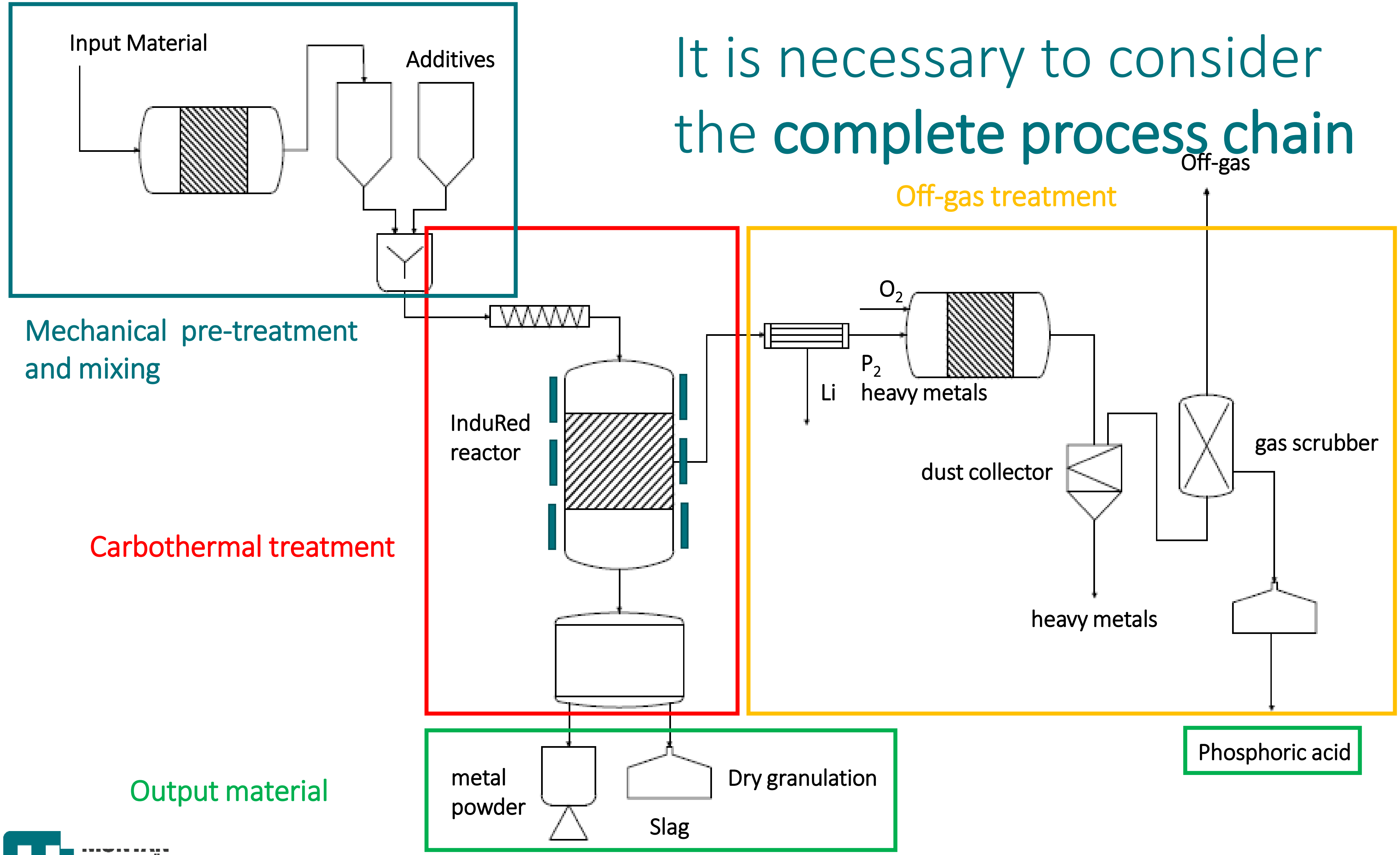
InduRed reactor in a new LIB recycling approach



PhD thesis: Lukas Wiszniewski (2024): Multidisciplinary development of a novel pyrometallurgical recycling concept for lithium-ion batteries (in progress)

