Advanced Chemical Precipitation Process for Sulfate Treatment with Gibbsite Recovery and Reuse

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Sulfate Treatment

- Major Technologies
  - Chemical precipitation [Desaturation process]
  - IX
  - Biological Treatment
  - Membrane [NF/RO]
  - Evaporation/Crystallization

- NF is a Popular Technology for Water Reuse Interest

- Handling of NF Reject is problematic.
Reduces Sulfate < 100 mg/L by Two Stage Process:

1st Stage: CaSO₄ Desaturation
SO₄ is reduced to <1500 mg/L

2nd Stage: Advanced Chemical Precipitation
SO₄ is reduced to < 100 mg/L

Treated effluent can potentially be reused.
1st Stage: CaSO$_4$ Desaturation

\[ \text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4 \]

2nd Stage: Advanced Precipitation Process

*Formation of Insoluble Complex [ETTRINGITE]*

- **Insoluble Complex Formation Reaction**
  \[ 3\text{CaO} + 3\text{Ca}^{2+} + 3\text{SO}_4^{2-} + 2\text{Al(OH)}_3 (s) + 28\text{H}_2\text{O} = 3\text{CaO. Al}_2\text{O}_3.3\text{CaSO}_4 . 31\text{H}_2\text{O} \]

- **Regeneration of the Reagent**
  \[ 3\text{CaO . Al}_2\text{O}_3.3\text{CaSO}_4 . 31\text{H}_2\text{O} + 6\text{H}^+ = 6\text{Ca}^{2+} + 3\text{SO}_4^{2-} + 2\text{Al(OH)}_3 (s) + 37 \text{H}_2\text{O} \]
General Concept

POND WATER → PRETREATMENT → NANOFILTRATION → NF PERMEATE

BACK TO POND (OPTION - I) → DESATURATION OF CaSO4 → OPTION II

TREATED WATER SO4 < 100 mg/l → ADVANCED PRECIPITATION PROCESS → CaSO4
Sulfate Desaturation Pilot Study

- Project Site: Copper Mine in South America
- Tailing Pond Water Contains High Sulfate and Calcium
- Need to Reduce Calcium and Sulfate
- Flow: 20gpm (5m³/hr)
Pond Water Characteristics:
- pH: 7.4
- Mg\(^{2+}\): 21 mg/L
- SO\(_4^{2-}\): 1830 mg/L
- Fe: 0.04 mg/L
- Mn: 0.17 mg/L
- Mo: 0.27 mg/L
- Al: 0.05 mg/L
- Na: 104 mg/L
- K: 124 mg/L

- Ca\(^{2+}\): 690 mg/L
- Alkalinity: 28 mg/L
- TDS: 3070 mg/L
- Cations: 40.02 meq/L
- Anions: 44.04 meq/L
Pretreatment Includes: Iron Coagulation, Multi-media filtration and Green Sand filtration

- Mo was reduced to < 0.05 mg/L
- Fe < 0.3 mg/L
- Mn < 0.05 mg/L
- SDI = 3

NF: Dow Filmtec [2 - NF 90 and 1 - NF 270]
NF Permeate – Sulfate Concentration and % Rejection - Pilot Study Data

Advanced Chemical Precipitation Process for Sulfate Treatment with Gibbsite Recovery and Reuse/10/29/2014
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Permeate</th>
<th>Discharge Std</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO4</td>
<td>35</td>
<td>250</td>
</tr>
<tr>
<td>Cl</td>
<td>80</td>
<td>200</td>
</tr>
<tr>
<td>Ca</td>
<td>25</td>
<td>60</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;0.1</td>
<td>5</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.01</td>
<td>5</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0.01</td>
<td>0.2</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.005</td>
<td>0.1</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.005</td>
<td>0.10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01</td>
<td>0.20</td>
</tr>
</tbody>
</table>

All concentrations are in mg/L
Precipitate $\text{SO}_4$ as $\text{CaSO}_4$

Use lime or lime/$\text{CaCl}_2$ as sources of $\text{Ca}^{2+}$

Determine the impact of sludge recirculation ratio on $\text{CaSO}_4$ nucleation and crystal growth

Ratio = Mass of solids [$\text{CaSO}_4$] in the recycle line/Mass of solids [$\text{CaSO}_4$] formed from the fresh wastewater [NF reject]

Goal was to reduce $\text{SO}_4$ to < 1,500 mg/L as $\text{SO}_4$ (theoretical solubility limit)
Sulfate Precipitation Process

REJECT WITH HIGH SULFATES (SO₄ 3200 and Calcium 1020 mg/l)

VEOLIA WATER PROPRIETARY (TURBOMIX REACTOR)

