Development and Optimisation of Extraction Technologies for CRM from Geothermal Brines

The CRM-geothermal project aims to develop effective, economically feasible and scalable technologies for the extraction of critical raw materials (CRMs) from geothermal brines without interfering with the heat extraction process. The work covers a range of complementary approaches, including adsorptive extraction using ion sieves, selective ion-exchange membranes, reversible adsorption using modified (bio-)polymers, bioextraction, helium extraction and gas diffusion electrocrystallisation (GDEx). These technologies, which are presented in further detail here below, provide the technological basis for combined CRM extraction by current geothermal operators and interested SMEs, supporting the development of new business models and enabling the valorisation of geothermal resources beyond heat production.

1. Adsorptive Extraction by Ion Sieves

In this task, the GFZ Helmholtz Centre for Geosciences (GFZ) and the Izmir Institute of Technology investigated the adsorptive extraction of lithium and strontium from geothermal fluids. For lithium ions, highly selective adsorption materials based on spinel manganese dioxide (λ-MnO_2) were applied, both with and without chitosan as a binder, as well as the less expensive γ-MnO_2. The adsorption performance of the materials was determined by recording adsorption isotherms, which were evaluated according to the Langmuir monolayer adsorption theory. Maximum adsorption capacities between 19 and 52 mg/g were achieved, in accordance with values reported in several studies in the literature. The adsorption capacity of γ-MnO_2 was considerably lower than that of λ-MnO_2, but its market price, depending on the quantity purchased, was also considerably lower. Alternatively, a hydrothermal synthesis procedure was developed to obtain spinel-type λ-MnO_2 from γ-MnO_2, resulting in a lithium uptake capacity of 23.1 mg/g, compared with 6.4 mg/g for γ-MnO_2. When λ-MnO_2 was bound to chitosan as a binder and granulated, the particle size increased from less than 1 µm to more than 1 mm, enabling flow-through processes.

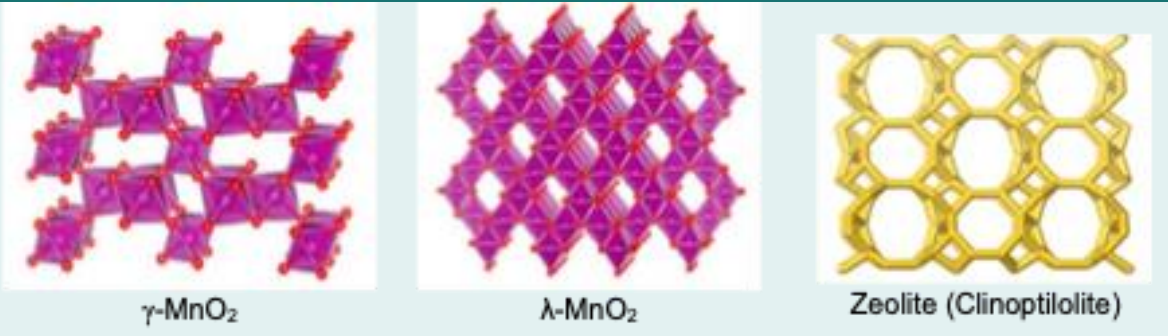

Figure 1. Crystal structures of two manganese dioxide morphologies and of clinoptilolite. (Mn: magenta and O: red).[1,2]

1. Pérez-Botella, E., Valencia, S., Rey, F., 2022. Zeolites in Adsorption Processes: State of the Art and Future Prospects. *Chem. Rev.* 122, 17647–17695. https://doi.org/10.1021/acs.chemrev.2c00140
2. Shin, J., Seo, J.K., Yaylian, R., Huang, A., Meng, Y.S., 2020. A review on mechanistic understanding of MnO_2 in aqueous electrolyte for electrical energy storage systems. *Int. Mater. Rev.* 65, 356–387. https://doi.org/10.1080/09506608.2019.1653520

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Dynamic flow-through adsorption experiments were carried out, providing a proof of concept for lithium adsorption using the spinel MnO_2-based materials in a flow-through process. The adsorption materials showed very high selectivity. An adsorption column with a filling volume between 100 and 400 mL was manufactured. The column was designed to withstand high temperatures and pressures and was corrosion-resistant, enabling flow-through experiments at elevated temperatures in a fixed-bed column setup.

