BrineRIS

Brines of RIS countries as a source of Critical Raw Materials and energy supply

EIT RM KAVA 8 Project

WP04 Recovery Technologies Testing

SOLVENT EXTRACTION OF LITHIUM FROM BRINE SOLUTIONS

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CHARACTERISATION OF GARKI BRINE

Li source	Li, ppm	Na, ppm	Ca, ppm	Mg, ppm	pH
Garki	65	96972	17475	871	5.5

evaporation

~500 ppm of Li → TARGET → > 6000 ppm Li

The solubility in H_2O, at 20°C:

NaCl 366 g/dm^3

LiCl 785 g/dm^3

Li_2CO_3 13.3 g/dm^3 ⟶ Li 2500 ppm

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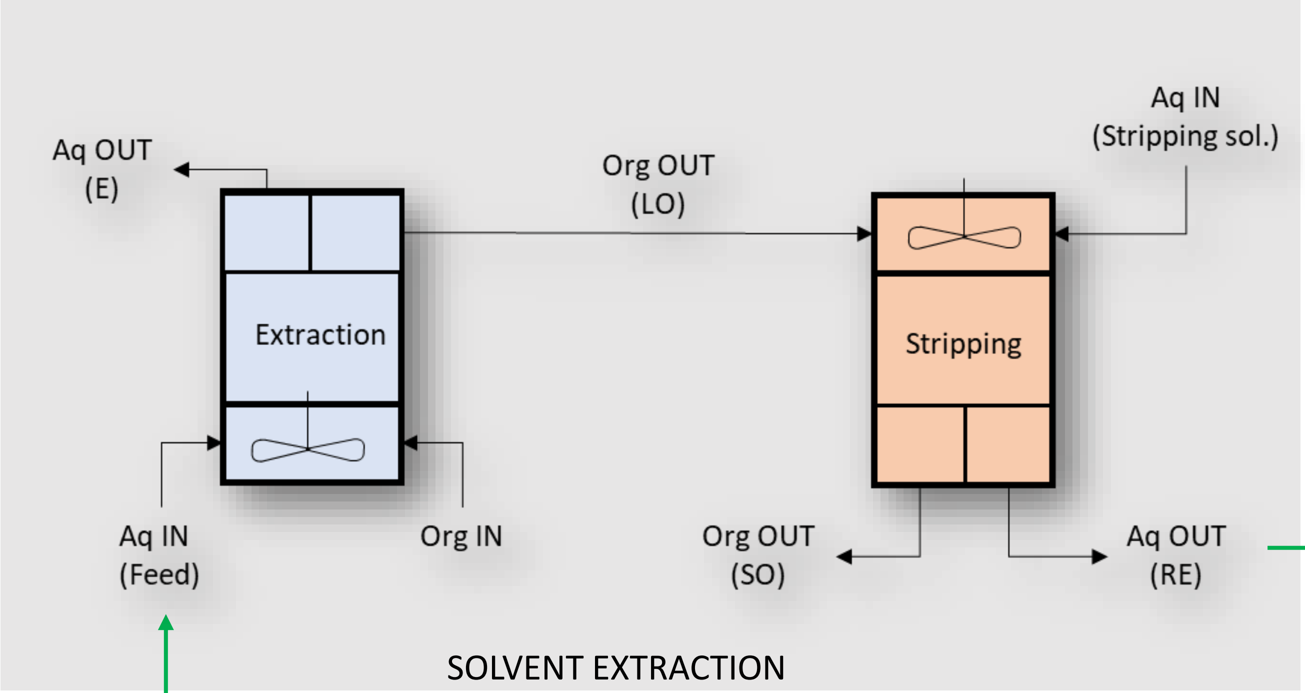
WUST CHEM - EXPERIMENTAL CONCEPT



PRECIPITATION

Li_2CO_3

Brines/
mine waters

CONCENTRATION
(evaporation)

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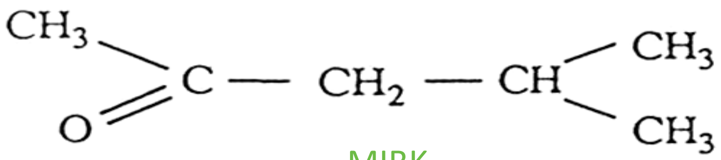
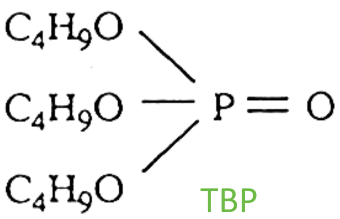
LITERATURE REVIEW – COMMON LITHIUM EXTRACTION SYSTEMS

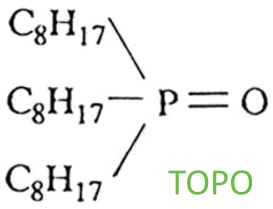
- **Tributyl phosphate + methyl isobutyl ketone (TBP + MIBK)**
- **Tri-octylphosphine oxides + β-diketones (TOPO + MEXTRAL 54-100)**



