

Development of a multistep process for battery-grade Li_2CO_3 production

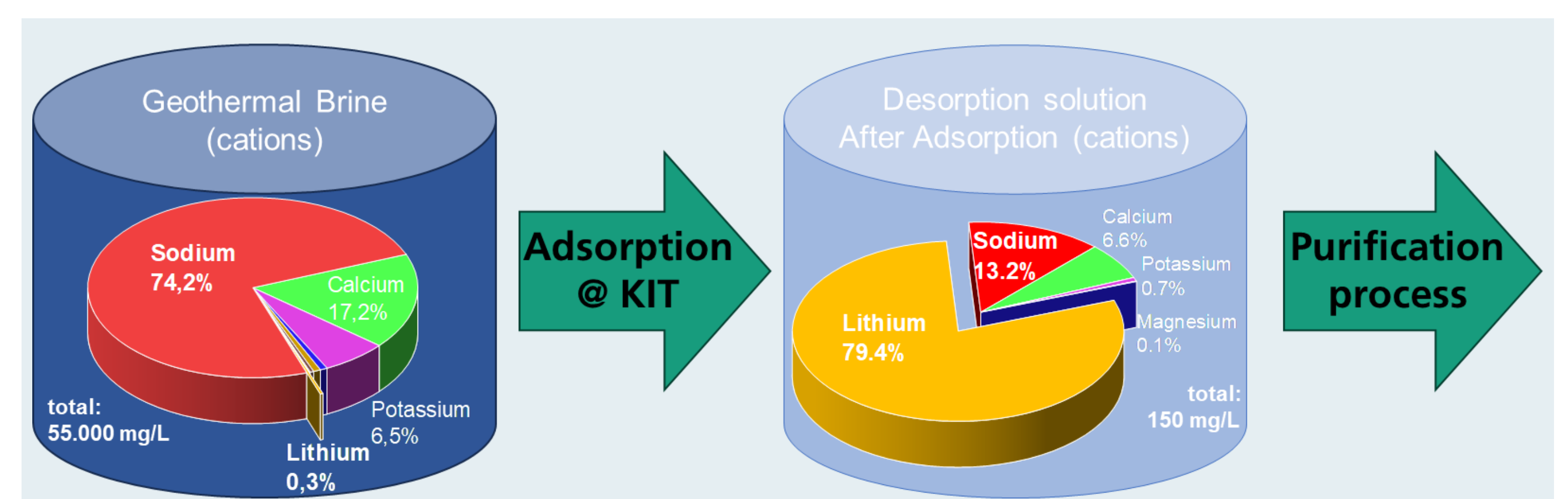
Lithium recovery from geothermal brines in the upper Rhine Valley



T. Skarke, M. Holzapfel, R. Hanich-Spahn, F. Klein
Fraunhofer-Institut für Chemische Technologie ICT, Joseph-von-Fraunhofer-Str. 7, 76327 Pfinztal (Germany)
Contact: tamara.skarke@ict.fraunhofer.de

Motivation

Global demand for lithium is increasing almost daily, largely due to the growing demand for lithium-ion batteries. However, the largest production sites are mostly located outside Europe and are concentrated in just a few countries, making Europe highly dependent on them. To counteract this, the EU has introduced sustainability regulations for batteries^[1] and is promoting the extraction of lithium from various raw materials within Europe. In addition to mineral deposits, the water from geothermal plants in the Upper Rhine Valley is also being considered as a potential lithium source.