Field tests at geothermal sites in Turkey were performed and evaluated. In field sorption tests conducted at the Tuzla Geothermal Power Plant, both γ-MnO_2 and commercial λ-MnO_2 were applied, and their applicability under actual geothermal brine conditions was confirmed. Cumulative desorption experiments showed that λ-MnO_2 gradually increased the lithium concentration, reaching ~1700 mg/L after eight cycles. A lithium-rich solid was precipitated from the enriched eluate, and XRD confirmed the presence of Li_2O_2; lithium accounted for approximately 75% of the total cationic content. Clinoptilolite zeolite was applied for strontium recovery; the ammonium acetate process enhanced performance, and successful strontium enrichment (~450 ppm) and precipitation of $SrSO_4$ were studied under field conditions.

2. Selective Ion-Exchange Membranes

In Deliverable D3.2, the University of Padua reports the development of an integrated, multi-step process for the selective extraction and purification of lithium (Li) and strontium (Sr) from geothermal brines, based on tailored ion-exchange materials and low-impact separation strategies.

The core of the approach is the use of sulfonated polyether ether ketone (SPEEK), an inexpensive and chemically robust polymer that can be engineered either as porous ion-exchange beads or as a water-soluble polymer. The porous ion-exchange SPEEK beads are used to selectively bind divalent cations (e.g. Ca^{2+}, Mg^{2+}, Sr^{2+}). Afterwards, soluble SPEEK efficiently captures monovalent species, including Li^+. This dual functionality enables a sequential and highly selective separation pathway.

The proposed extraction process begins with the selective removal of divalent cations from the raw brine using SPEEK-based beads. This step exploits the stronger binding affinity of divalent cations and is optimised through a cascade of short contact stages, maximising divalent ion uptake while minimising lithium losses. The beads are subsequently regenerated using concentrated HCl, yielding a concentrated chloride mixture from which Sr can be recovered. Strontium is selectively precipitated as $SrSO_4$ via a solvent-assisted route, achieving a purity of approximately 80%.

Following divalent ion removal, the Li-enriched brine is treated with water-soluble SPEEK to concentrate monovalent cations without relying on energy-intensive evaporation. Regeneration of the water-soluble SPEEK produces a concentrated solution of monovalent chloride species, which is then dried. Lithium is subsequently selectively extracted using a minimal amount of anhydrous ethanol, which preferentially dissolves LiCl over NaCl and KCl. After solvent removal, Li is obtained as LiCl with a purity of about 96%.

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The overall process is designed according to green chemistry principles: it employs low-cost and widely available chemicals (e.g. HCl, NaOH, ethanol), minimises water and solvent consumption, and avoids the formation of harmful by-products. Importantly, most process streams, including ion-exchange materials and solvents, can be recycled, while residual brines and salts can be safely re-injected into the aquifer.

