Origin and Extraction of Andean Salars

Lithium and Boron Recovery from Salt brines and Salt flats in Chile and Bolivia
Introduction

- World Li demand expected to rise 60% in next five years
- Andean Salar have 23.2 MMT recoverable lithium. By comparison, mineral reserves are 8.8 MMT.
- Salar de Uyuni alone, contains 5.4 MMT estimated reserve
Problem Statement

• **Benefits - Salar de Uyuni**
  - contains 20% of recoverable Li reserves
  - A potential source of boron

• **Problems - Salar de Uyuni extraction**
  - 3600m altitude
  - High Mg/Li ratio (16-22:1) creates evaporation problems
  - Li content (<0.08%) is low compared to other salt flats. Thus greater concentration process is needed

• **Standard evaporation/concentration process needs to be modified**
Agenda

- Location & Geochemical Origin of Andean Salar
- Salar de Uyuni Brine Composition
- Salar de Uyuni Modified Extraction Process
- Analyzer/StudioSC Facilities Simulation
General facts

- 130 salars
  - Argentina (≈30)
  - Bolivia (35)
  - Chile (65)
- Area from 0.04 to 10,000 km$^2$
- Geologic Requirements
  - Internal drainage basin
  - Evaporation rates higher than drainage rates
    - Evaporation – 1000 to 2500 mm/yr
    - Precipitation – 5 to 500 mm/yr
Fig. 2 Cross section from the Pacific Ocean through the Andes Cordillera (at latitude UTM northing 7400000). 1: Pacific Ocean; 2: Coast Range; 3 and 4: Central Valley or Atacama Desert (3: fossil salars, 4: pediplanes or alluvial fans); 5: Precordillera (Domeyko Range); 6 and 7: Pre-Andean Depression (6: Cordillera de la Sal, 7: salar de Atacama); 8, 9, and 10: Andes Cordillera (8: basement, 9: ignimbrite plateau, 10: stratovolcanoes); 11: present salars; 12: hypothetical ancient buried salars
Geochemical Origin

- Water Inflow
  - Rain, runoff, springs, seeps, rivers, underground

- Ion source
  - Rain
    - Atmospheric salts
  - Rock Weathering
    - Runoff of volcanic rock
  - Subsurface Recycling of dissolved brines
  - Subsurface Recycling of water through salt deposits

Fig. 3 Morphology of Andean salars (modified from Risacher and Fritz 1991)
### Brine Composition of Salar de Uyuni and other Salt flats

<table>
<thead>
<tr>
<th>Source</th>
<th>Na</th>
<th>Cl</th>
<th>K</th>
<th>Mg</th>
<th>Ca</th>
<th>SO4</th>
<th>B</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salar de Uyuni, Bolivia</td>
<td>100</td>
<td>190</td>
<td>16</td>
<td>17</td>
<td>3</td>
<td>22</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Salar de Uyuni, Bolivia</td>
<td>70</td>
<td>50</td>
<td>12</td>
<td>7</td>
<td>0.3</td>
<td>16</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Salar de Atacama, Chile</td>
<td>90</td>
<td>190</td>
<td>24</td>
<td>10</td>
<td>0.5</td>
<td>16</td>
<td>0.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Hombre Muerto, Argentina</td>
<td>100</td>
<td>160</td>
<td>5</td>
<td>1</td>
<td>0.5</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Bonneville, US</td>
<td>80</td>
<td>140</td>
<td>5</td>
<td>4</td>
<td>0.1</td>
<td>8</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Zabuye, China</td>
<td>70</td>
<td>100</td>
<td>17</td>
<td>0.03</td>
<td>0.1</td>
<td>8</td>
<td></td>
<td>0.5</td>
</tr>
</tbody>
</table>
Lithium concentration in Salar de Uyuni brine

Brine Composition

Distribution of lithium in the interstitial brine of the upper 10 m (modeled by ArcGIS using Kriging)

10,000 km2 area
Salar de Uyuni Analysis Results

Assumption: 300 mg/l $\text{HCO}_3^{-1}$, 6.6 pH, and 5C

### Scaling Tendencies

<table>
<thead>
<tr>
<th>Solids</th>
<th>Tendency</th>
</tr>
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<tbody>
<tr>
<td>CaSO4.2H2O</td>
<td>1.00000</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.00000</td>
</tr>
<tr>
<td>CaSO4</td>
<td>0.971050</td>
</tr>
<tr>
<td>NaCl2H2O</td>
<td>0.837525</td>
</tr>
<tr>
<td>H2O</td>
<td>0.700862</td>
</tr>
<tr>
<td>Na2SO4.10H2O</td>
<td>0.546220</td>
</tr>
<tr>
<td>CaCO3</td>
<td>0.490825</td>
</tr>
<tr>
<td>CaCO3</td>
<td>0.353139</td>
</tr>
<tr>
<td>KCl</td>
<td>0.311916</td>
</tr>
<tr>
<td>Na2SO4.CaSO4</td>
<td>0.260675</td>
</tr>
<tr>
<td>B(OH)3</td>
<td>0.256009</td>
</tr>
<tr>
<td>CaSO4.0.5H2O</td>
<td>0.228997</td>
</tr>
<tr>
<td>K2SO4.CaSO4.1H2O</td>
<td>0.206718</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>0.144112</td>
</tr>
</tbody>
</table>