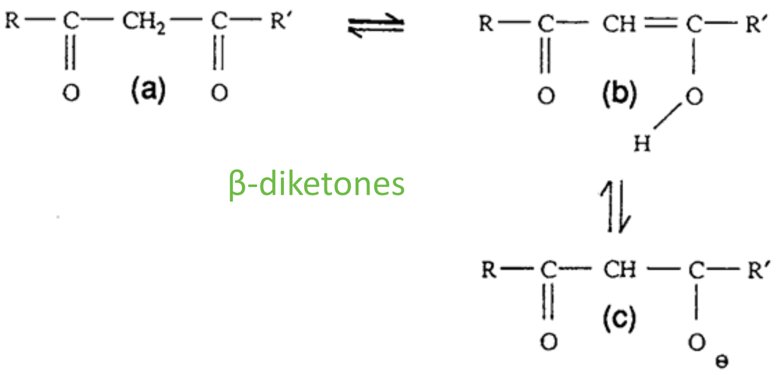
MIBK



TBP



TOPO



β-diketones

Main factors in SX:

- Type & concentration of extractant
- Type & concentration of diluent
- A/O ratio
- pH_{eq}
- Stirring speed
- Extraction kinetics
- Type & concentration of stripping agent

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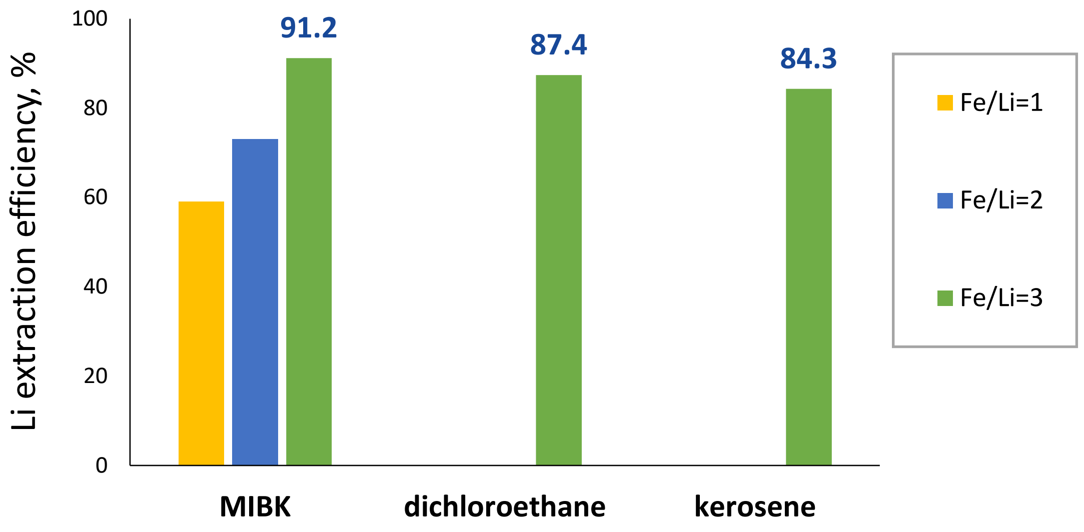
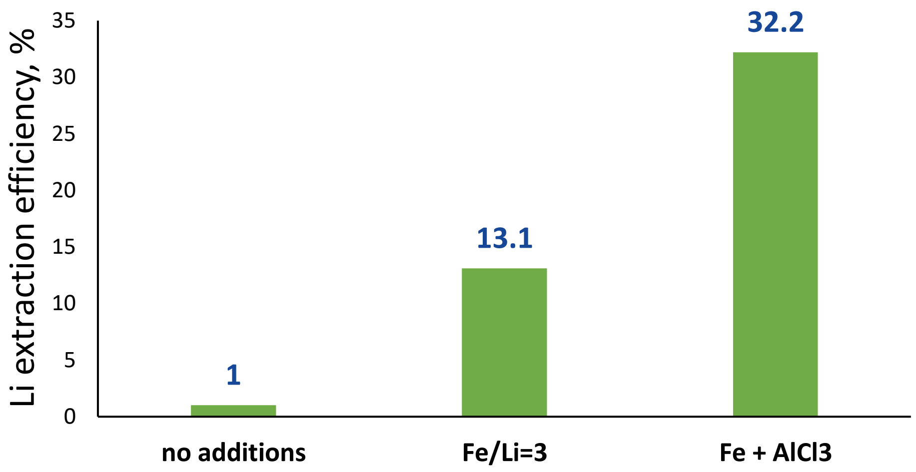
LITHIUM EXTRACTION SYSTEM: TBP + MIBK

Aq: Sol.1 Org: 60% TBP/$FeCl_3$ + diluent



Sol. 1: ~1 g/L Li + 70 g/L Na

Aq: SZ4 Org: 60% TBP/$FeCl_3$ + MIBK



S4Z: evaporated Garki brine, ~500 ppm Li + elemental matrix (saturated sol.)

Constraints:

- Co-extractants ($FeCl_3$ & $AlCl_3$) are needed for succesful Li extraction.
- Additions of co-extractants results in salting out before and during extraction stage.
- Additional cleaning step would be necessary before stripping stage.
- The rich elemental matrix presents significant difficulties in the solvent extraction of lithium.
- Li extraction efficiency is not satisfactory, even with addition of co-extractants.

