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Die Ressourcenuniversität. Seit 1765.

dorfner ANZAPLAN

CHEMIE TU Bergakademie Freiberg

Carbonation of lithium-containing primary and secondary raw materials using CO_2

CO_2-LiPriSek

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GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung

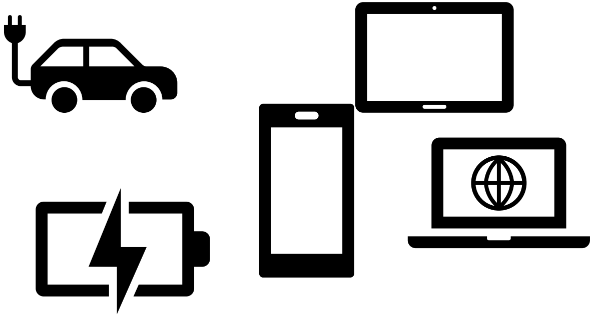
Projektträger Jülich
Forschungszentrum Jülich

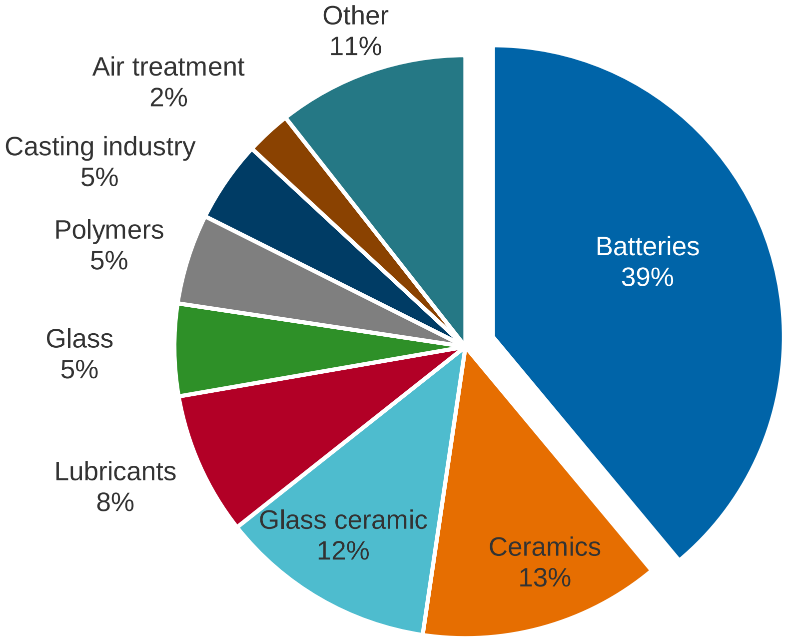
Why lithium recovery?

Motivation of the project

Lithium

- A synonym for energy transition
- A strategic raw material
- Uneven distribution of global lithium deposits
- Main application field: energy storage