### Species Output (True Species)

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>Aqueous</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/L</td>
<td>g/L</td>
<td>g/L</td>
</tr>
<tr>
<td>Ca+2</td>
<td>0.37142</td>
<td>0.380095</td>
<td>0.0</td>
</tr>
<tr>
<td>Cl-1</td>
<td>190.037</td>
<td>194.475</td>
<td>0.0</td>
</tr>
<tr>
<td>H2O</td>
<td>869.493</td>
<td>889.802</td>
<td>0.0</td>
</tr>
<tr>
<td>HCO3-1</td>
<td>0.207684</td>
<td>0.212535</td>
<td>0.0</td>
</tr>
<tr>
<td>Mg+2</td>
<td>16.297</td>
<td>16.6775</td>
<td>0.0</td>
</tr>
<tr>
<td>Na+1</td>
<td>87.6115</td>
<td>89.0579</td>
<td>0.0</td>
</tr>
<tr>
<td>SO4-2</td>
<td>13.8061</td>
<td>14.2309</td>
<td>0.0</td>
</tr>
<tr>
<td>K+1</td>
<td>15.3417</td>
<td>15.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Li+1</td>
<td>0.820799</td>
<td>0.83997</td>
<td>0.0</td>
</tr>
<tr>
<td>B3O3(OH)4-1</td>
<td>0.417424</td>
<td>0.427174</td>
<td>0.0</td>
</tr>
<tr>
<td>B(OH)3</td>
<td>2.25064</td>
<td>2.30321</td>
<td>0.0</td>
</tr>
<tr>
<td>B(OH)3Cl-1</td>
<td>2.43951</td>
<td>2.49649</td>
<td>0.0</td>
</tr>
<tr>
<td>CaSO4.2H2O</td>
<td>12.3508</td>
<td>0.0</td>
<td>12.6393</td>
</tr>
<tr>
<td>NaCl</td>
<td>39.0628</td>
<td>0.0</td>
<td>39.9752</td>
</tr>
<tr>
<td>Total (by phase)</td>
<td>1250.61</td>
<td>1227.2</td>
<td>52.6145</td>
</tr>
</tbody>
</table>

Fourteen phases at or close to saturation

52.6 g/l solids computed to exist in brine
Extracting Lithium and Boron from Brine

- **Standard Process**
  - Evaporate brine to 6% Lithium
  - Remove Mg using CaO
  - Remove Ca using Na2SO4
  - Remove Li using Na2CO3

- **Complications**
  - High magnesium complicate evaporation step
    - Li-Carnallite is reported when Li exceeds 4%
    - Borate adsorbs on Mg(OH)₂ surface
Extraction Process for Salar de Uyuni

Low Mg, High Li Process


Salar de Uyuni Proposed

Diagram showing the extraction process for Salar de Uyuni, focusing on the modified extraction process for lithium recovery.

Key steps include:
- Solar Ponds
- Bittern Brine
- Evaporator S/L/V Separation
- Ca Precip S/L Separation
- Mg Precip S/L Separation
- Li Precipitation Separation Washing Drying
- Li2CO3
- Solar Ponds
- Carbonation
- Reflux
- Evaporation
- Li2CO3
- Boron Recovery
- Mg(OH)2 CaSO4.2H2O
- CO2
- Residual Ca, Mg, Na Salts
Evaporation Step – Avoid Li-Carnallite

- Evaporation path is black dotted line
- 3-5% Li\(^+\) is potential concentration goal
- Li-carnallite precipitates ~2% Li\(^+\)
- Thus, Mg\(^+2\): Li\(^+\) ratio in original brine needs to be reduced

SIMULATION RESULTS
Extraction Process for Salar de Uyuni


Simulation Steps

1. Add Ca(OH)$_2$ to brine and precipitate Mg$^{+2}$
2. Add Na$_2$(COO)$_2$ to filtered liquid and precipitate Ca$^{+2}$
3. Evaporate filtered liquid to precipitate NaCl/KCl, etc.: Concentrate Lithium to 3-6%
4. Add Na$_2$CO$_3$ to concentrate and precipitate Li$_2$CO$_3$
5. Compute Lithium Recovery and Boron fate
Ca(OH)$_2$ Addition
Predictions vs. Experimental data (Uyuni-2)