LITHIUM EXTRACTION SYSTEM: MEXTRAL 54-100 + TOPO in KEROSENE

RESEARCH OBJECTIVES:

1. LACK OF SELECTIVITY OF THE EXTRACTION SYSTEM FOR LITHIUM !
2. WHAT IS THE EFFICIENCY OF LITHIUM EXTRACTION?
3. IS IT POSSIBLE TO REGENERATE LOADED ORGANIC PHASE?
4. IS IT POSSIBLE TO CONCENTRATE LITHIUM TO TARGET LEVEL BY CHANGE OF VOLUME PHASE RATIO (A/O)?

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GOAL 1. MODIFICATION OF EXPERIMENTAL CONCEPT

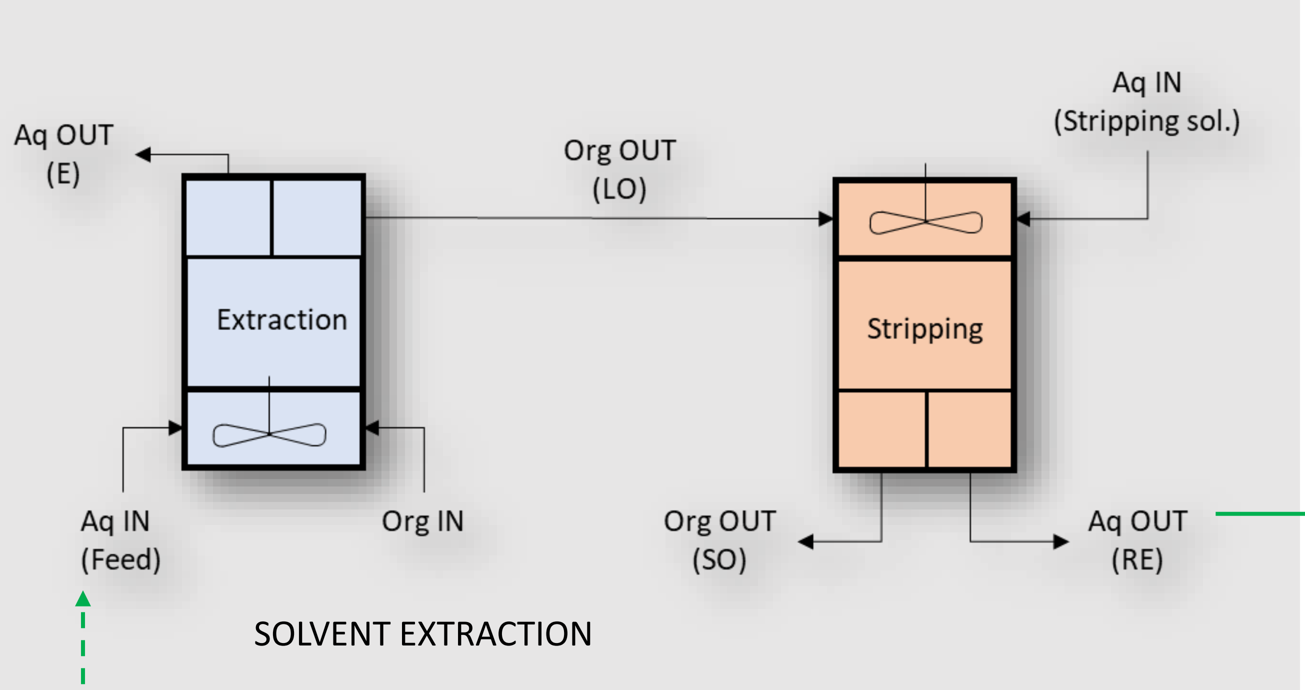
Brines/
mine waters

PRECIPITATION of Ca & Mg

OR

SELECTIVE SEPARATION of Li

CONCENTRATION (evaporation)



PRECIPITATION

Li_2CO_3

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GOAL 1. SOLUBILITIES of Ca & Mg COMPOUNDS

Solubility S [g/100 g H_2O]			
Oxalates		**Hydroxides**	
$CaC_2O_4 \cdot H_2O$	$7.36 \cdot 10^{-4}$	$Ca(OH)_2$	0.173
$MgC_2O_4 \cdot H_2O$	0.038	$Mg(OH)_2$	$1.22 \cdot 10^{-3}$
$Li_2C_2O_4 \cdot H_2O$	6.6	LiOH	12.7