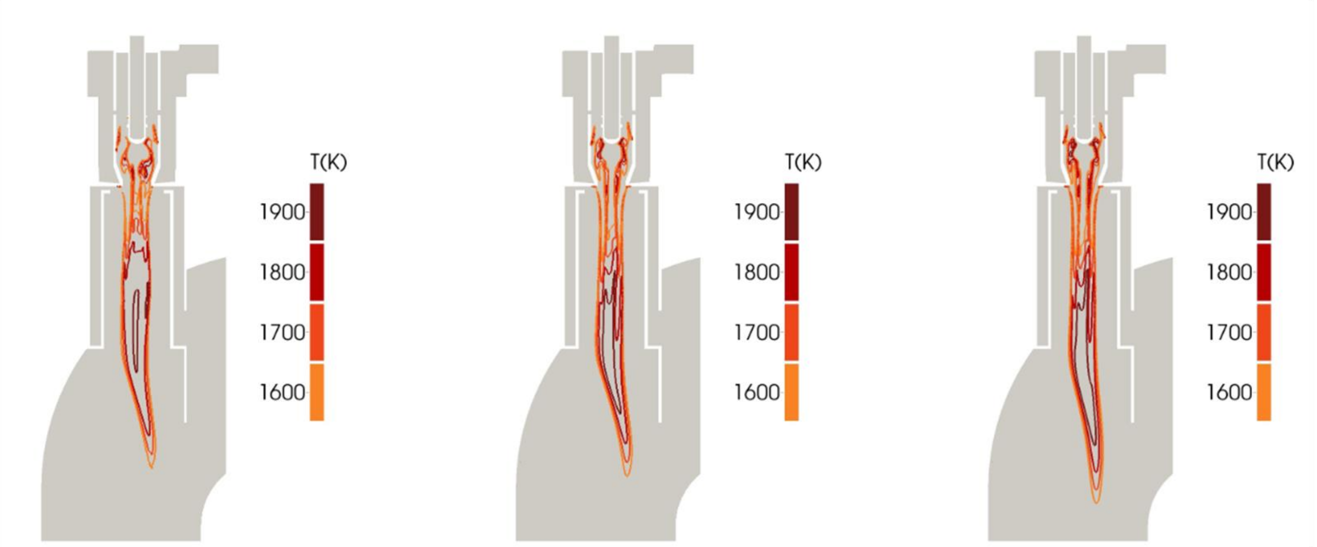
European Patent 4 114 997 (Number: 21 708 619.8)
„Apparatus and process for thermal treatment of raw material containing lithium compounds and phosphorus compounds, method of recovering lithium and/or phosphorus from residue material of lithium-ion batteries“

It is necessary to consider the **complete process chain**



Challenge Hydrogen enriched gases: Burner technology

- Low NOx burner with H2 enriched natural gas
  - Increase Hydrogen Content → Increase in observed maximum Ter