Conservative ions

Mg$^{+2}$ and Ca$^{+2}$

Experiments run at 22C, 1atm. Field conditions will be ~5-10C and ~0.7atm
Ca(OH)$_2$ Addition

Predictions vs. Experimental data (Uyuni-2)

Experiments run at 22°C, 1 atm. Field conditions will be ~5-10°C and ~0.7 atm

pH, SO$_4^{2-}$, and Boron

List of solid phases formed

- **Significant**
  - Mg(OH)$_2$ (40 g/l)
  - CaSO$_4$.2H$_2$O (40 g/l)
  - Ca$_2$B$_6$O$_{11}$.9H$_2$O (4 g/l)

- **Minor**
  - CaCO$_3$
  - Mg$_2$B$_6$O$_{11}$.15H$_2$O
  - NaCl
Ca(OH)$_2$ addition, Solids

Extraction Simulation
Na-Oxalate Addition (Uyuni1)
Evaporation Step

Na\(^+\) and K\(^+\) concentration, g/l

SO\(_4\)^{-2}\) concentration, g/l

Concentration factor

*The author boiled the samples at atmospheric conditions. Evaporation in the field will be at \(-10^\circ C\) and 0.7 bar*
Evaporation Step

*The author boiled the samples at atmospheric conditions. Evaporation in the field will be at ~10°C and 0.7 bar.*

**Cl⁻ concentration, g/l**

**B concentration, g/l**

Concentration factor
### Summary of Results

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Li</th>
<th>B</th>
<th>Cl</th>
<th>SO4</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lime Precipitation</strong></td>
<td>93</td>
<td>16</td>
<td>14.0</td>
<td>0.3</td>
<td>0.8</td>
<td>0.36</td>
<td>190</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>OLI Calc (U2)</td>
<td>95</td>
<td>17</td>
<td>20.1</td>
<td>0.0</td>
<td>0.8</td>
<td>0.2</td>
<td>200</td>
<td>0.4</td>
<td>1000mL</td>
</tr>
<tr>
<td><strong>Oxalate Precipitation</strong></td>
<td>115</td>
<td>16</td>
<td>&lt;0.05</td>
<td>0.2</td>
<td>0.8</td>
<td>0.2</td>
<td>196</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>OLI Calc (U2)</td>
<td>116</td>
<td>18</td>
<td>0.00</td>
<td>0.0</td>
<td>0.8</td>
<td>0.2</td>
<td>198</td>
<td>0.1</td>
<td>960</td>
</tr>
<tr>
<td><strong>Evaporation to 20 g/L Li</strong></td>
<td>56</td>
<td>53</td>
<td>&lt;0.05</td>
<td>0.4</td>
<td>19.8</td>
<td>2.9</td>
<td>201</td>
<td>20.2</td>
<td></td>
</tr>
<tr>
<td>OLI Calc (U2)</td>
<td>60</td>
<td>53</td>
<td>0.00</td>
<td>0.0</td>
<td>20.1</td>
<td>3.8</td>
<td>219</td>
<td>10.6</td>
<td>36</td>
</tr>
<tr>
<td><strong>Evaporation to 30 g/L Li</strong></td>
<td>38</td>
<td>41</td>
<td>&lt;0.05</td>
<td>0.7</td>
<td>30.3</td>
<td>4.2</td>
<td>216</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td>OLI Calc (U2)</td>
<td>38</td>
<td>44</td>
<td>0.00</td>
<td>0.0</td>
<td>30.1</td>
<td>2.4</td>
<td>229</td>
<td>12.3</td>
<td>24</td>
</tr>
</tbody>
</table>

*The author boiled the samples at atmospheric conditions. Evaporation in the field will be at ~10C and 0.7 bar
Simulating using StudioSC
Lithium Recovery, 87%
Conclusions

• Mg must be removed prior to evaporation, otherwise
  • Li-carnallite forms
  • B(OH)$_4$ adsorbs on Mg(OH)$_2$ (not predicted by OLI)
• Complications between Predicted and measured results
  • OLI MSE Database did not contain Mg- and Ca-oxalates
  • Experiments at Lab T/P, not field T/P
    ■ Predicted B-phases not observed in experiments
    ■ Li predicted to precipitate before 5% concentration
• Case run using V9.0 Brine Facilities
  • Simplifies work, but limited to final input conditions
• Waiting on additional published data from Chonnam National University