Oilfield produced water as an alternative source of selected chemical elements

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Geothermal Lithium Networking Event
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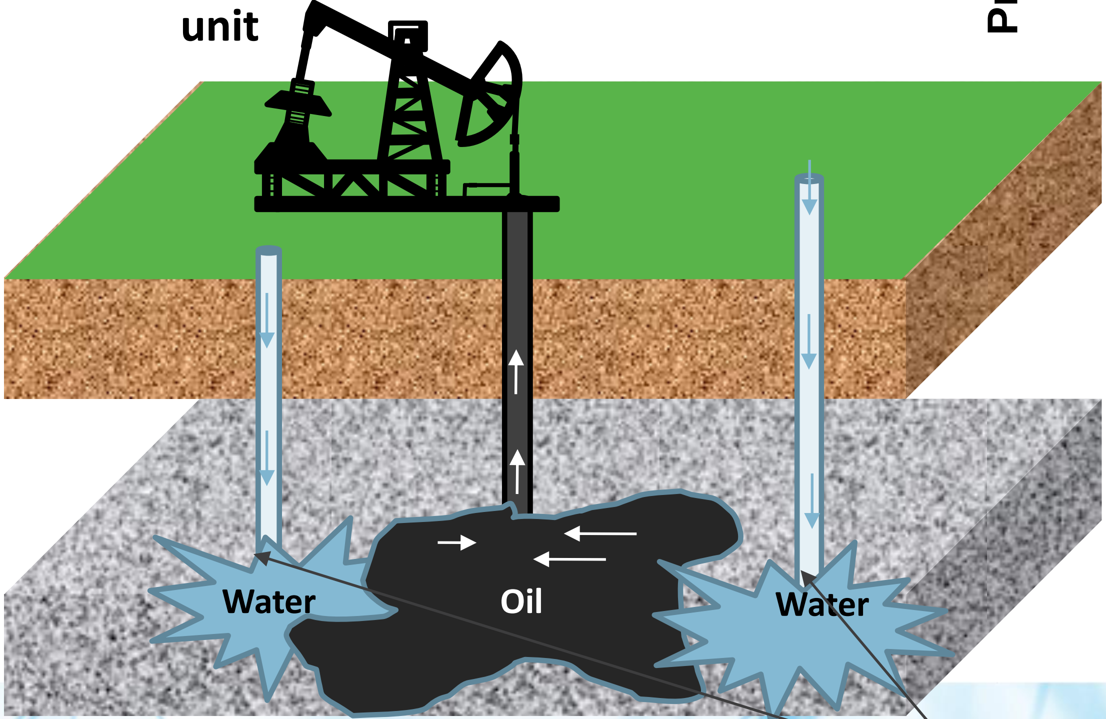
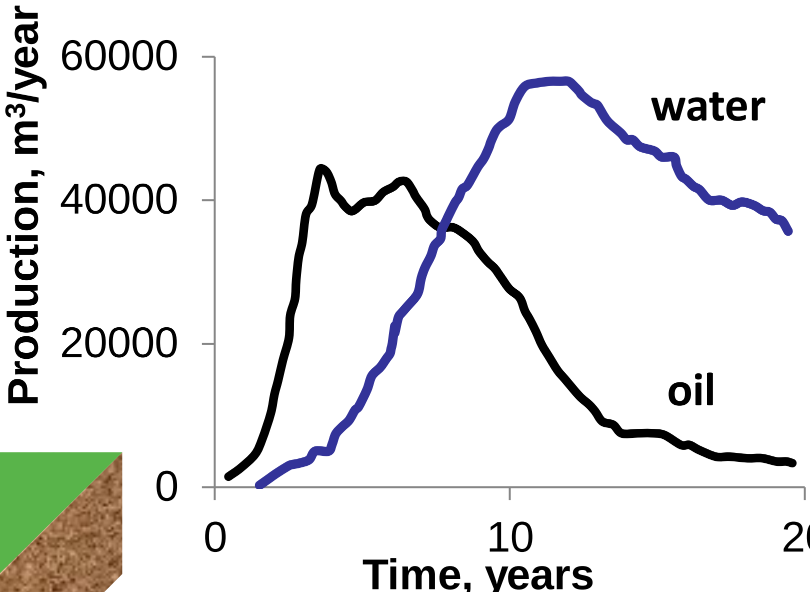
Rzeczpospolita Polska
Narodowe Centrum Badań i Rozwoju