Natural Gas | 30 % H_2 | 50 % H_2

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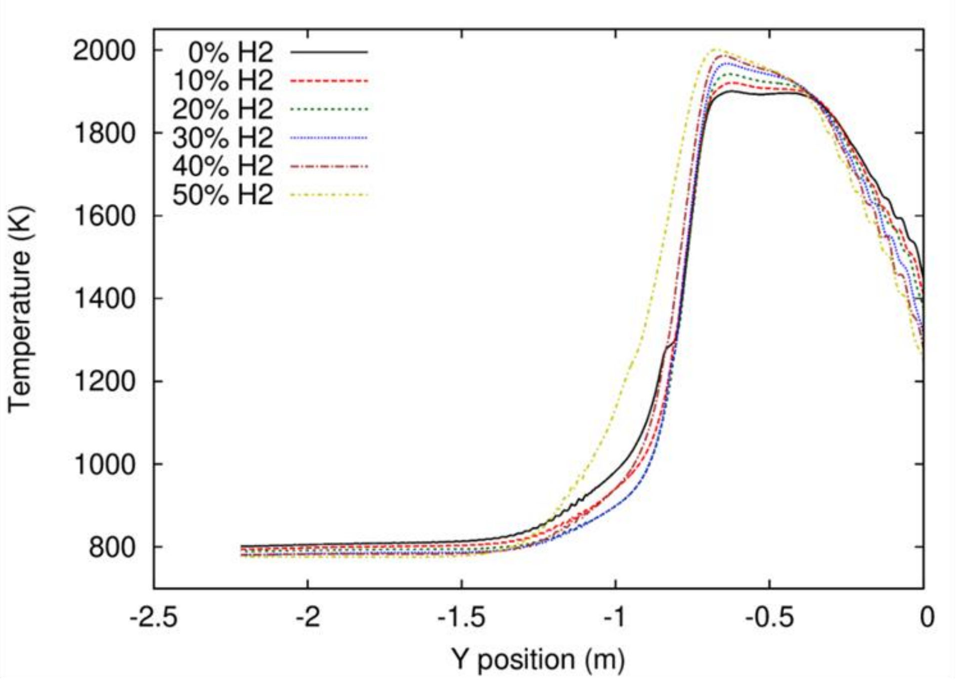
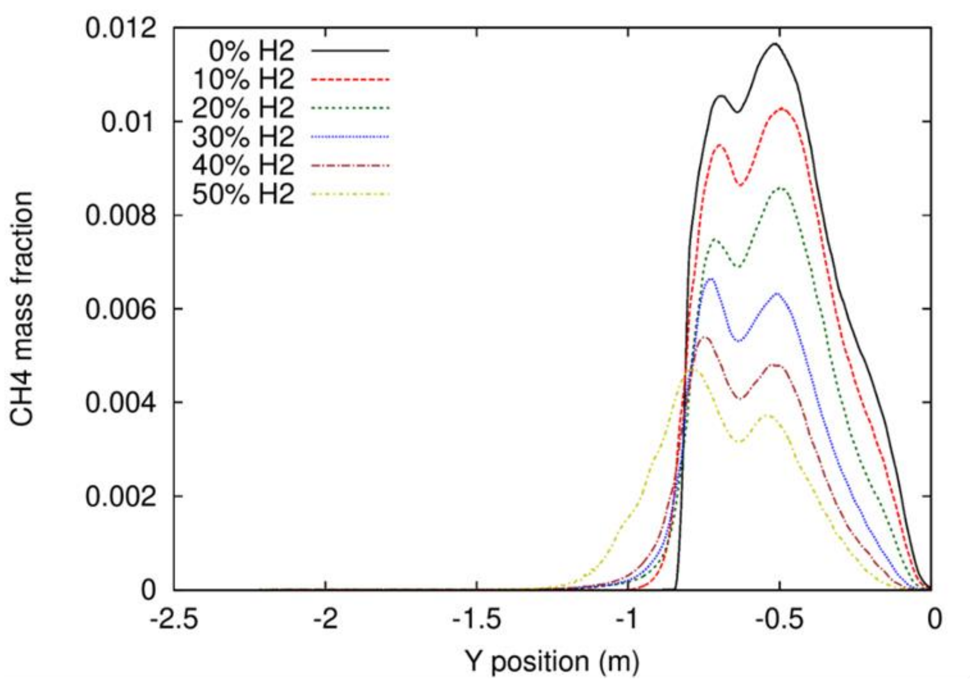
Challenge Hydrogen enriched gases: Burner technology