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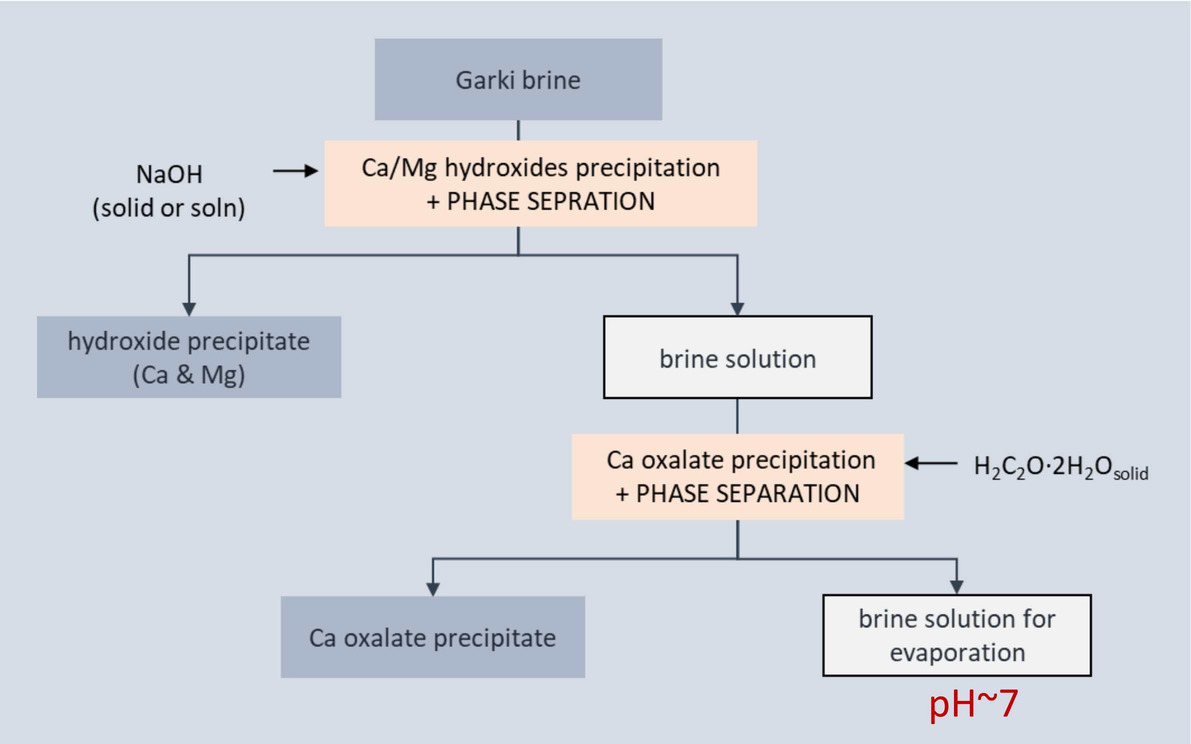
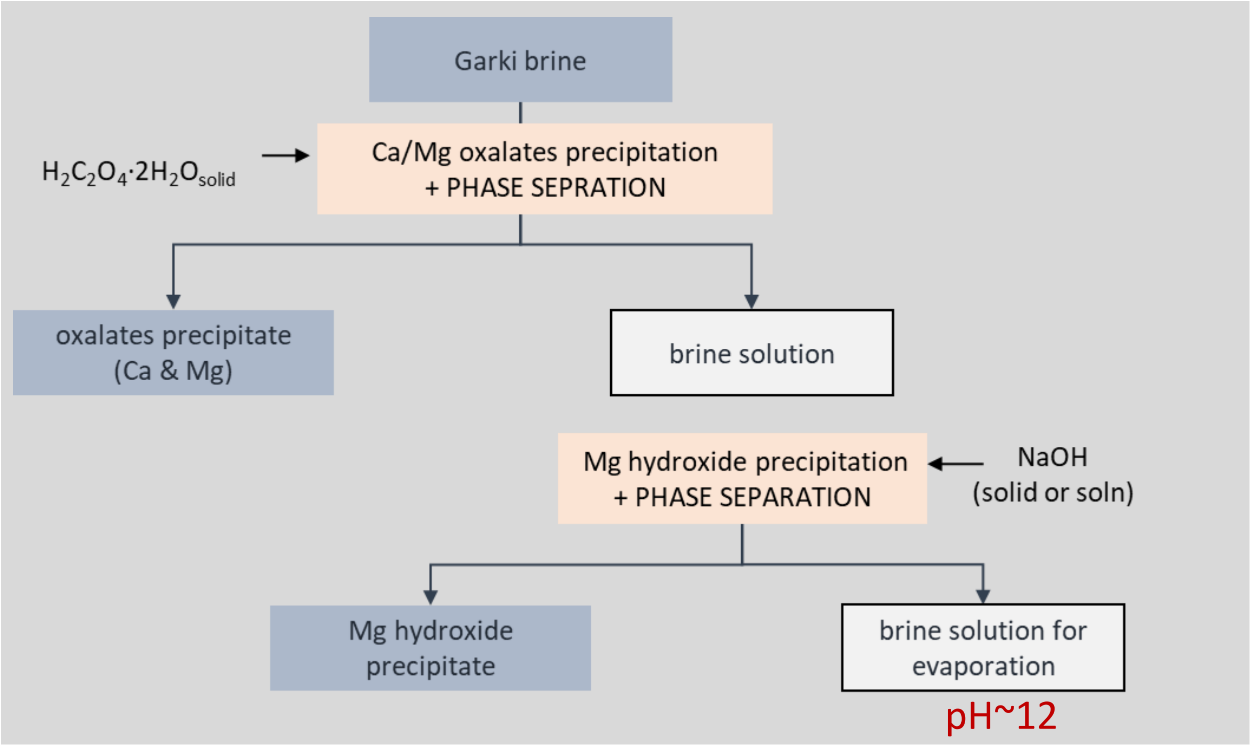
GOAL 1. TREATMENT of GARKI BRINE TOWARDS Ca & Mg REMOVAL

hydroxides → oxalates sequence



oxalates → hydroxides sequence



- pH of aqueous phase after precipitation determines further steps before SX
- The hydroxide → oxalates sequence is more economical due to lower reagents consumption