Four-Step purification and recovery process for Li_2CO_3

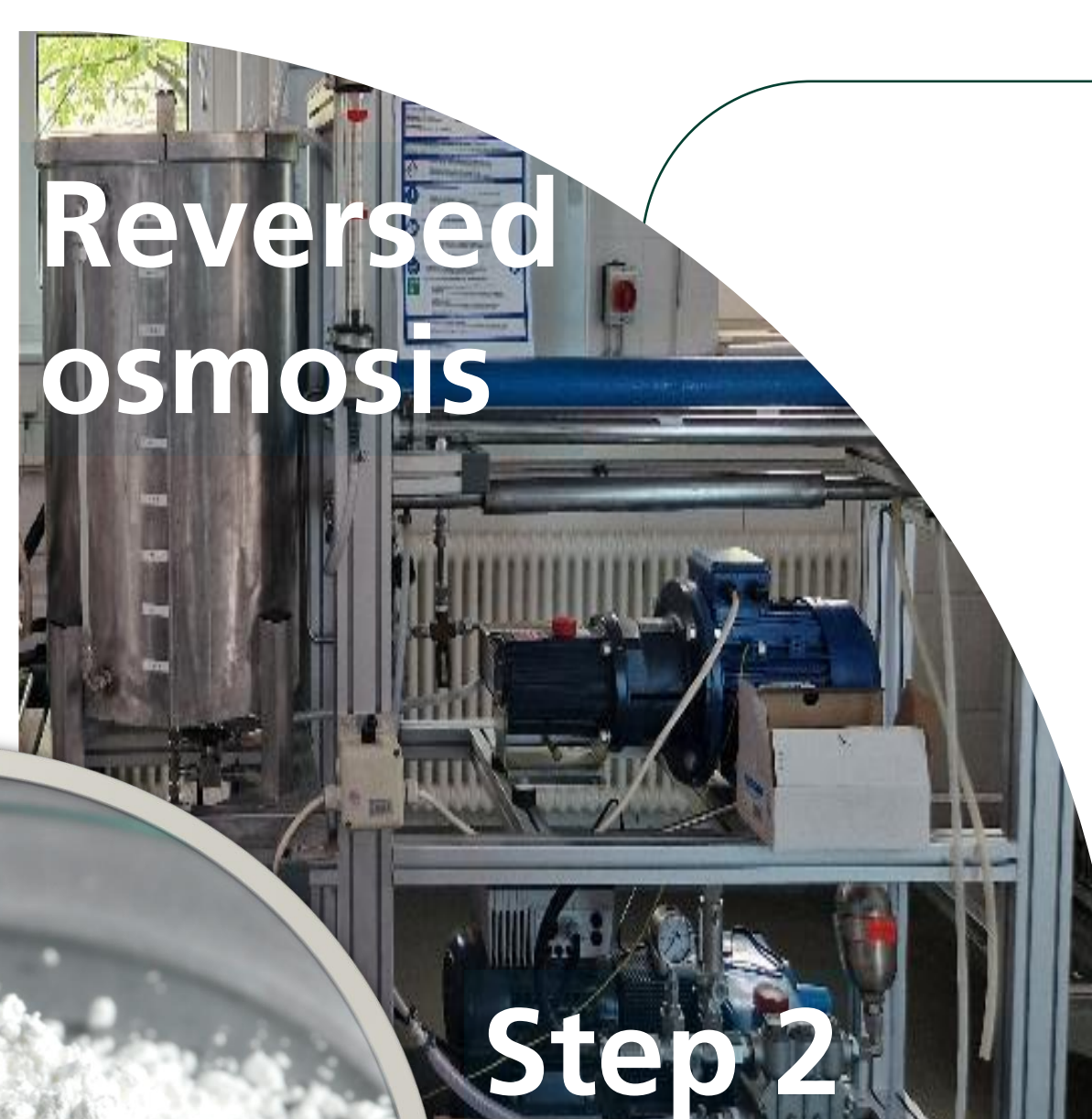
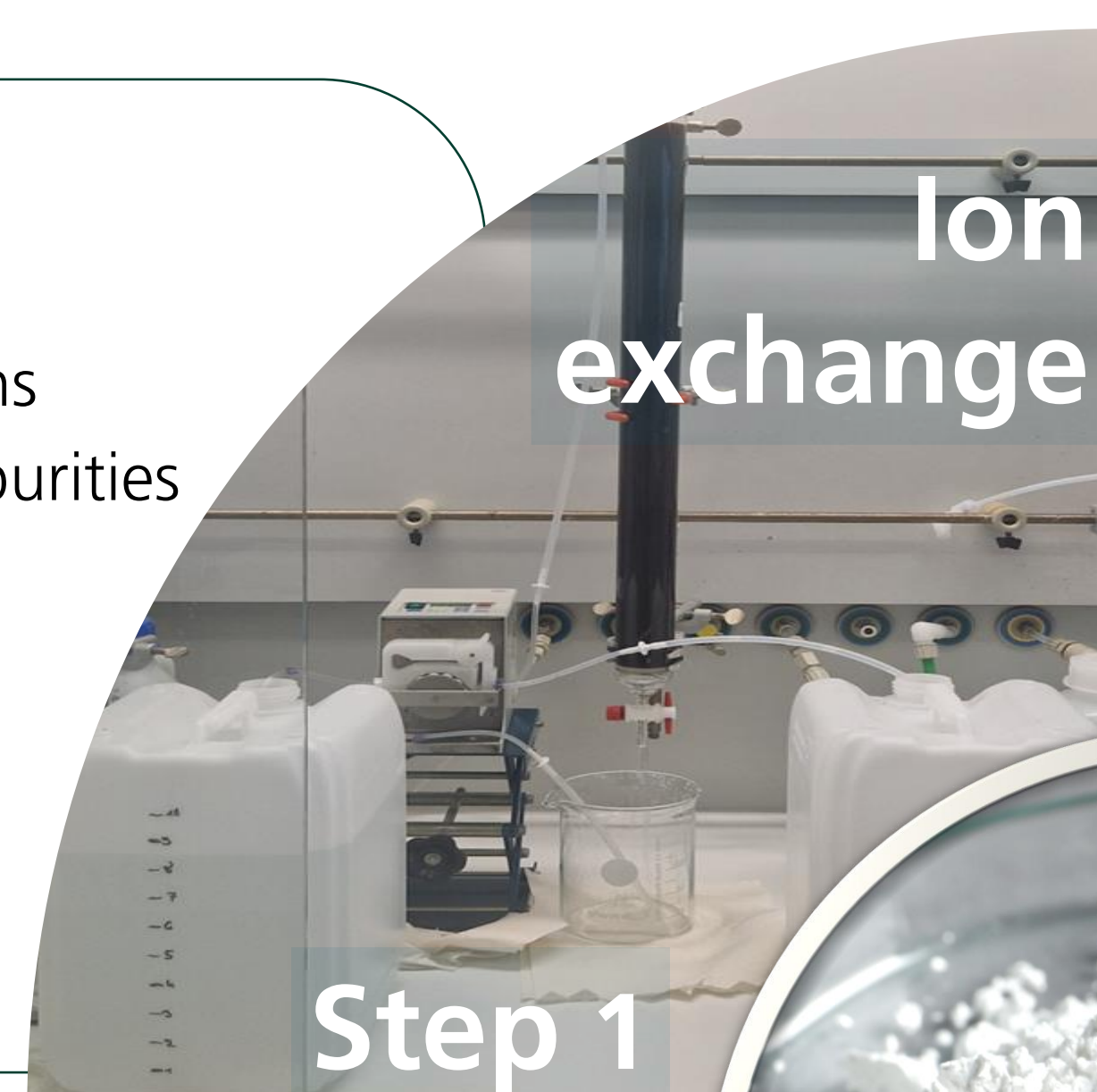
1. Additional purification