Natural Gas → 1896 K

Natural Gas + 50 % H_2 → 1986 K





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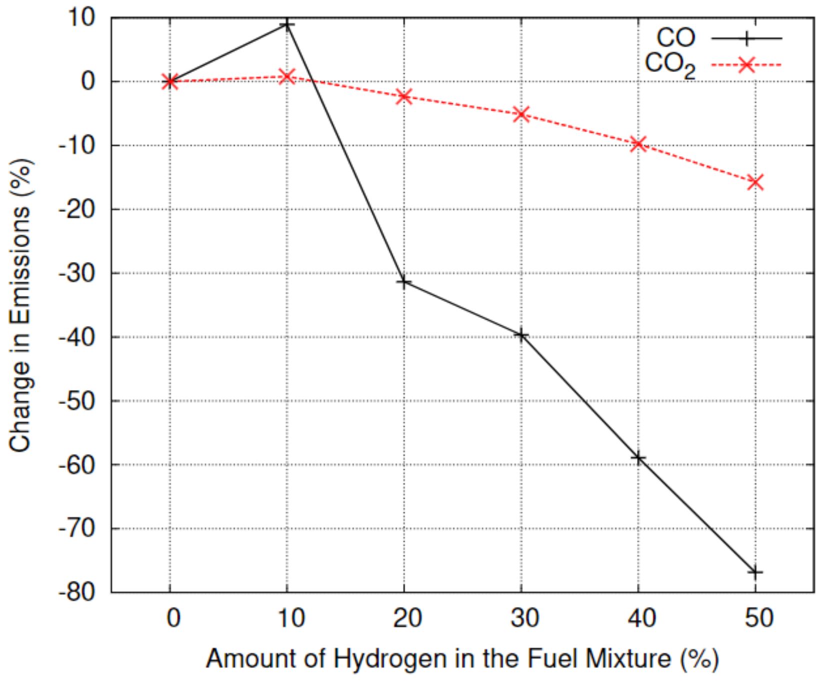
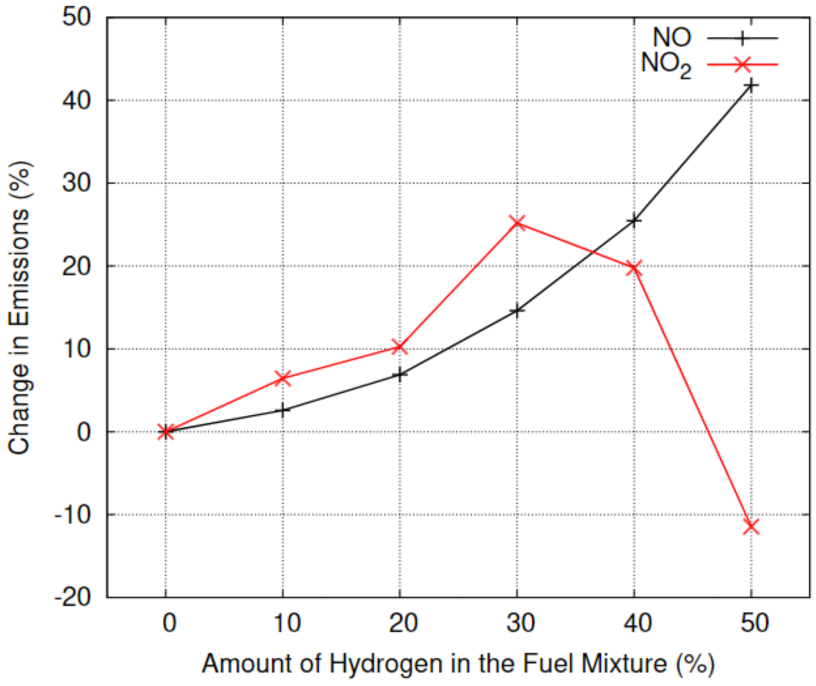
Challenge Hydrogen enriched gases: Burner technology