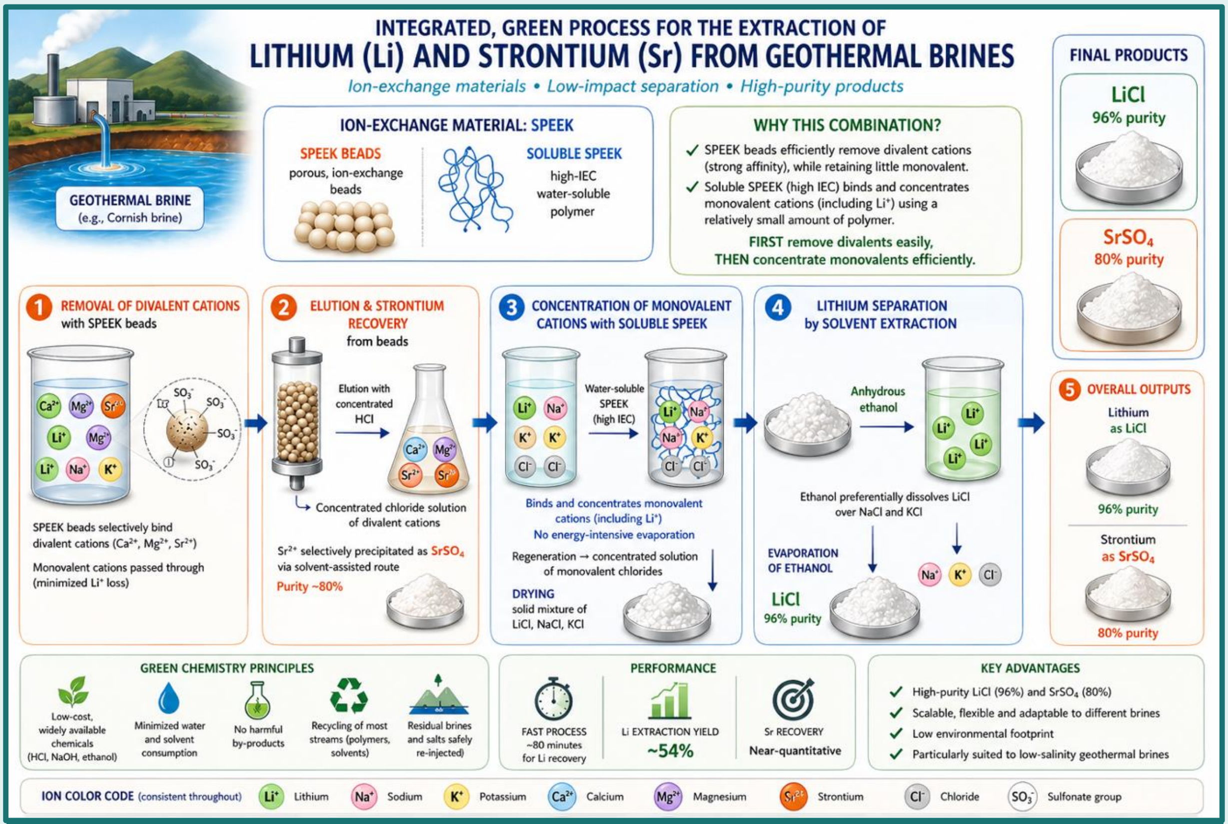

Figure 2: Integrated green process for the extraction of lithium and strontium from geothermal brines.

From a performance standpoint, the process is fast (approximately 80 minutes for Li recovery), exhibits moderate lithium extraction yields (~54%), and achieves near-quantitative recovery of strontium. Although additional steps for Sr recovery increase complexity and energy demand, the overall methodology provides a scalable, flexible and environmentally sustainable framework for lithium extraction from geothermal resources, particularly suited to low-salinity brines.

3. Selective Reversible Adsorption Using Modified (Bio-)Polymers

In this task, the GFZ Helmholtz Centre for Geosciences (GFZ) investigated the selective adsorption of critical raw materials (Mg^{2+}, Rb^{+}, Sr^{2+}, Ga^{3+}, Ge^{4+}) from geothermal brines using modified polymers as adsorbents under realistic geothermal conditions.

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First, biopolymers (chitosan, starch and cyclodextrins) were modified with crown ethers (CR) using microwave-initiated graft polymerisation. Thirty different compounds were successfully produced (≤ 84%). Adsorption tests at salinities of up to 2 M NaCl showed capacities of 25–30% for Mg^{2+}, Rb^{+} and Sr^{2+} at an initial CRM concentration of 1 mM.

The second approach investigated the impregnation of polystyrene resins with CR. Cation-exchange resins (such as Dowex® 50 WX) were used for this purpose. The impregnated resins showed higher adsorption, with up to 90% for Sr^{2+} and Mg^{2+} in a NaCl matrix > 1 M.

The highest Sr adsorption in 1 M NaCl (25%) was achieved using the 50WX8 resin with a mesh size of 50–100. Rubidium was preferentially adsorbed by 50WX2 resins modified with DC18C6, reaching 11%. In a 0.1 M NaCl matrix, Ge^{4+} was only minimally and non-selectively adsorbed, regardless of the resin modification. The highest Ga adsorption in 1 M NaCl (75%) was achieved with the 50WX8 resin (mesh size 50–100) modified with 18C4N2.

The regeneration of the adsorbents was tested through desorption experiments in various acids. The best results were obtained using 3% HNO_3. After six hours of stirring at room temperature, the metals were almost completely recovered into the liquid phase.