Advantages:

- High selectivity for targeted cations
- Effective reduction of divalent impurities

Key metrics:

- Flow rate: 1 L / h
- Column length: 0.5 m
- Impurity reduction: 60-90 %
- Divalent ions: 95 %



2. Concentration

Advantages:

- Efficient and fast separation
- Simple application
- No dangerous waste

Key metrics:

- Flow rate 0.5-2 L / min
- Concentration factor: 5-24
- Lithium recovery ≥ 99 %

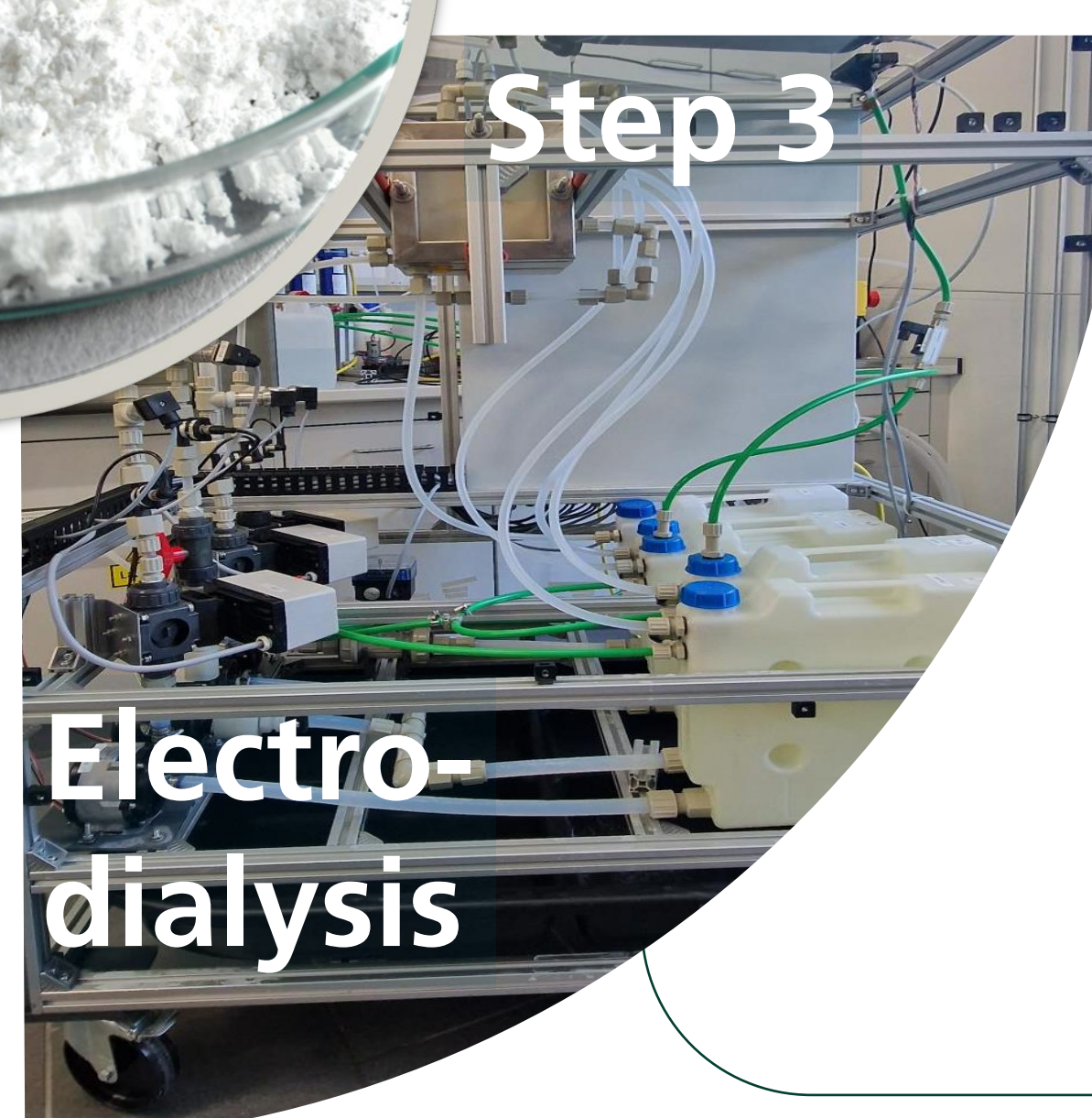
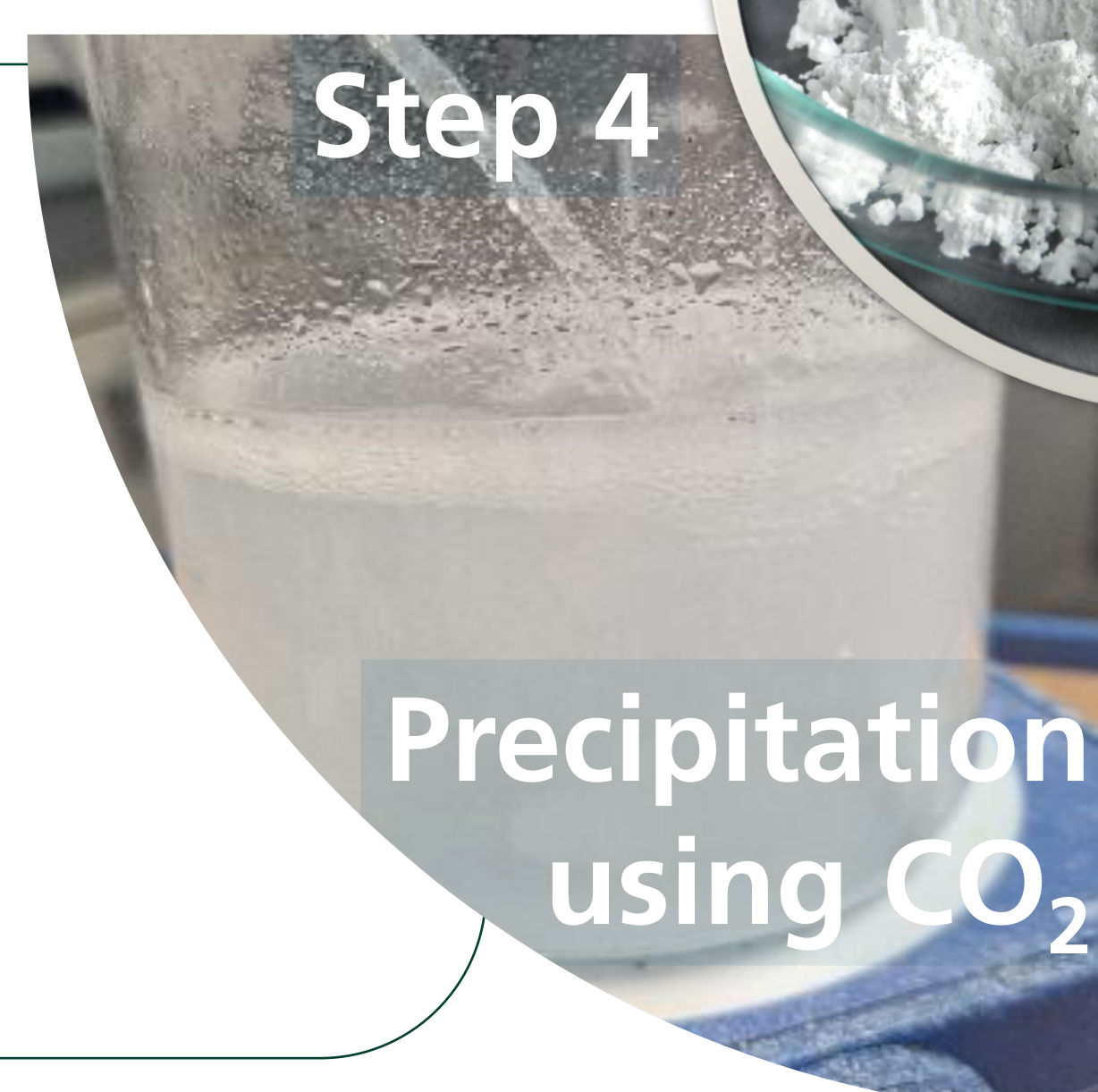
4. Li_2CO_3 recovery