The crucial importance of water handling in oilfield operations

Forecasted production of the reservoir brine in 2022: 80 million m^3 of brine daily



Fluid recovery profile from a selected oil well



(source: doi.org/10.1093/ijlct/cts049)

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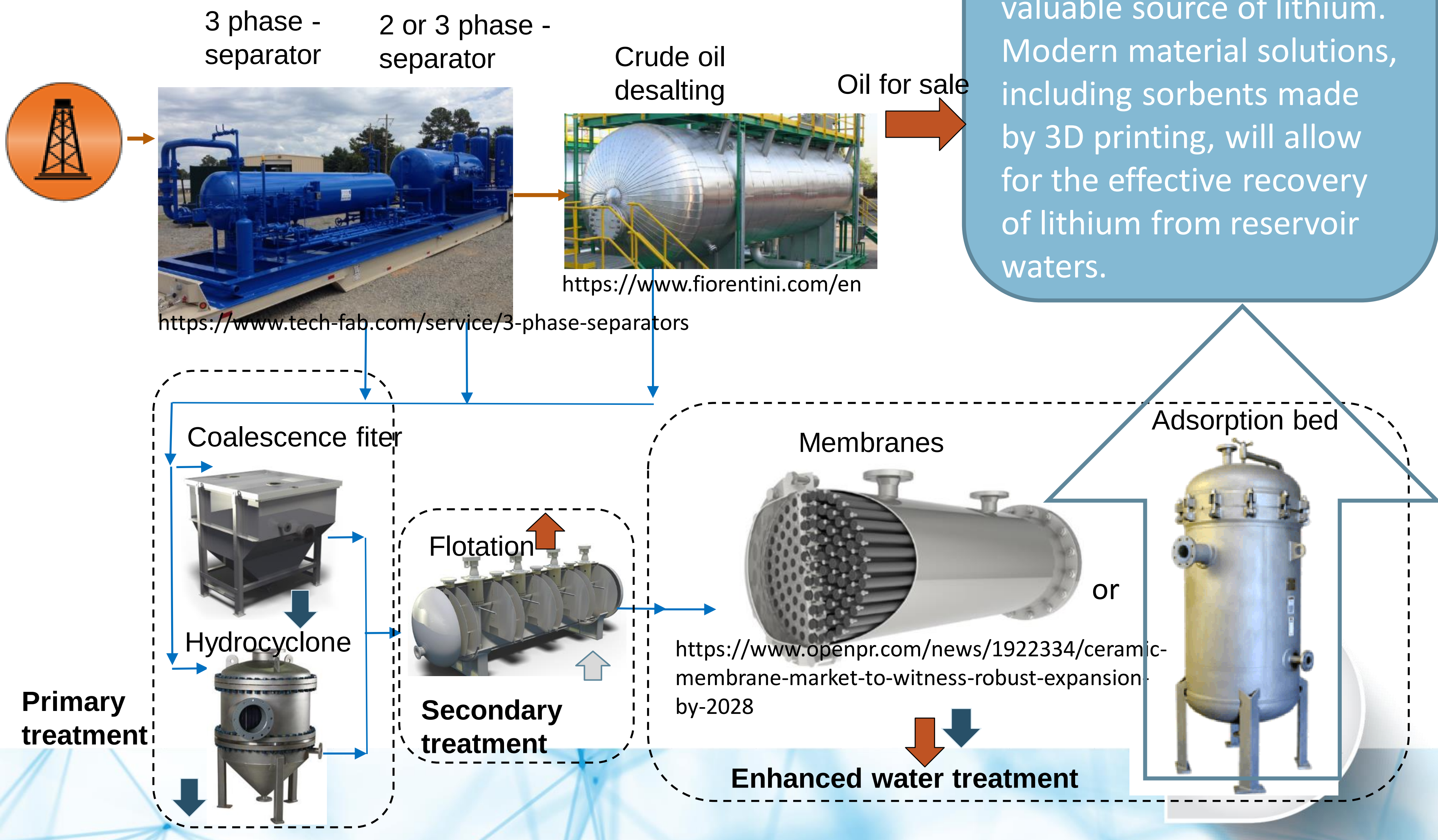
Typical water treatment scheme

Reservoir brines, produced along with crude oil and natural gas, can be a valuable source of lithium. Modern material solutions, including sorbents made by 3D printing, will allow for the effective recovery of lithium from reservoir waters.