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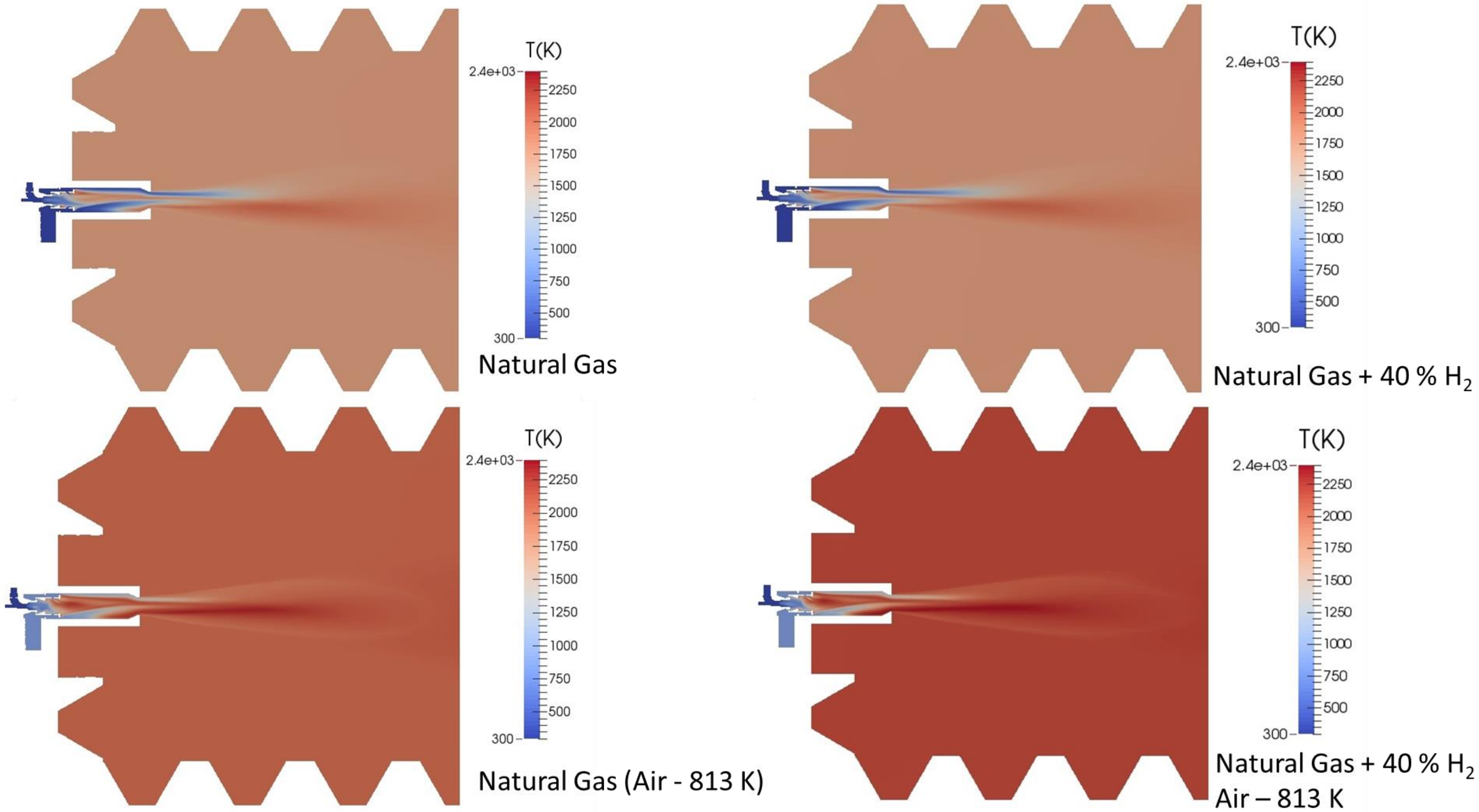
Challenge Hydrogen enriched gases: Burner technology



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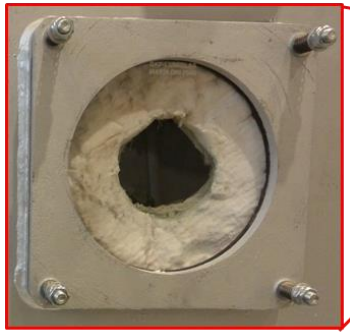
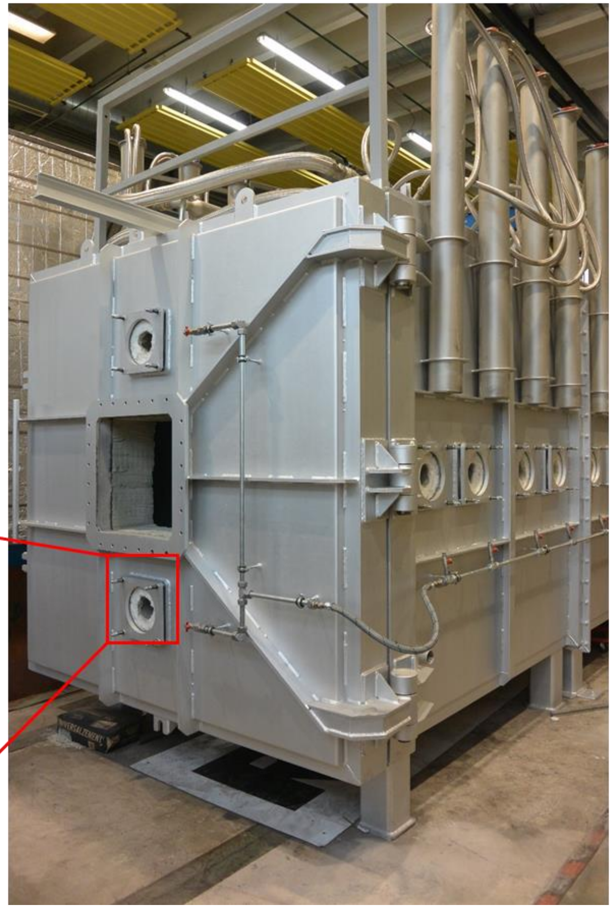
TPT Burner Test Facility