Advantages:

- No further additives needed for pH control
- Product precipitates as white powder, low impurities

Key metrics:

- Still under optimization
- Battery grade purity ≥ 99 %**



3. Lithium transfer

Advantages:

- Efficient separation and recovery
- No additives needed (pH, corrosion)
- LiOH as resulting solution facilitate the Li_2CO_3 production

Key metrics:

- Flow rates: 2-3 L / min
- Max. LiOH concentration: 72.1 g/L
- Current densities : 5-70 A/m²

Methodology

Synthetic desorption solutions (50 L) produced by KIT and EnBW^[2] were used as feed. Each process step was performed batchwise:

- 1. Ion Exchange** – cation exchange resin, loaded with LiOH, regenerated with HCl.
- 2. Reverse Osmosis** – spiral-wound thin-film composite membrane (2.8 m² surface).
- 3. Electrodialysis (Bipolar Membranes)** – three-chamber setup, with LiOH as product and HCl as side-product.
- 4. CO_2 Precipitation** – Conversion to Li_2CO_3 via CO_2 sparging, followed by filtration, washing, and drying to battery-grade purity ($> 99\%$).

LiCORNE

The EU project LiCORNE is part of the Horizon 2020 cluster and consists of 16 partners from research institutions and industry across Europe and beyond. The project aims to extract battery-grade lithium chemicals from three European sources: mineral deposits (pegmatite), geothermal energy water from the Rhine Graben, and aged cathode material from batteries. Various environmentally friendly and sustainable processes for lithium extraction will also be tested. The various extraction methods, from mining to the finished product, will be evaluated in parallel through LCA and LCC studies.

Further Competences in Lithium Processing

In addition to the presented process chain, ICT provides further methods that could be applied for lithium recovery:

- Supercritical CO_2 precipitation – selective carbonate formation
- Advanced membrane techniques – e.g. nanofiltration for divalent ion separation
- Free-Flow Electrophoresis (FFE) – innovative approach to separate lithium from sodium

Outlook

The next steps could be as follows:

- Testing of real desorption solutions
- Increase in turnover, Up-scaling
- Further cost reduction

We would like to thank our partners:

- Energie Baden-Württemberg AG ENBW
Laura Herrmann, Joscha Fürniß
- Karlsruher Institut für Technologie KIT
Martina Gamba, Fabian Jeschull
- LiCORNE-Consortium



[1] New EU regulatory framework for batteries Setting sustainability requirements, EPRS | European Parliamentary Research Service, [https://www.europarl.europa.eu/RegData/etudes/BRIE/2021/689337/EPRS_BRI\(2021\)689337_EN.pdf](https://www.europarl.europa.eu/RegData/etudes/BRIE/2021/689337/EPRS_BRI(2021)689337_EN.pdf)

[2] L. Herrmann, H. Ehrenberg, M. Graczyk-Zajac, E. Kaymakci, T. Kölb, L. Kölb, J. Tübke, Lithium recovery from geothermal brine – an investigation into the desorption of lithium ions using manganese oxide adsorbents, Energy Adv. 2022, 1, 877, DOI: 10.1039/D2YA00099G.



Funded by the European Union under Grant Agreement No 101069644. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.