The aim of the Complithium project

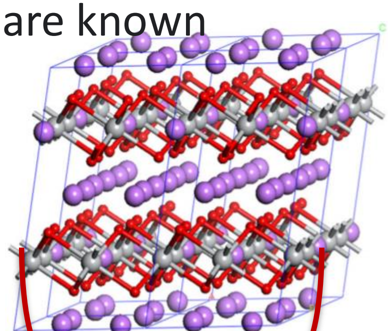
The aim of the project is to develop a technology for the recovery of lithium and potable water from waste reservoir brines based on combined sorption-membrane techniques. The proposed solution is a process innovation on a national and global scale. The elements of the novelty are:

- high-porosity sorbents made with the 3D printing technique for lithium recovery with improved selectivity and sorption capacity;
- nanofiltration membranes modified with crown ethers for the simultaneous production of desalinated water and sorption of residual lithium from brines.

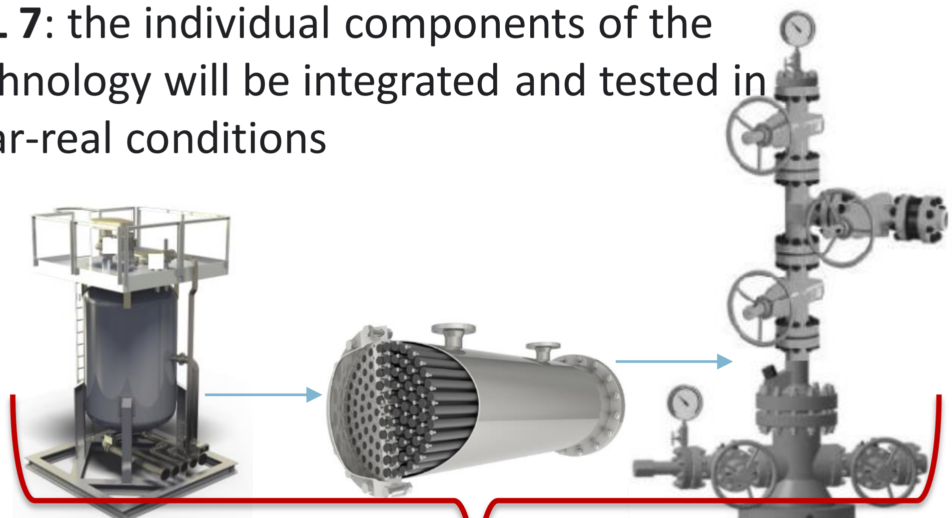
Technological readiness level

before starting the project implementation: **TRL 2**: the basic principles of operation of individual system components and process limitations are known

at the end of the project implementation: **TRL 7**: the individual components of the technology will be integrated and tested in near-real conditions

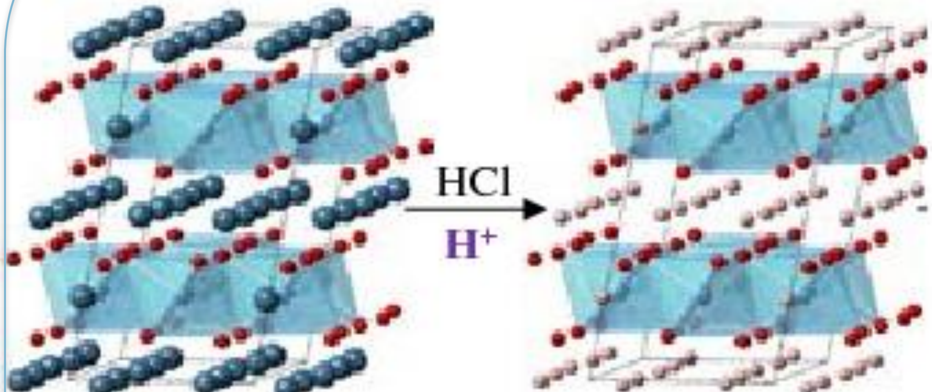


(source: DOI: 10.1007/s11581-015-1393-3)