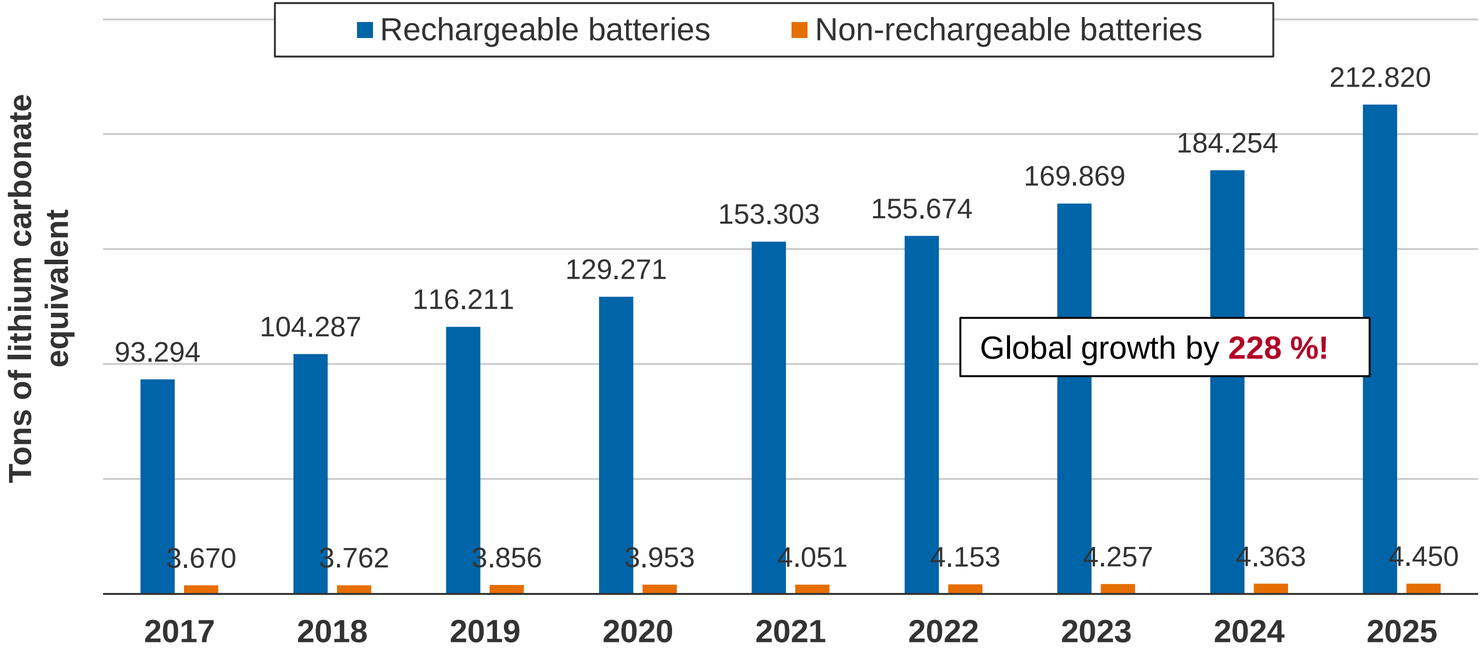




https://de.statista.com/statistik/daten/studie/159921/umfrage/verwendungszwecke-von-lithium-auf-dem-weltmarkt/

Motivation

Increasing demand for lithium ion batteries (LIBs)



https://de.statista.com/infografik/14998/weltweiter-lithiumbedarf-fuer-batterien/

Aim of the project CO_2-LiPriSek

Recovery of Lithium from:

Primary resources
- Use of local raw materials
  - Zinnwaldite
  - Lepidolite
  - Spodumene

COOL-Process

Secondary resources
- Spent lithium-ion batteries
  - $LiCoO_2$
  - $LiNi_xCo_yAl_zO_2$
  - $LiFePO_4$

Li_2CO_3
(battery grad >99.5%)