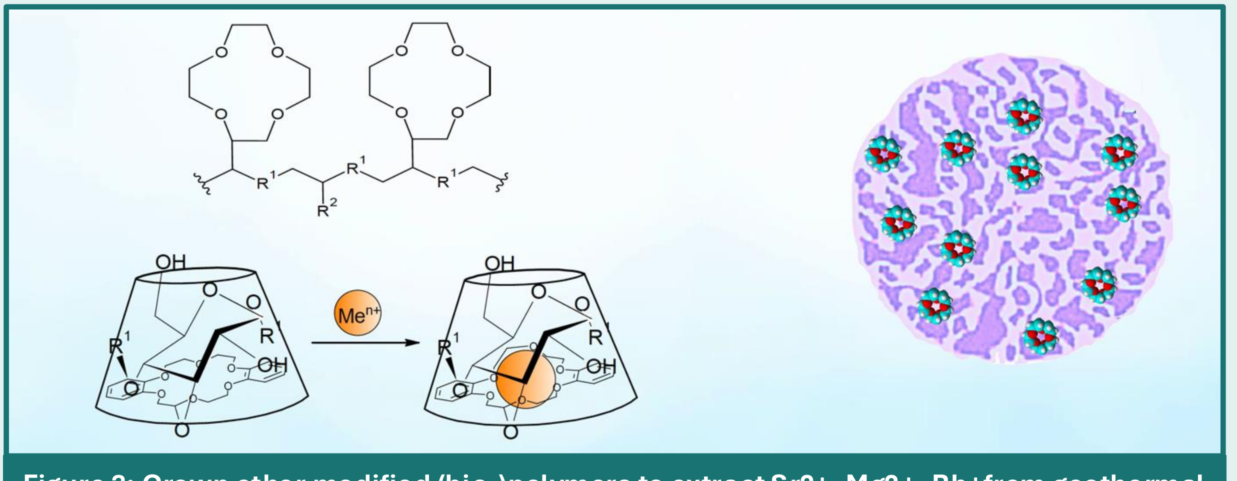

Figure 3: Crown ether modified (bio-)polymers to extract Sr2+, Mg2+, Rb+from geothermal brine. Left: Graftingon Biopolymers (Chitosan, starchand cyclodextrin). Right: Impregnation of Amberlite resin.

4. Bioextraction: Proof-of-Concept Oxalogenesis–Oxalotrophy Pathway for Biorecovery of Li and Sr

Oxalogenesis and oxalotrophy are both processes performed by microbes. Oxalogenesis consists of the production of oxalic acid (OA), a low-molecular-weight organic acid (LMWOA), by fungi and plants. Oxalotrophy consists of the use of OA by bacteria as both carbon and energy sources, leading to the conversion of OA into CO_2. Both processes are naturally combined into a pathway called the oxalate-carbonate pathway (OCP), which has been described in soils where it has a profound effect on pH and the solubility of selected metals.

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OA is a strong LMWOA (pKa1: 1.25; pKa2: 4.2), and its conjugate base, oxalate, is known as an effective chelator of cations, forming insoluble complexes with elements such as Ca^{2+} or Mg^{2+}. Notably, oxalate does not form such complexes with Li, allowing it to remain in solution in its presence. On the other hand, the conversion of OA to CO_2 during oxalotrophy leads to a local increase in pH, which can result in carbonate precipitation if the pH increases above 8. In soils with high Ca^{2+} contents, this may lead to the conversion of atmospheric CO_2 into $CaCO_3$.

In this deliverable, the University of Neuchâtel explored whether an industrial OCP could be engineered by replacing Ca^{2+} with Li^+ (or Sr^{2+}). In other words, the researchers tested how oxalogenesis and oxalotrophy affected the solubility of Li and Sr contained in geothermal brines, in order to transfer them from a mixed and solubilised form within the brine to a pure and precipitated form for their recovery.

The overall biorecovery approach was tested on Li^+ and consisted of the following steps: 1) OA production by a fungal strain, 2) fluid filtration with oxalic acid in order to remove impurities such as Ca, and 3) Li immobilisation as Li-carbonates via fluid alkalinisation by bacterial oxalotrophy. The data obtained demonstrated the feasibility of this pathway.