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GOAL 2. EXTRACTION RESULTS - EXAMPLES

<table>
<tr><th>No.</th><th>Aqueous Feed</th><th>Organic Feed</th><th>%E</th></tr>
<tr><td>SX 44.1</td><td rowspan="3">F14:~500 ppm Li
pH_{ini}~5</td><td>Org1: 20% TOPO + 10% Mextral 54-100</td><td>0.0</td></tr>
<tr><td>SX 44.2</td><td>Org2: 20% TOPO + 20% Mextral 54-100</td><td>0.0</td></tr>
<tr><td>SX 44.3</td><td rowspan="2">Org3: 20% TOPO + 30% Mextral 54-100</td><td>4.5</td></tr>
<tr><td>SX 46.1</td><td rowspan="3">F15: ~500 ppm Li
pH_{ini} ~11→ pH_{eq} ~ 6</td><td>33.4</td></tr>
<tr><td>SX 46.4</td><td>Org5: 20% TOPO + 40% Mextral 54-100</td><td>36.5</td></tr>
<tr><td>SX 46.5</td><td>Org6: 20% TOPO + 50% Mextral 54-100</td><td>36.8</td></tr>
<tr><td>SX 46.8</td><td>F15A:~500 ppm Li
pH_{ini}~12 → pH_{eq} ~ 9</td><td rowspan="3">Org1: 20% TOPO + 10% Mextral 54-100</td><td>97.6</td></tr>
<tr><td>SX 46.9</td><td>F15B:~500 ppm Li
pH_{ini}~14→ pH_{eq} ~ 13</td><td>99.1</td></tr>
<tr><td>SX 47</td><td rowspan="2">F16:~500 ppm Li
pH_{ini}~11 → pH_{eq} ~ 9</td><td>98.9</td></tr>
<tr><td>SX 47.1</td><td>Org7: 10% TOPO + 10% Mextral 54-100</td><td>43.8</td></tr>
<tr><td>SX 49</td><td>S8Z: ~500 ppm
pH_{ini}~12 → pH_{eq} ~ 12</td><td>Org1: 20% TOPO + 10% Mextral 54-100</td><td>93.6</td></tr>
</table>

Diluent: kerosene, A/O = 1, extraction time 10 min, disengagement < 2min, SX49 - A/O = 3/1

F14/F16 – synthetic brine, F15 – semi-synthetic after Ca&Mg removal, S8Z – natural brine after Ca&Mg removal and evaporation

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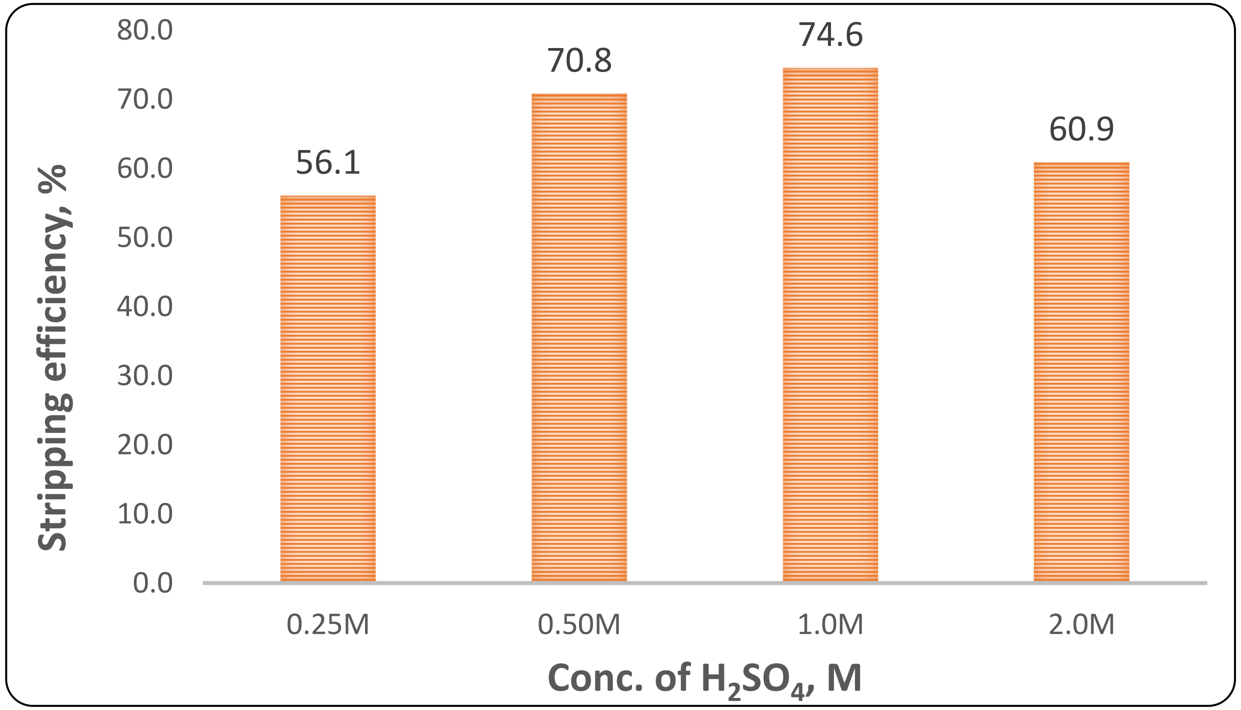
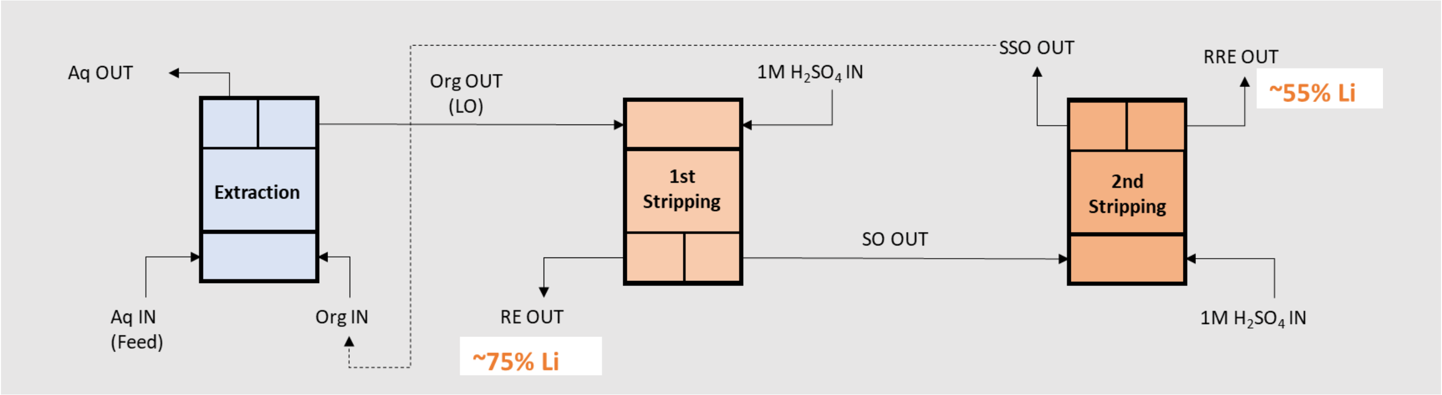
GOAL 3. STRIPPING OF LITHIUM