Lithium recovery

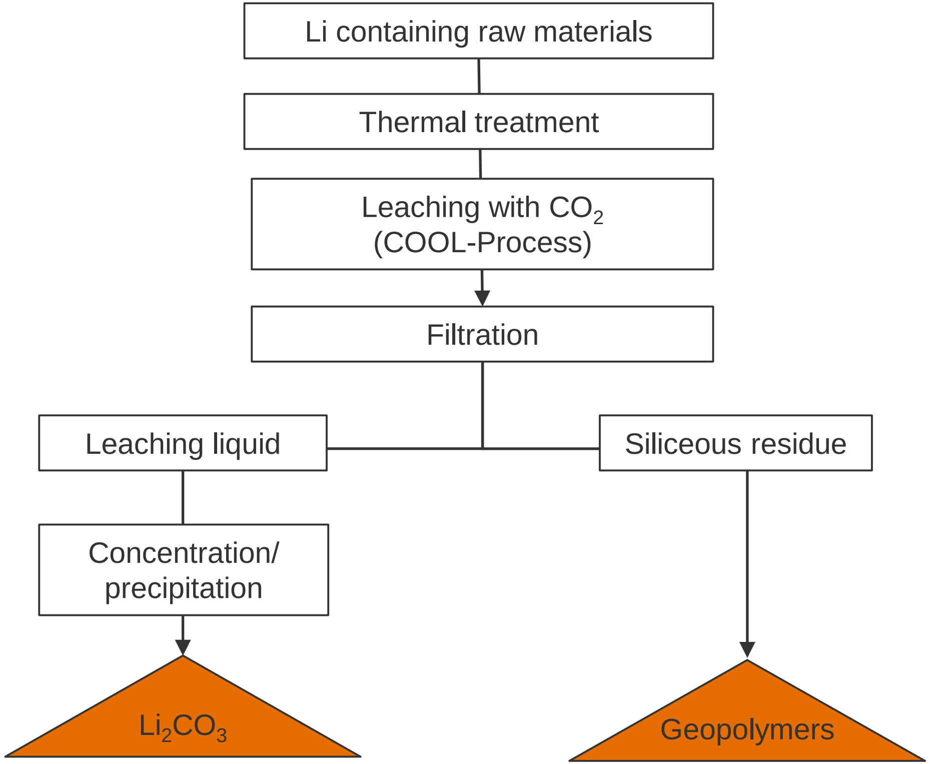
Innovative alternative

COOL-Process

- Leaching with supercritical CO_2 (sc-CO_2)
- Advantages:
  - ✓ Low chemicals cost
  - ✓ No complex waste water treatment
  - ✓ High selectivity for Li
  - ✓ No addition of further precipitation agent
  - ✓ High purity of precipitated Li_2CO_3 → *bg*-grade without further purification
  - ✓ No Lithium losses → Circulation of the mother liquor
  - ✓ Utilization of solid residue (mainly silicate) for production of geopolymers → holistic valorisation of raw material → No landfill required