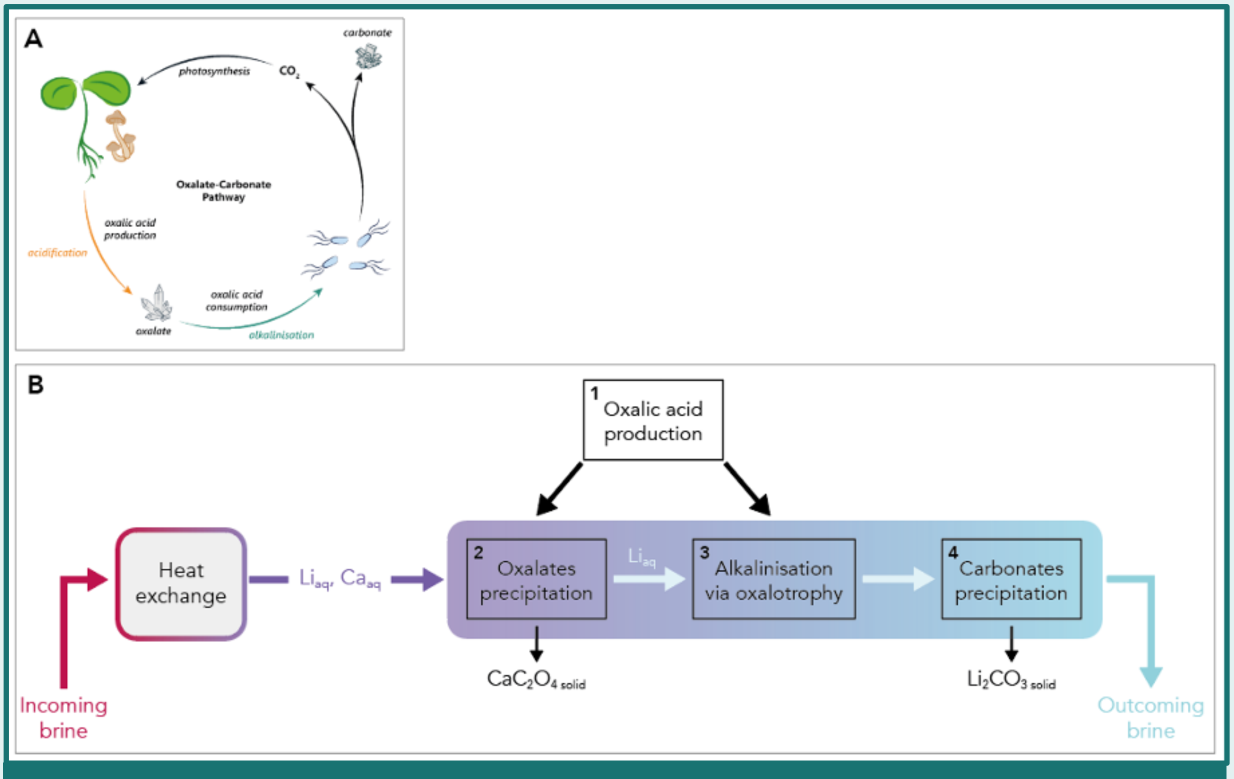

Figure 4: Oxalogenesis–Oxalotrophy Pathway for Biorecovery of Li and Sr.

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A strain of the fungus *A. niger* was able to produce OA, using saccharose as a carbon source, at concentrations compatible with the next step in the pathway, i.e. at least 10 g/L. Fluid cleaning with OA in order to remove Ca (and other elements) via oxalate precipitation was possible for brines containing up to 54 g Ca/L, which corresponds to the high-salinity synthetic brine that the project partners agreed upon as the experimental test solution. Li precipitation as a result of oxalotrophy, using a strain of the bacterium *Pandoraea* sp., proved to be a critical step, since both experimental and geochemical models showed a favoured formation of Li-phosphate over Li-carbonates. Finally, the application of this biorecovery approach to Sr was inferred based on Sr-oxalate and Sr-carbonate solubility indices. It showed its feasibility, but this remains to be tested in the laboratory.

5. Effectiveness of Microbial Biorecovery of Metals from Geothermal Brines

This section presents experimental evidence, investigated by the University of Neuchâtel, challenging the technical feasibility and effectiveness of microbial biosorption of metals from geothermal brines, using both lithium (Li^{2+}) and lead (Pb^{2+}) as proof-of-concept examples. It also highlights the challenges associated with turning effective biosorption into an actual biorecovery approach in the specific context of geothermal operations.

Biosorption consists of the reversible immobilisation of a compound (for instance, a metal in solution) by binding to the external surfaces of microbial biomass. This can result from chemical adsorption to cell wall compounds or to extracellular polymeric substances (EPS) secreted by microbes during biofilm growth.

Lithium biosorption was first assessed using Gram-positive bacteria (*Bacillus subtilis*, *Glutamicibacter mysorens*, and *Priestia megaterium*) and simple Li^{2+} solutions at 3 ppm. Here, Li^{2+} was immobilised via complexation on cell wall teichoic acids.

Batch experiments showed effective transfer of Li^{2+} from solution to biomass, with performance dependent on both bacterial strain and biomass-to-fluid ratio. *Bacillus subtilis* demonstrated consistently high Li^{2+} uptake, while *P. megaterium* exhibited particularly high Li^{2+} binding per cell in some tests.