Ca⁺², SEED

VEOLIA WATER PROPRIETARY SOLID / LIQUID SEPARATOR (MULTIFLO)

TREATED WATER SO₄ < 1500 mg/l

SLUDGE RECYLE

CaSO₄ SLUDGE FOR DISPOSAL

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CaSO₄ Precipitation as a Function of Sludge Recirculation Ratio

### Sulfate in Untreated Reject: 3200 mg/L

<table>
<thead>
<tr>
<th>Sludge Recycle Ratio</th>
<th>20:1</th>
<th>15:1</th>
<th>10:1</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9.3</td>
<td>9.3</td>
<td>9.2</td>
<td>9.3</td>
</tr>
<tr>
<td>Sulfate, mg/L</td>
<td>1,250</td>
<td>1,100</td>
<td>1,200</td>
<td>2000</td>
</tr>
</tbody>
</table>

Used: Turbomix® Reactor with 30-minutes reaction time followed by MULTIFLO™ for solid/liquid separation
Further Reduction of Sulfate to < 100 mg/L

Advanced Precipitation Process

Formation of Insoluble Complex [ETTRINGITE]

- Insoluble Complex Formation Reaction
  \[3\text{CaO} + 3\text{Ca}^{2+} + 3\text{SO}_4^{2-} + 2\text{Al(OH)}_3(s) + 28\text{H}_2\text{O} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}\]

- Regeneration of the Reagent
  \[3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O} + 6\text{H}^+ = 6\text{Ca}^{2+} + 3\text{SO}_4^{2-} + 2\text{Al(OH)}_3(s) + 37\text{H}_2\text{O}\]
Sulfate Treatment Schematic
(Advanced Precipitation/Ettringite Process)

1. **LIME OR CaCl2**
2. **SEED**
   - **TURBOMIX WITH MULTIFLO**
   - **SO4 < 1800 mg/l**
   - **SATURATED SOLUTION OF CaSO4**
   - **TO SLUDGE DEWATERING UNIT**
   - **SLUDGE RECYCLE**

3. **LIME (OPTIONAL)**
4. **ALUMINUM**
   - **TURBOMIX**
   - **SLUDGE RECYCLE**
   - **ACID**

5. **MULTIFLO**
   - **SO4 < 100 mg/l**

6. **TREATED WATER**
   - **SO4 < 100 mg/l**

7. **REGENERATION TANK**

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Pilot Results

Process Optimization with Fresh Gibbsite

- Influent Sulfate: 1500 mg/l
- PH: 11.5
- Increased Chemical Dosage

PH: 11.8

DATE
9/5/13 9/6/13 9/7/13 9/8/13 9/9/13 9/10/13 9/11/13 9/12/13 9/13/13 9/14/13

EFFLUENT SULFATE, mg/l (AVG)
Pilot Results

Sulfate Reduction with Regenerated Gibbsite

- Date: 9/3/13 to 11/2/13
- Effluent Sulfates, mg/l (AVG)
- X-axis: Date
- Y-axis: Effluent Sulfates, mg/l (AVG)
Pilot Results

Effluent Aluminum Concentration

<table>
<thead>
<tr>
<th>DATE</th>
<th>Effluent Aluminum, mg/l (AVG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9/13/13</td>
<td>0.05</td>
</tr>
<tr>
<td>9/18/13</td>
<td>0.1</td>
</tr>
<tr>
<td>9/23/13</td>
<td>0.15</td>
</tr>
<tr>
<td>9/28/13</td>
<td>0.3</td>
</tr>
<tr>
<td>10/3/13</td>
<td>0.35</td>
</tr>
<tr>
<td>10/8/13</td>
<td>0.25</td>
</tr>
<tr>
<td>10/13/13</td>
<td>0.2</td>
</tr>
</tbody>
</table>

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Ettringite Particle Size Distribution
Ettringite Reactor Sludge
- Ettringite (Major)
- Calcite and Gypsum (Minor)

Recovered Gibbsite Sludge
- Gypsum (Major)
- Calcite (Minor)
- Amorphous (predominant): Gibbsite/Aluminum Hydroxide \( . \) XH20
Ettringite Crystals in Ettringite Reactor Effluent Sample
Recovered Aluminum Sludge Sample

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Process Flow Diagram

FEED WATER CONTAINING SULFATES
FLOW = 4.5 m³/h
SO₄ = 2300 mg/l

PRETREATMENT

NF (60% Recovery)
FLOW = 1.8 m³/h
SO₄ = 5700 mg/l

1st STAGE PRECIPITATION
SLUDGE RECIRCULATION
CALCIUM SULFATE SLUDGE

NF PERMEATE
FLOW = 2.7 m³/h
SO₄ = 35 mg/l

2nd STAGE PRECIPITATION
ALUMINUM RECOVERY
TREATED WATER
FLOW = 1.35 m³/h
SO₄ = 150 mg/L

FINAL EFFLUENT
FLOW = 4.05 m³/h
SO₄ = <75 mg/l
INLET SULFATE CONCENTRATION
(PILOT STUDY AT GOLD MINE SITE: South Africa)
PRELIMINARY PILOT RESULTS FROM GOLD MINESITE: South Africa