Lithium recovery

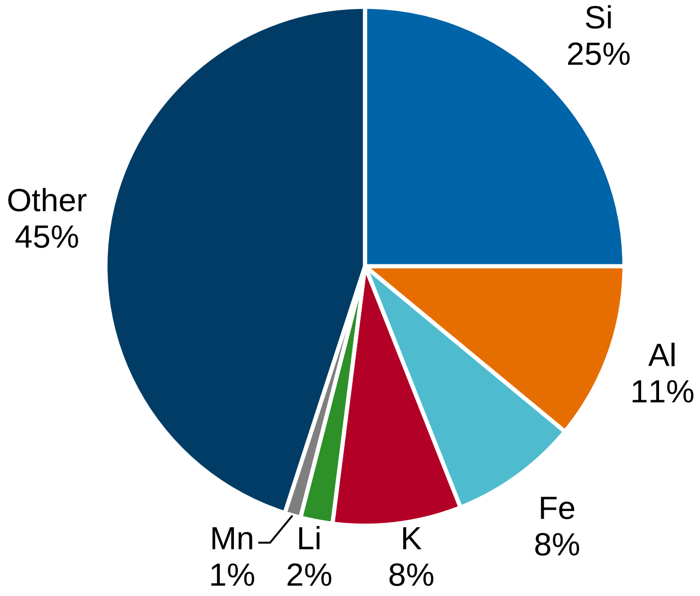
COOL-Process

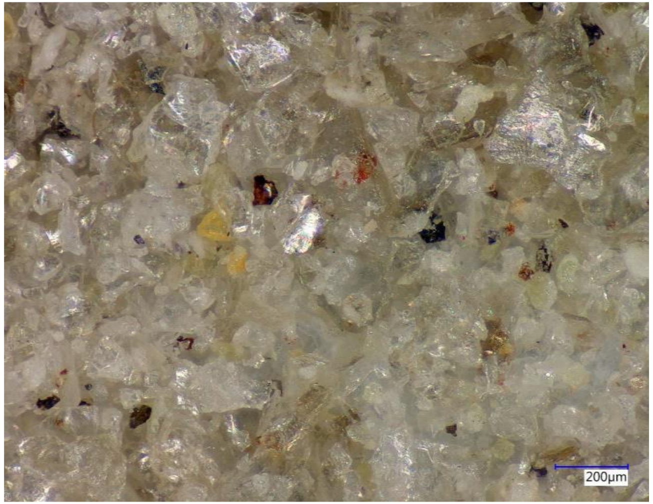


Lithium recovery

COOL-Process

Zinnwaldite





COOL-Process

Zinnwaldite

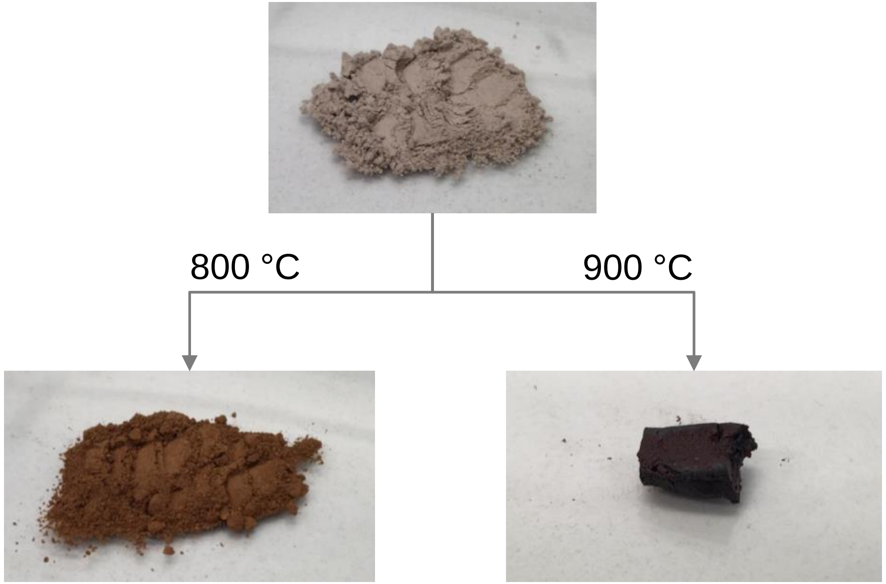
Thermal treatment

- Aim:
  - Uniformation of different Li raw materials to one single Li-species
  - Phase transformation to ß-spodumene ($LiAlSi_2O_6$)
  - Simultaneous removal of the fluorine content