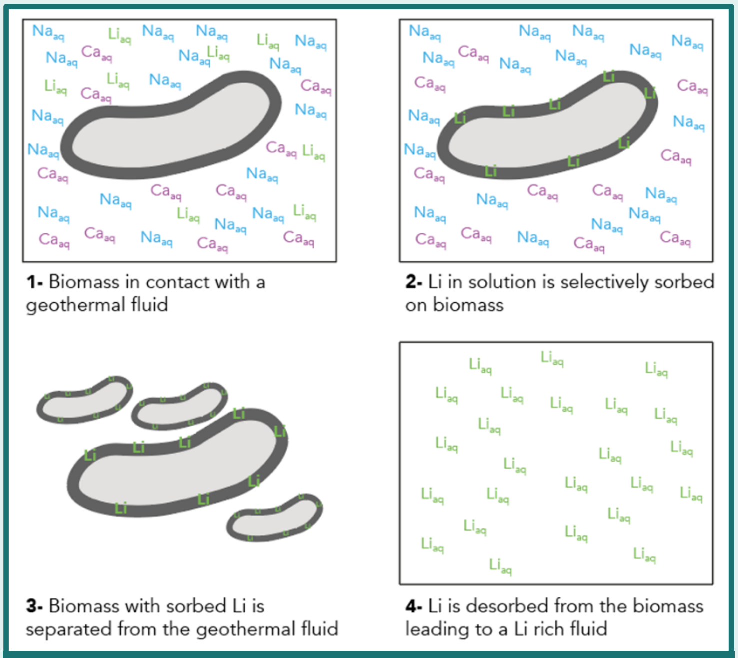

Figure 5: Microbial biorecovery of lithium from geothermal fluids.

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Lithium bound to the biomass was successfully recovered using filtration followed by *aqua regia* digestion, confirming that biosorption is reversible and that Li^{2+} can be recovered in solution using standard analytical and metallurgical methods.

The approach was extended to Gram-negative, chemolithoautotrophic bacteria (*Thiobacillus* spp.), which bind metals via EPS in biofilms. Preliminary bioreactor tests using a natural geothermal fluid from Cornwall (Li ≈ 40 mg/L, total salinity ≈ 6 g/L, pH 7) showed that approximately 6 µg Li^{2+} could be captured per 10^{10} cells without nutrient addition. Lithium recovery from the biomass was not assessed yet. While Li^{2+} uptake per cell was lower than for some Gram-positive strains, the robustness and industrial relevance of *thiobacilli* make them promising candidates. In addition, the use of continuous-flow systems optimised for low-salinity geothermal fluids demonstrated scalable potential. Based on laboratory data with B. subtilis, a maximum theoretical Li^{2+} immobilisation of approximately 1 kg per year could be reached from a continuously operated 100-L reactor with a low-salinity geothermal fluid.

In addition to Li^{2+}, the researchers also evaluated Pb^{2+} biosorption under relevant geothermal conditions, i.e. at high pressure and temperature. We used biomass of *Penicillium citrinum*, a fungal strain isolated from a geothermal brine sample. While pressure and temperature did not inhibit biosorption, high NaCl concentrations were identified as the primary limiting factor, since most biosorption sites were primarily occupied by elements at the highest concentration. However, without any NaCl, Pb^{2+} was effectively sorbed. This finding is critical, as it highlights salinity as a key constraint for in situ biosorption strategies.

Overall, these experiments showed that microbial biosorption of CRM from geothermal brines is technically feasible, compatible with continuous operation and potentially scalable. However, further optimisation of biosorption for the biorecovery of CRM is required. First, the influence of salinity and pH on biosorption efficiency and the selectivity of target CRM over other less interesting elements shall be assessed. Second, once biosorption has been optimised, different recovery schemes for the transfer of the sorbed CRM of interest shall be assessed. As a result, future work will focus on process optimisation, potentially with extremophilic microorganisms, and pilot-scale upscaling in collaboration with industrial partners.

6. Helium Production from Geothermal Fluids

Helium is considered a critical raw material and is regarded as an indispensable gas for various industries, e.g. in the medical sector, aircraft construction, electronics and fibre-optics fabrication. Currently, natural gas deposits are the only relevant resource for this rare element, and cryogenic distillation is a common technology for helium extraction and enrichment. An alternative source of helium could be the gas phase extracted from geothermal production fluids. In the framework of the EU-funded project “CRM-geothermal”, the potential of this alternative helium production was evaluated by the GFZ Helmholtz Centre for Geosciences (GFZ).