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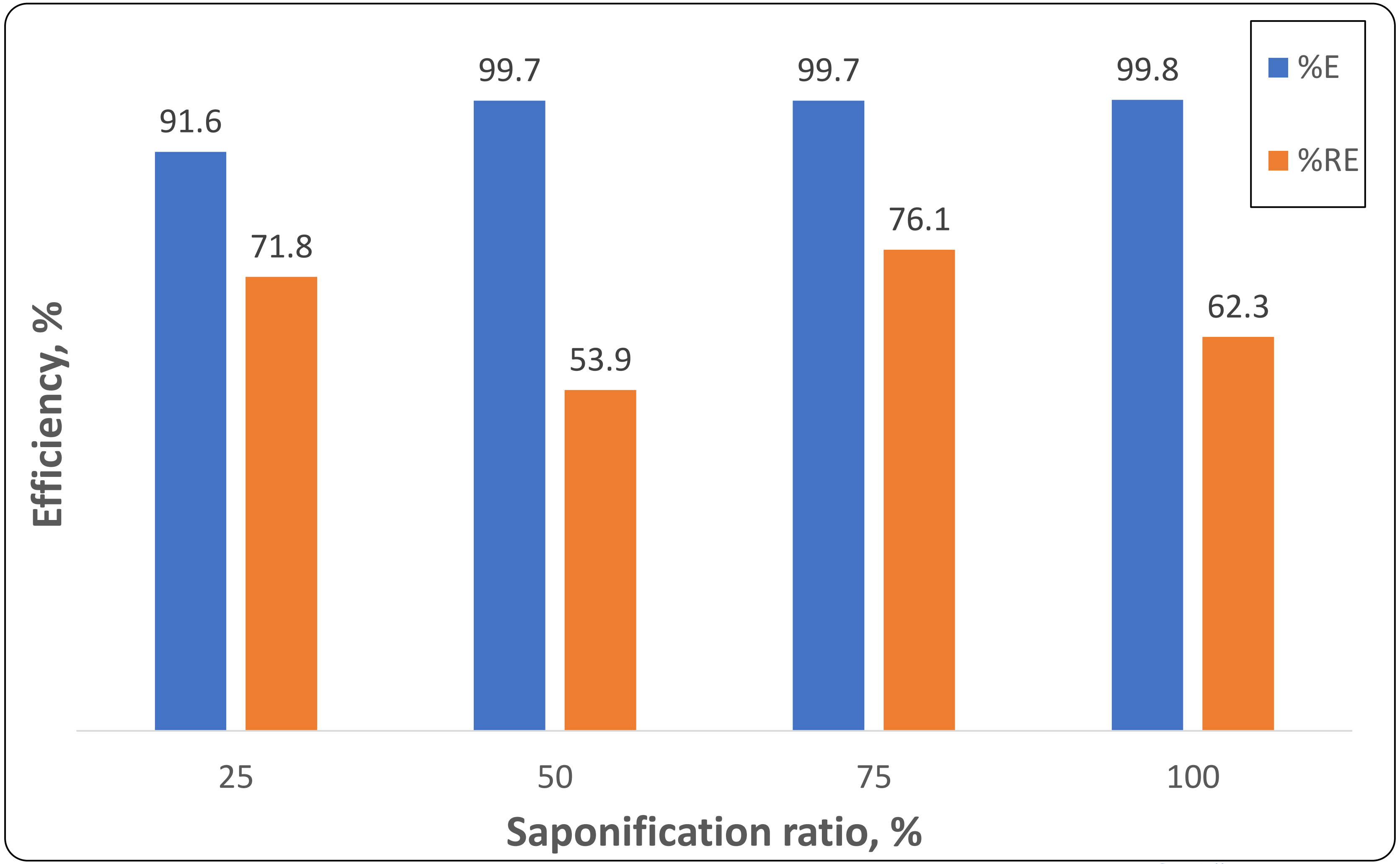