COOL-Process

Zinnwaldite

Thermal treatment

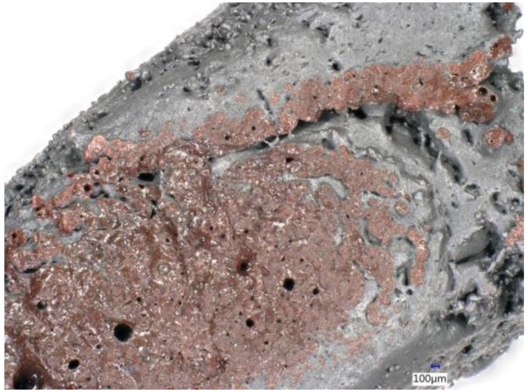


COOL-Process

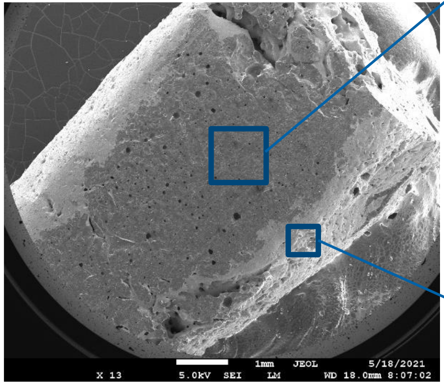
Zinnwaldite

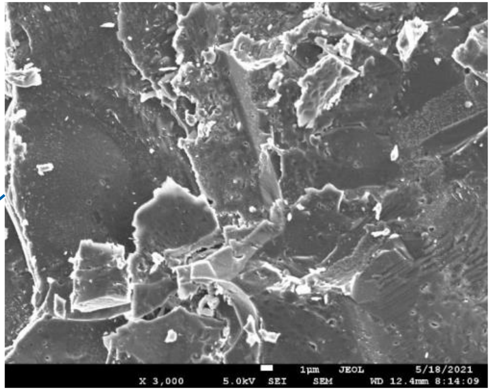
Thermal treatment: 900 °C

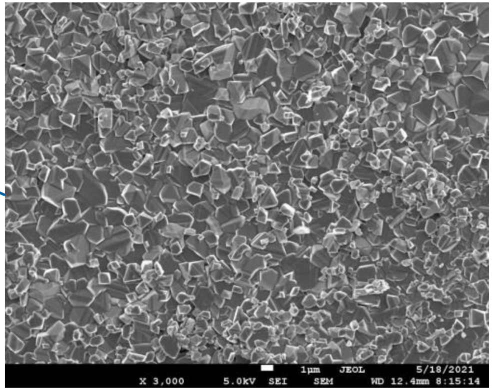
Digital Microscope



Scanning electron microscope







COOL-Process

Zinnwaldite

Leaching with sc-CO_2

- Aim:
    - Selective Mobilisation of Lithium
- Optimization of process parameters by design of experiment (DOE)

Factor	-	0	+
Temperature [°C]	170	200	230
Residence time [h]	2	3	4
Liquid-solid-ratio [mL/g]	20	50	80

- In Summer 2021: Execution of DOE → adaption to other ores and simultaneous leaching of different Li-ores

COOL-Process

Geopolymers: Utilization silicate residue

Geopolymers

- Inorganic, calcium-free polymers based on silicon and aluminum oxide
- CO_2-free cement

Silicate residue from COOL-Process

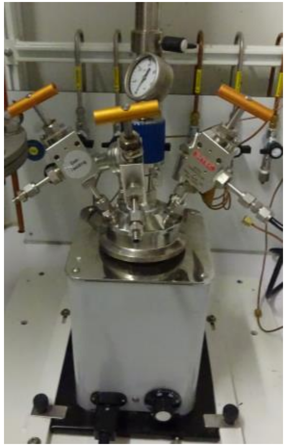
- First trials were successful
- Formation of a pressure resistant tablet
- Further trials to follow when COOL process for zinnwaldite has been optimised

COOL-Process

Black mass

Black mass

- Origin: BMW i3 LIB
- Was collected after discharging and mechanical pretreatment (crushing, milling)



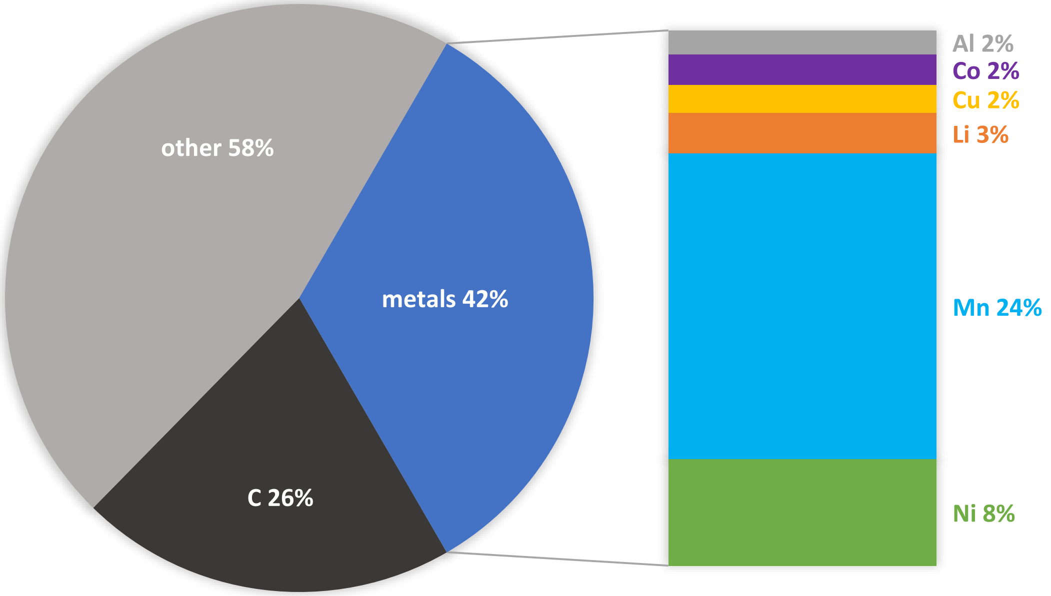
COOL-process

- Process parameter optimised by means of design of experiments (DOE) like 3^3 Box-Behnken Design
  - Temperature 150-230 °C
  - Residence time 2-4 h
  - Ratio solid-liquid: 11-33 g black mass per L water
- Leaching were carried out in an autoclave