The work included the sampling and analysis of gases from various geothermal sources in Europe and East Africa to investigate the helium content of these sources. Based on these results, a gas extraction unit was tested to efficiently separate gases from geothermal brines without interrupting the production process.

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Polymer membranes in a closed system were used for this purpose. For further helium enrichment, activated molecular sieves were successfully tested. The laboratory studies were supplemented by field tests conducted during production tests at a drill site in Cornwall (UK).

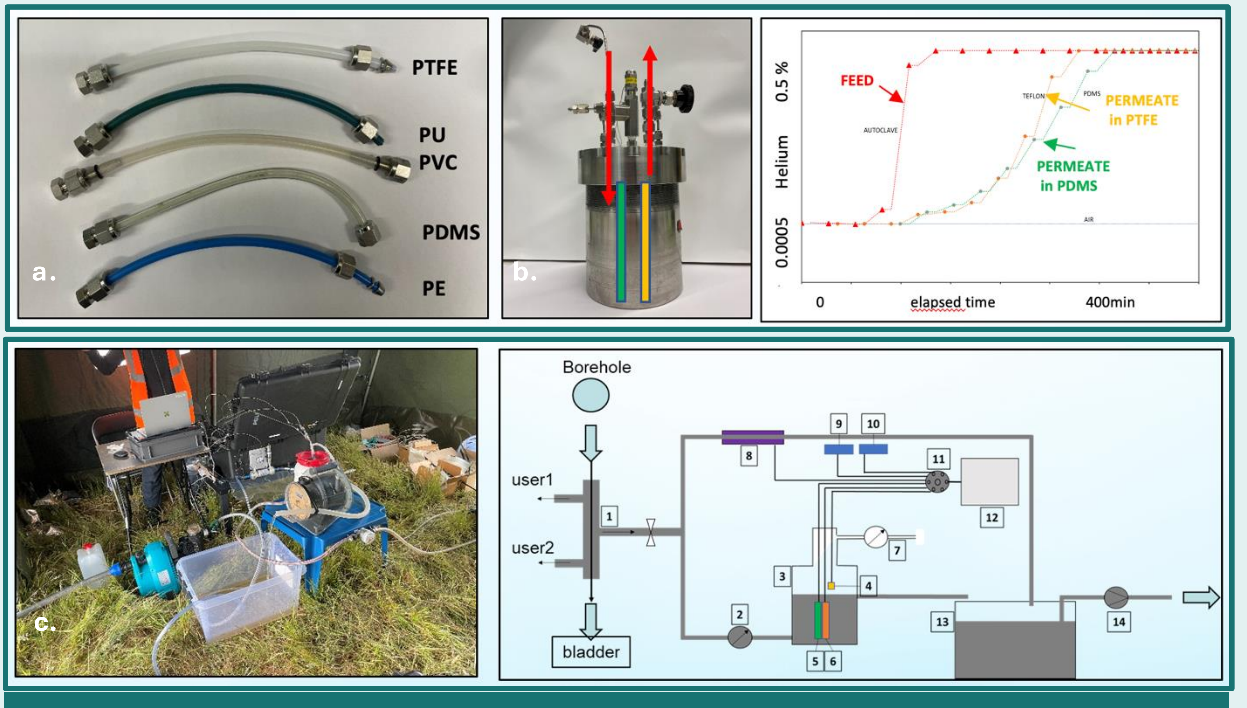

Figure 6: The potential of membrane technology to separate gas from geothermal fluids during plant operation was validated in lab and field experiments.
a. Lab tests of various polymeric membranes in autoclave experiments. b. Helium supplied (FEED) -> fast permeation for all polymers -> Helium in PERMEATE within hours in equlibrium with FEED. c. Field test at Cornish Lithium production well. Successful separation of whole gas phase from geothermal water.

7. Gas Diffusion Electro-Crystallisation (GDEx)

The Flemish Institute of Technological Research (VITO), Belgium, has implemented Gas Diffusion Electrocrystallisation (GDEx) technology for the selective extraction of lithium from geothermal brines. It is an innovative electrochemical process for the reactive precipitation of metals in solution using oxidising or reducing agents produced in situ by the electrochemical reduction of a gas in a gas-diffusion electrode (GDE).