Al(OH)₃:SO₄ Ratio VS Effluent SO₄ Conc

Effluent Sulfates Conc (mg/l) vs Al(OH)₃:SO₄ Ratio.
Advanced Chemical Precipitation Process for Sulfate Treatment with Gibbsite Recovery and Reuse/ 10/29/2014
Cost Comparison ($/1,000 gal) Chemical & Power

- Advanced Chemical Precipitation Process with Gibbsite Recovery & Reuse
- **Chemical & Power**: $1.98 [0.38 euro/m³]
- **Without Gibbsite Recovery**: $3.85 [0.75 euro/m³]
Conclusions

- NF with Proper Pretreatment is Capable of Reducing Sulfate to < target Limit of 250 mg/L
- More than 98% Sulfate Rejection Was Achieved
- 1st Stage Desaturation Process:
  Sulfate from NF Reject can be Reduced to < 1500 mg/L in presence of a Seed Material with Proper Sludge Recirculation Ratio.
- Seed material be Added Only Once during the Crystallization Process
- Sulfate Removal is a combination of Chemical Precipitation and Adsorption Process.
Conclusions

• More than 95% Gibbsite was recovered and reused in the Ettringite Process
  ○ Using 95% recovered Gibbsite and 5% fresh Gibbsite, reduced dissolved to less than 100 mg/L
○ Important Process parameters:
  ○ pH
    ○ Reaction Time
    ○ Ca : SO₄ ratio & Al : SO₄ ratio
    ○ Sludge recirculation with an optimized Solids ratio
    ○ Mass of solids in the recycle line per mass of solids generated by the fresh wastewater
Thank You!
## Cost Comparison ($/1,000 gal) Chemical & Power

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Unit Cost U.S. $/ton</th>
<th>EVP/Crys(^{(a)})</th>
<th>IX(^{(a)})</th>
<th>Ettringite with Gibbsite Recovery(^{(b)})</th>
<th>Ettringite without Gibbsite Recovery(^{(b)})</th>
<th>Outotec Process</th>
<th>BaCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda Ash (100% Pure)</td>
<td>300</td>
<td>1.99</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Sulfuric Acid (100% Pure)</td>
<td>280</td>
<td>0.2</td>
<td>1.85</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Lime (100% Pure)</td>
<td>180</td>
<td>0</td>
<td>1.08</td>
<td>0.97</td>
<td>1.02</td>
<td>2.02</td>
<td>0</td>
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<tr>
<td>Flocculant (100% Pure)</td>
<td>5,000</td>
<td>0.01</td>
<td>0.05</td>
<td>0.07</td>
<td>0.05</td>
<td>0.1</td>
<td>0</td>
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<tr>
<td>Power</td>
<td>0.10/kw.hr</td>
<td>1.48</td>
<td>0.27</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
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<tr>
<td>Aluminum Trichloride Hexahydrate (as 23% Al₂O₃)</td>
<td>800</td>
<td>0</td>
<td>0</td>
<td>0.16</td>
<td>2.64</td>
<td>2.64</td>
<td>0</td>
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<tr>
<td>Calcium Chloride (100% Pure)</td>
<td>600</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Hydrochloric Acid (100% Pure)</td>
<td>600</td>
<td>0</td>
<td>0</td>
<td>0.54</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>CO₂ (100% Pure)</td>
<td>200</td>
<td>0</td>
<td>0</td>
<td>0.04</td>
<td>0.04</td>
<td>0.14</td>
<td>0</td>
</tr>
<tr>
<td>BaCl₂ (98% Pure)</td>
<td>2,600</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>41.5</td>
</tr>
<tr>
<td>Na₂Al₂O₄ (20% Al₂O₃)</td>
<td>400</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.86</td>
<td>0</td>
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<tr>
<td>Total $/1,000 gal (€/m³)</td>
<td>3.68 (€0.71)</td>
<td>3.25 (€0.63)</td>
<td>1.98 (€0.38)</td>
<td>3.85 (€0.75)</td>
<td>7.21 (€1.38)</td>
<td>41.6 (€8.07)</td>
<td></td>
</tr>
</tbody>
</table>


\(^{(b)}\) Pilot Study conducted by Veolia Water Solutions & Technologies, 2011-2012.