COOL-Process

Black mass

Composition

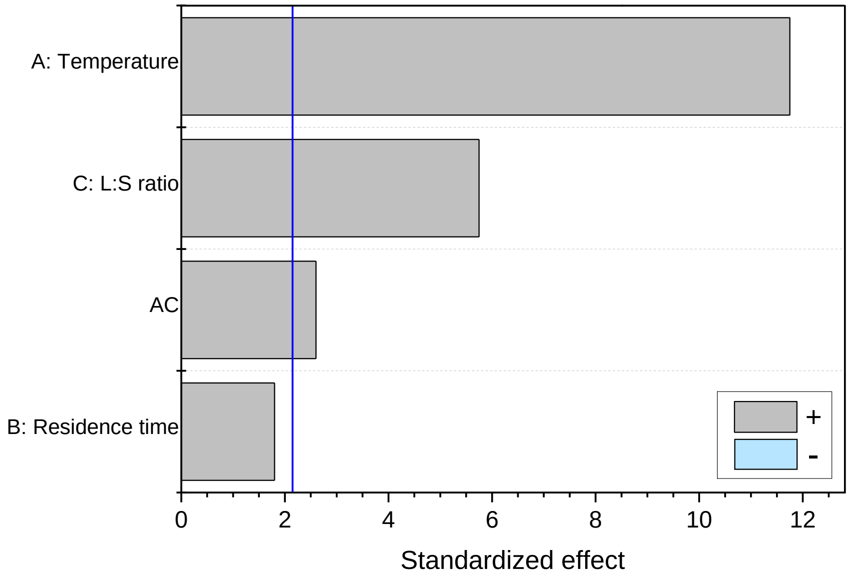


COOL-Process

Results of DOE

Effects on Li mobilisation

- Temperature has the highest effect (linear)
- Liquid-solid ratio showed the second highest effect
- Residence time only poor effect