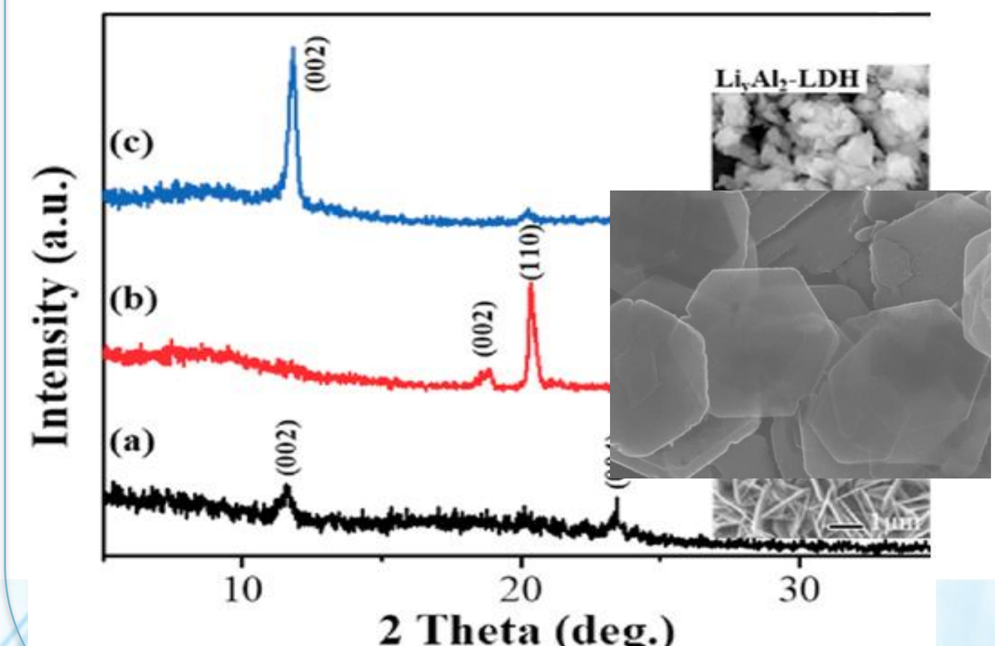


Lithium-selective sorbents - Al, Mn and Ti oxides and hydroxides

Layered H_2TiO_3 i $Li_x{}^{*}Al_2(OH)_6Cl_x$



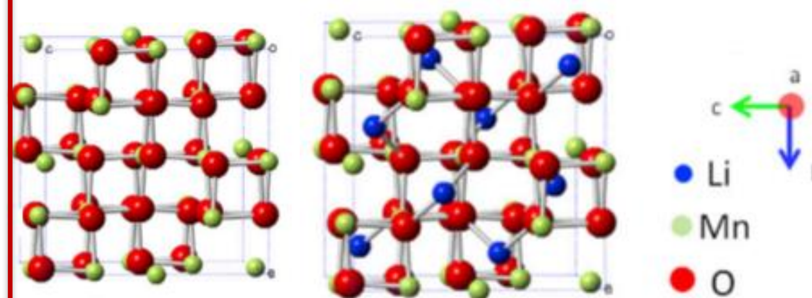
(source: doi:10.1039/c4dt00467a)

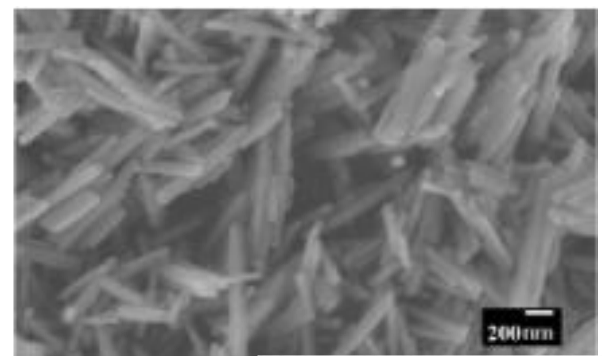


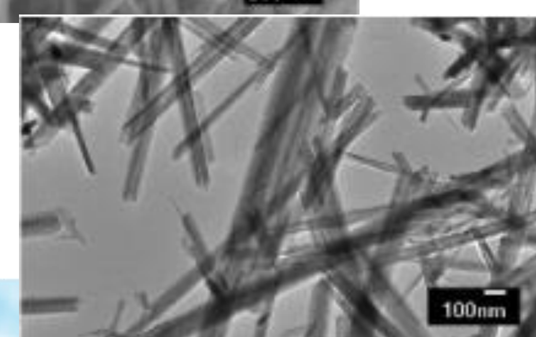
(source: doi.org/10.1016/j.solidstatesciences.2020.106488