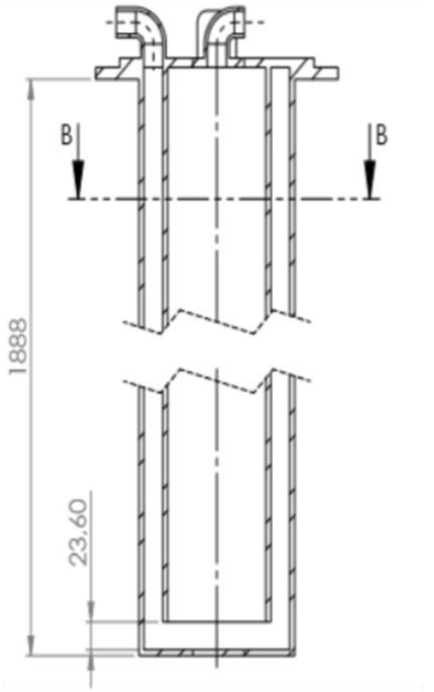
Gas supply system:
- 5 to 120 Nm³/h natural gas
- 4 to 100 m³/h H_2 or CO_2
- 60 Nm³/h to 1200 Nm³/h air
- 10 to 190 Nm³/h O_2

Measurement ports:
- 23 ports
- air cooled for optical measurements
- Spring-loaded flange





Cooling system:
- 14 water cooled elements
- Up to 851 kW cooling power



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Safety related parameters Hydrogen vs. Methane

Kenngröße	Wasserstoff	Methan
Untere Explosionsgrenze	4,0 Vol.-% (Mol-%)	4,4 Vol.-% (Mol-%)
Obere Explosionsgrenze	77,0 Vol.-% (Mol-%)	17,0 Vol.-% (Mol-%)
Sauerstoffgrenzkonzentration	4,3 Vol.-% (Mol-%)	9,9 Vol.-% (Mol-%)
Maximaler Explosionsdruck	8,3 bar	8,1 bar
K_G	800 bar m s^{-1}	52 bar m s^{-1}
Normspaltweite	0,29 mm	1,14 mm
Mindestzündenergie	0,017 mJ	0,23 mJ
Zündtemperatur	560 °C	595 °C

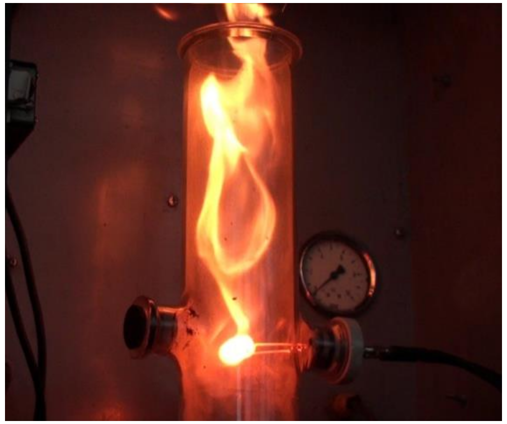
V. Schröder *et al.*, Sicherheitstechnische Eigenschaften von Erdgas-Wasserstoff-Gemischen, BAM, 2016

Raupenstrauch H., „Sicherheitstechnische Fragestellungen in Zusammenhang mit der Energiewende", Energieforschungsgespräche Disentis/CH, 2023

Process- and Plant Safety Research Group

Process and Plant Safety

- **Fire & Explosion Prevention**
- **Education**
- **Combustion and Safety Lab**