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The localised electrochemical reactions are carefully controlled by a unique GDE, and atmospheric air is used as the main chemical reactant for the controlled precipitation of lithium-containing compounds from geothermal brines. Compared with conventional metal extraction methods, GDEx offers several key advantages. Through careful regulation of process parameters such as pH, ionic strength, gas composition and applied potential, the technology enables the targeted formation of CRM-based compounds with minimal reliance on external chemical reagents. This significantly reduces the environmental footprint typically associated with CRM extraction, which often involves intensive chemical treatments and the use of toxic additives.

The initial experiments were performed on synthetic solutions to optimise the parameters. Subsequently, geothermal brines and leachate solutions were treated using the optimised experimental parameters. Experiments on different brine sources showed impressive results, removing over 95% of the lithium. A downstream synthesis process was successfully implemented on the recovered lithium to convert it into lithium carbonate.

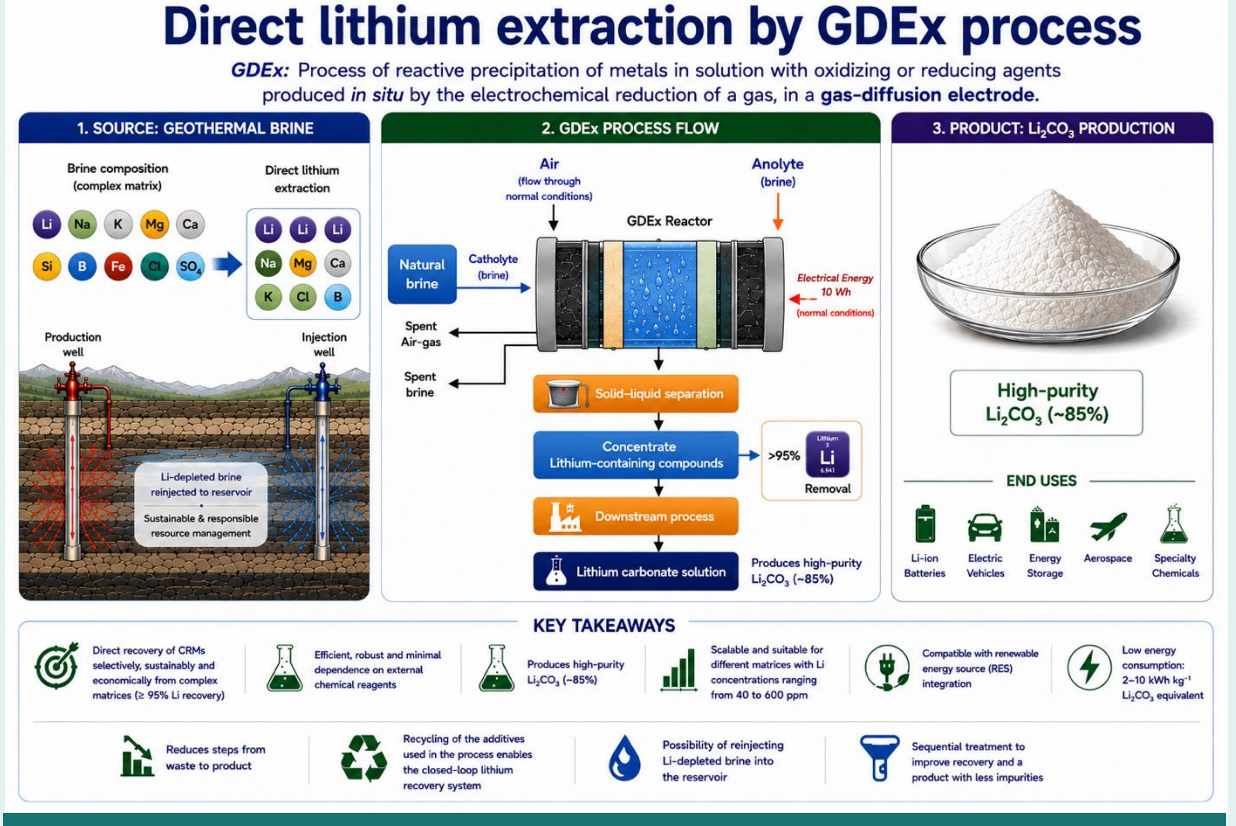

Figure 7: Direct lithium extraction by GDEx process.

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More information:

Deliverable 3.4: Report on proof-of-concept oxalogenesis-oxalotrophy pathway for biorecovery of Li and Sr

Deliverable 3.6: Report on membrane-based gas extraction from brine

Other deliverables will be made available in due time at:
https://crm-geothermal.eu/deliverables/

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