MnO_2 nanotubes

Lithium sorption → Li





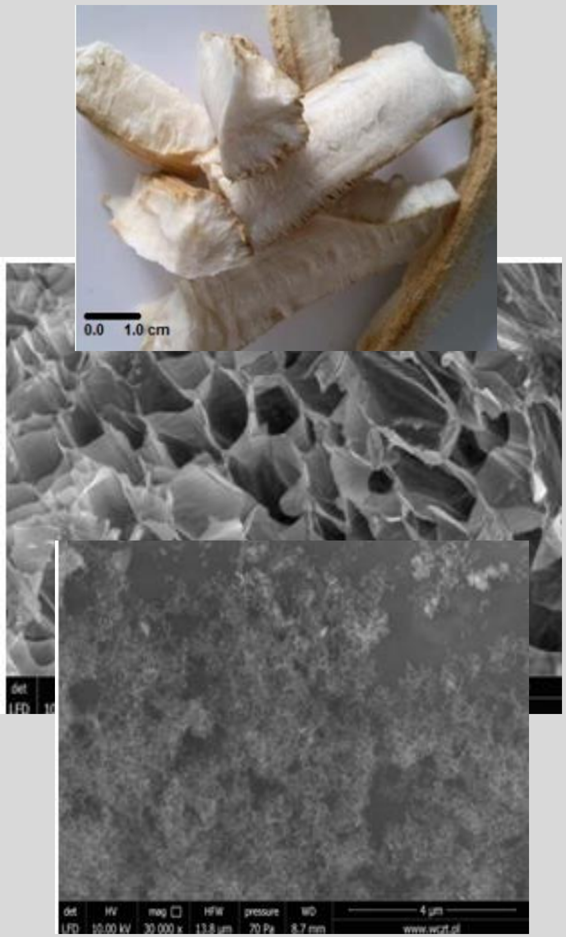


(source: doi.org/10.1016/j.isci.2020.101768)

Commercial sorbents manufactured by 3D printing

Operational problem: how to apply light and dusty powders on an industrial scale?