MONTAN UNIVERSITÄT LEOBEN WHERE RESEARCH MEETS THE FUTURE

TPT S!DS

Interdisciplinary Master Degree

NAME: Safety and Disaster Management

ACADEMIC DEGREE: Master of Science

DURATION: 4 Semester

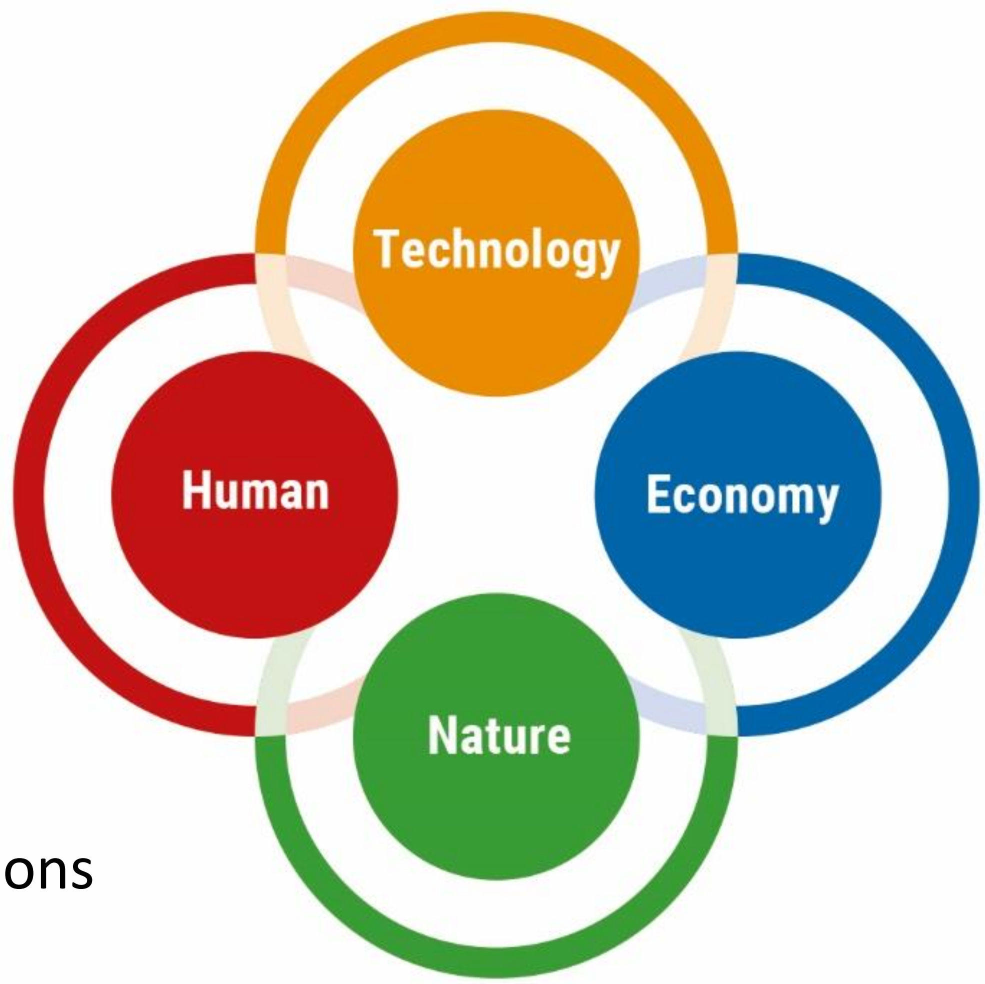
LANGUAGE: English

ADMISSION: Open to all disciplines (Bachelor level)

ORDINARY STUDY: Conceivable as part-time study

<u>Developing Interdisciplinary Competence:</u>

- Linking TECHNOLOGY, ECONOMY, NATURE, HUMAN
- Targeted seminars and trainings focused on intersections



Thanks to ...

- My colleagues at TUC for the warm welcome and great hospitality, esp. Professor Evan Diamadopoulos

Thanks to …

- Dr. Susanne Feiel for helping me organizing this stay at TUC
- Rector Peter Moser for supporting me

Credit: Foto Freisinger

Credit: MUL/Martina Stöbbauer

Thanks to …

- To my HTPT group for their great work and for preparing so many slides …

Thanks to …

- To my wife Brigitte

Appologize for not supporting my team these days …

- **FC Caterpillarshrub** fighting for winning the university championship again

MONTAN UNIVERSITÄT LEOBEN

THANK YOU FOR YOUR ATTENTION!

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… keep on running!

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