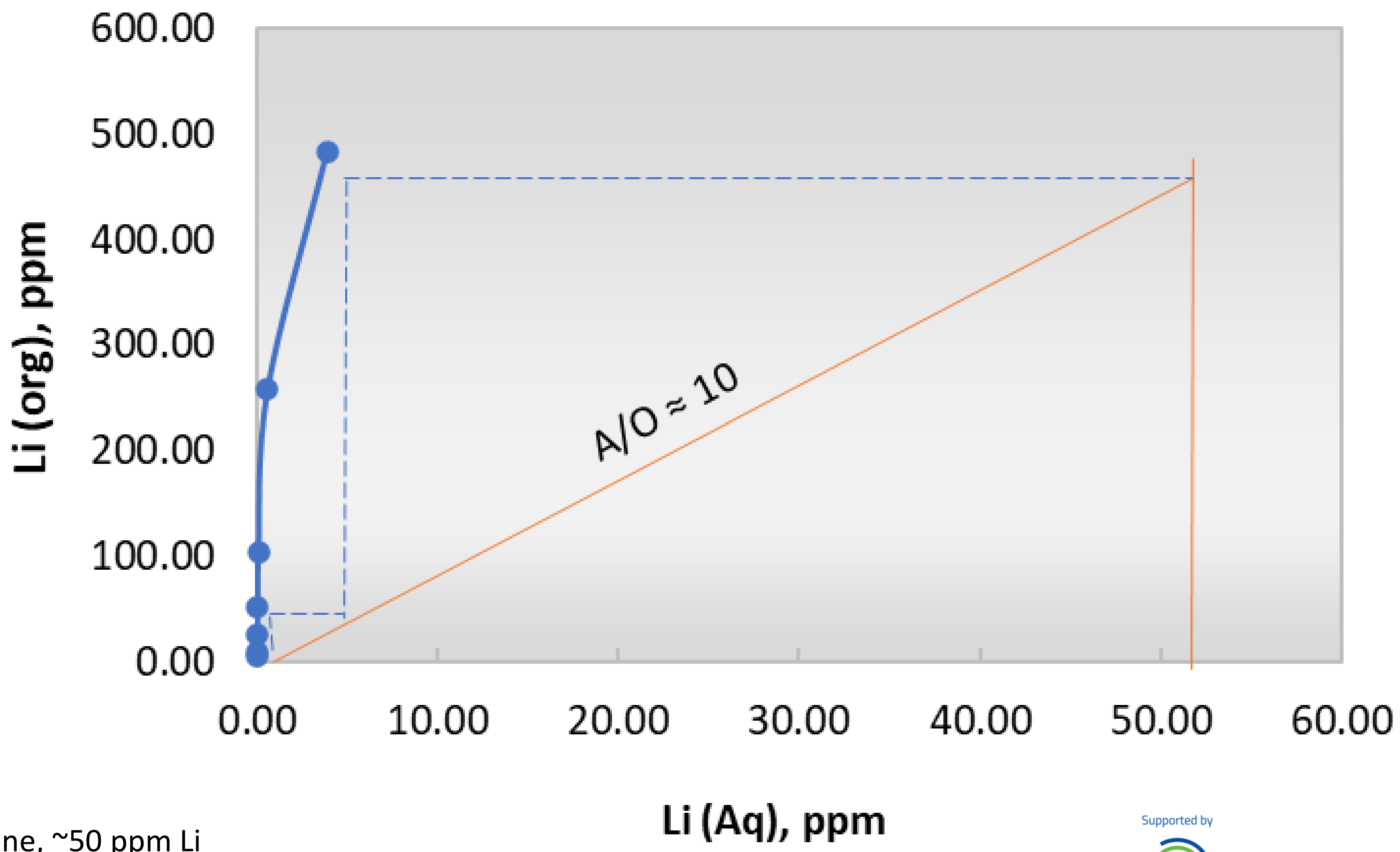
GOAL 3. EFFECT OF ORGANIC PHASE SAPONIFICATION