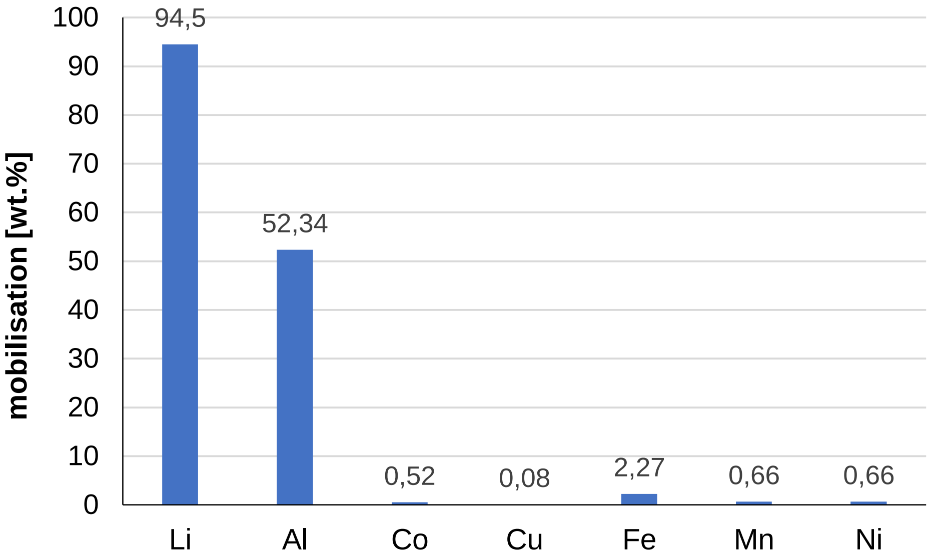


COOL-Process

Results of DOE

Optimum

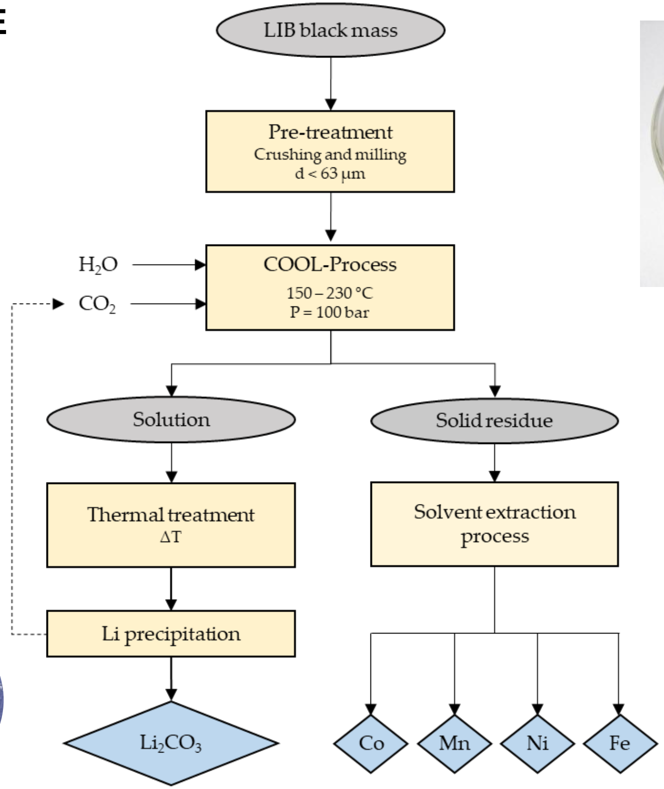
- Highest Li mobilisation at:
  - 230 °C, 4 h, 11 g black mass per liter water
- Highest Li mobilisation: **94.5 wt.%**
- Special feature: **selective Li mobilisation**



COOL-Process

Results of DOE

Recycling process scheme



Li_2CO_3
Purity: **99.8 wt.%**
→ Battery grade

Summary

- COOL-process allows Li recovery from primary and secondary resources
- Thermal treatment of raw material allows simultaneous processing of different ores
- Li recycling from spent LIBs → selective mobilisation of Li from LIBs → **94.5 wt.% Li mobilisation**
- Product is **Li_2CO_3** in **battery grade** (99.8 % purity) without further purification → direct use for production of new LIBs possible → **circular economy**
- Solid residue of COOL-process with ores: Production of **Geopolymers** → CO_2-free cement!

Publication

Publication in Journals

- S. Pavón, D. Kaiser, R. Mende, M. Bertau (2021) The COOL-Process - a selective approach for recycling lithium batteries. *Metals* **11**, 259, DOI: 10.3390/met11020259
- D. Kaiser, S. Pavón, M. Bertau (2021) Recovery of Al, Co, Cu, Fe, Mn, and Ni from spent LIBs after Li selective separation by the COOL-Process Part 1: Leaching of solid residue from COOL-Process; submitted
- S. Pavón, D. Kaiser, M. Bertau (2021) Recovery of Al, Co, Cu, Fe, Mn, and Ni from spent LIBs after Li selective separation by COOL-Process – Part 2: Solvent extraction from sulphate leaching solution; submitted

Conferences

- Oral presentation: D. Kaiser, S. Pavón, R. Mende, M. Bertau „Selective production of lithium carbonate from black mass“ WastEng2020, 31.05-04.06.2021, digital

Outlook

- Optimisation COOL-Process for different Li-ores
- Testing of further black mass (e.g. $LiFePO_4$)
- Scale-Up of COOL-Process up to 2 L autoclave volume
- Optimisation of production of Geopolymers from silicate residue
- LCA of COOL-Process

Thank you for your attention!

CO2WIN Use Carbon Sustainably

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