Inspiration: spongy sunflower pith modified with nanoparticles

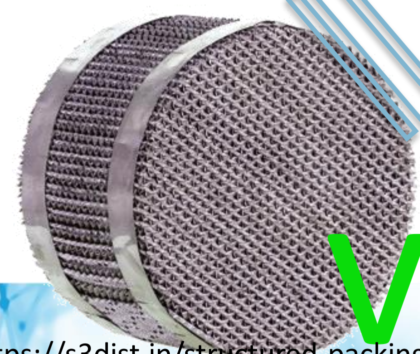


Solving the operational problem

Typical extrusions/pellets

X

Structured packing



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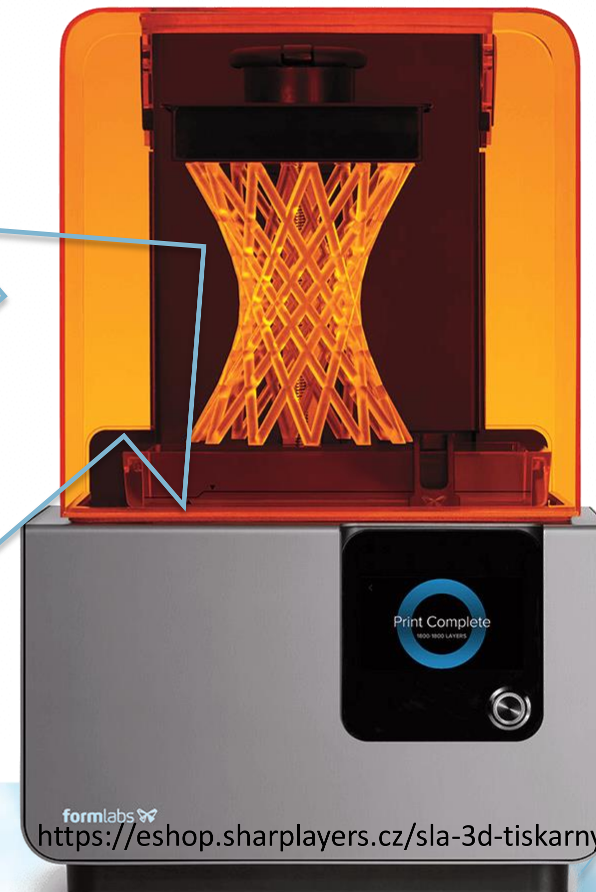
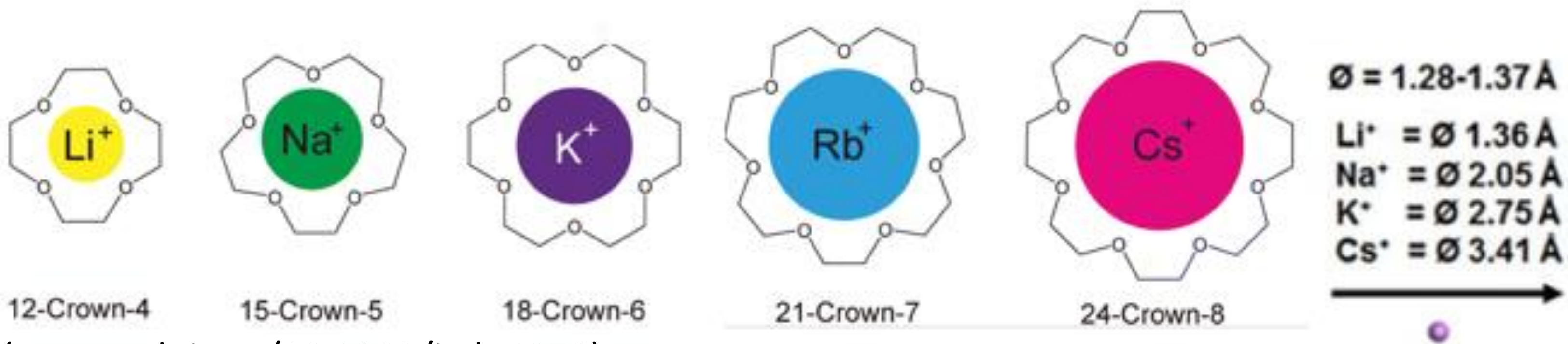
https://s3dist.in/structured-packings/

DLP/SLA printer



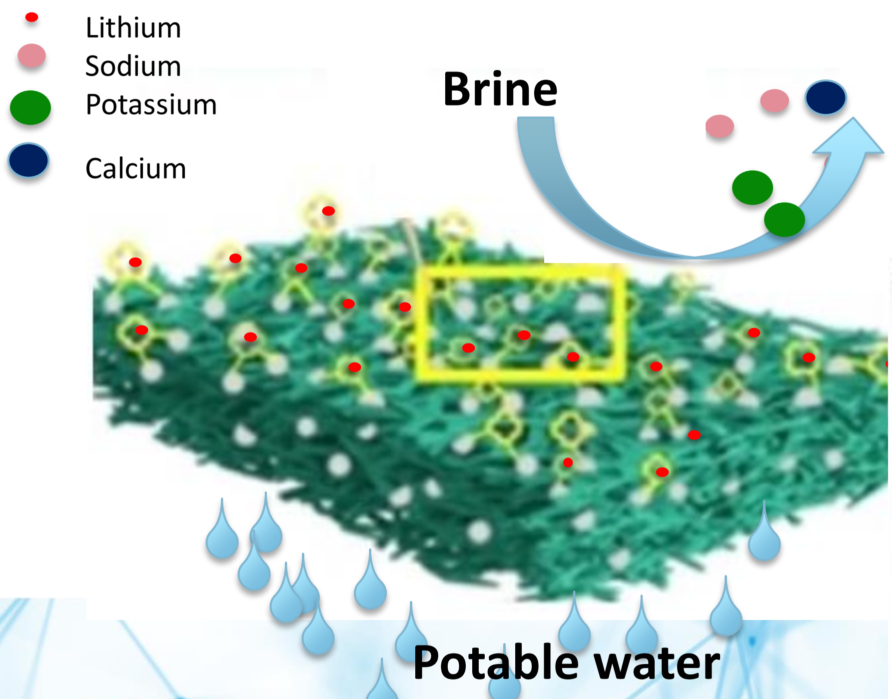
https://eshop.sharplayers.cz/sla-3d-tiskarny

Ceramic membranes modified with crown ethers



(source: doi.org/10.1002/jctb.4976)