GOAL 4. CONCENTRATION OF Li BY CHANGING A/O RATIO McCABE-THIELE DIAGRAM



Aq: synthetic brine, ~50 ppm Li
Org: 20% TOPO + 10% Mextral 54-100, A/O: 1/10 – 10/1, t=10min

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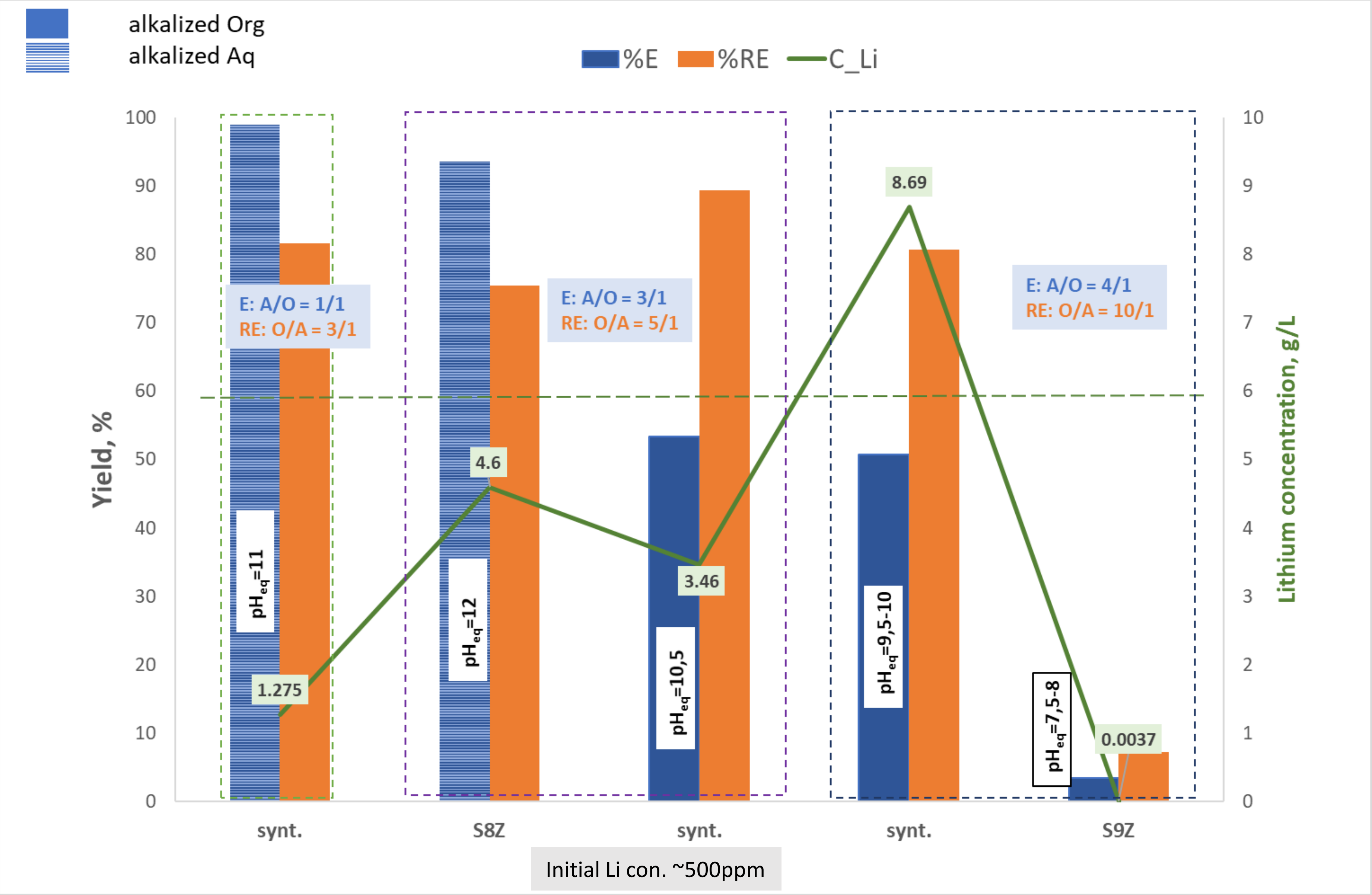
GOAL 4. CONCENTRATION OF Li BY CHANGING A/O RATIO



S8Z, S9Z – natural brine after Ca&Mg removal and evaporation, ~500 ppm Li

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CONCLUSIONS

- The Mextral /TOPO extraction mixture can effectively concentrate lithium from brines, even those with low lithium content. Adjusting the aqueous-to-organic (A/O) ratio can enhance lithium concentration, but large brine volumes are required due to the low initial lithium levels.
- Pre-treatment of brines is essential to remove competing ions that may be co-extracted with lithium and reduce overall recovery.
- High lithium recovery can be achieved using alkaline brines or saponified organic solutions, provided the equlibrium pH is carefully controlled.
- SX is suitable for purified lithium solutions with varying compositions, and its performance can be optimized by adjusting parameters such as pH, A/O ratios, and the type of organic phase to achieve high lithium recovery.
- The SX method shows potential for industrial-scale application. By carefully optimizating process parameters, it is possible to ensure the proces works efficiently on a larger scale.
- Laboratory-scale results cannot reliably predict process kinetics, energy consumption, or overall economic feasibility in larger-scale operations. These factors must be carefully evaluated through pilot-scale testing.

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Thank you!

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