Mechanism of Li-selective membrane

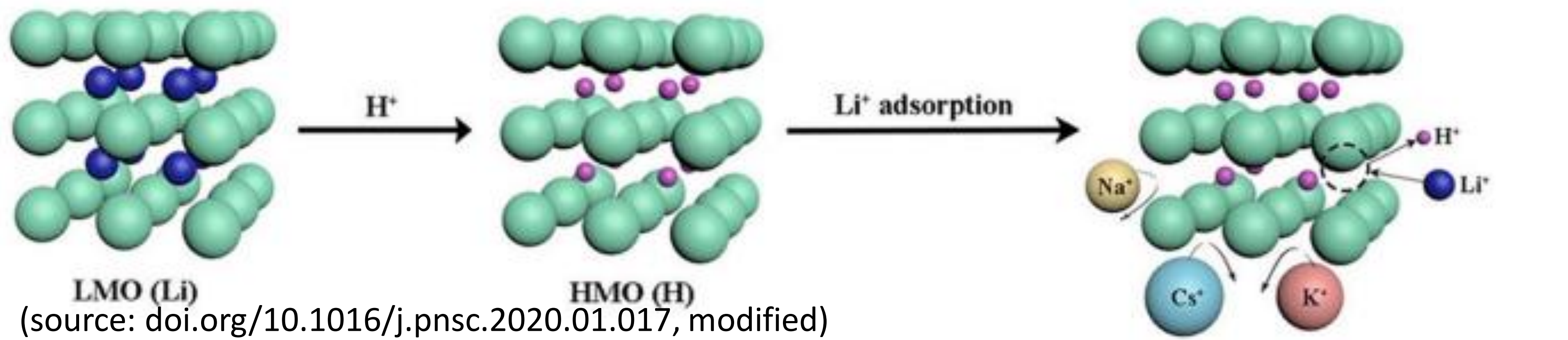


(source: doi.org/10.1002/slct.201904836, modified)

(source: doi.org/10.1016/S0015-1882(11)70118-5)

Manganese-based adsorbents

Behavior of manganese-based ion sieves



(source: doi.org/10.1016/j.pnsc.2020.01.017, modified)

Lithium ions are introduced into the manganese compound to form a spinel structure through heat treatment. Subsequently, the lithium ion is extracted from the spinel structure by acid treatment, with a proton replacing Li^+ to form a lithium ion sieve without changing the crystal structure. In the presence of multiple ions, the lithium ion sieve has the ability to screen and remember a target ion, which is called the ‘ion sieve effect’.

In this study $LiMn_2O_4$ was synthesized according to method described by K. Sato, D. Poojary, A. Clearfeld in „The surface structure of the proton-exchanged lithium manganese oxide spinels and their lithium-ion sieve properties”.

Reservoir water chemistry and its impact on lithium recovery

https://en.ahmadullins.com/publiclist/produced-water/produced-water-treatment

Lithium recovery from a „model" water (1M LiCl in distilled water) using $LiMn_2O_4$ powder was 27 mg/g.

For real reservoir water the sorption capacity (SC) was 15 mg/g.

At pH = 10 the sorption capacity was 20 mg/g, at pH=4 → 3 mg/g.

Li:Mg ratio 1:1000 → SC = 8 mg/g
Li:Ca ratio 1:1000 → SC = 19 mg/g
Li: Na ratio 1:10000 → SC = 18 mg/g
Li:Fe ratio 1:100 → SC = 22 mg/g

pH		5.8
Conductivity	[mS/cm]	163
Density	[kg/m^3]	1103
Total dissolved solids	[mg/dm^3]	156412
General hardness	[mg $CaCO_3$ /dm^3]	51788
H_2SiO_3	[mg/dm^3]	100
SiO_2	[mg/dm^3]	77
Na^+	[mg/dm^3]	31201
K^+	[mg/dm^3]	5931
Li^+	[mg/dm^3]	120
Ca^{+2}	[mg/dm^3]	18667
Mg^{+2}	[mg/dm^3]	1267
Ba^{+2}	[mg/dm^3]	2
Sr^{+2}	[mg/dm^3]	163
Fe^{+2}	[mg/dm^3]	257
Mn^{+2}	[mg/dm^3]	4
Cl^-	[mg/dm^3]	89120
SO_4^{-2}	[mg/dm^3]	2301
HCO_3^{-2}	[mg/dm^3]	110

Thank you for attention

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