Wisconsin Case Studies: Using Rare Earth Chloride to Reduce Phosphorus to Ultra-Low Limits

By: Joseph Carlston
Product Development Scientist

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Discussion Outline

- **Rare Earth Technology Introduction**
  - What are rare earths?
  - Rare earths vs. traditional P removal

- **Preliminary Lab Studies**

- **Plant Trials**
  - Equipment Set-up
  - Facility processes
  - Trial results

- **Conclusions / Summary**
Rare earth elements are located in the lanthanide series (plus Sc and Y) of the periodic table.

- Most prominently known for high strength, permanent magnets
- Unique reactivity with oxyanions, such as phosphate
Typical Rare Earth Markets

**Chemicals & Oxides**
- Automotive (catalysts)
- Ceramics
- Chemical catalysts
- Consumer electronics
- Glass polishing
- Internal sales of magnetic materials
- NiMH Batteries
- Petroleum refining
- Phosphors / Displays / Energy Efficient Lighting
  - Pigments
- Wastewater Treatment

**Magnetic Materials**
- Automotive
- Computing / Networking
- Consumer electronics
- Home Appliances
- HVAC systems
- Industrial Automation
- Office Automation
- Renewable Energy Systems
- Telecommunications

**Rare Metals**
- Aerospace
- Catalysts
- Electronics
- LED Lighting
- Lithium Batteries
- Phosphors / Displays
- Solar Power Cells
- Super Alloys
- Superconductivity platforms
- Wireless Communications
Uses for Lanthanum & Cerium

Traditional Markets
- Glass Polishing
- Hybrid Vehicle Batteries
- Catalytic Converters
- Advanced Optics

Emerging Markets
- Recreation Water
- Wastewater
Why RE is different than traditional coagulants

- Precipitate is CePO$_4$ (Rhabdophane)
- Forms ionic bonds
- Preferentially reacts with phosphorus
- Achieves a 1:1 molar ratio of Ce:PO$_4$

Forms Fe/AlOOH and Fe/Al(OH)$_3$ intermediates to adsorb P

Phosphate adsorbs on the surface of the floc (surface chemistry)
• Rare earth chloride solution

• Active Ingredient: Cerium Chloride (CeCl$_3$)
  – Concentration: 31.5%

• Density: 12.4 lbs/gal

• Freezing Point: -40°C

• pH: 3.5
  – Non-hazardous rating

• Compatible with existing equipment
Molar Ratios of Coagulants Versus Final Concentration P
2.5 mg/L PO₄-P Starting Concentration

- CeCl₃
- FeCl₃
- Fe₂(SO₄)₃ (as Fe)
- Alum (as Al)
- PAC (as Al)
- AlCl₃ (as Al)
- ACH (as Al)
Molar Ratios of Coagulants Versus Final Concentration P
1 mg/L PO₄-P Starting Concentration

- CeCl₃
- FeCl₃
- Fe₂(SO₄)₃ (as Fe)
- Alum (as Al)
- PAC (as Al)
- AlCl₃ (as Al)
- ACH (as Al)
Coagulant Comparison – Varying Initial P

Coagulant Required to Reduce P to 0.1 mg/L

Molar Ratio of Metal Required (Ce/Fe/Al:P)

Initial P Concentration (mg/L PO₄-P)
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Molar Ratio REE:P</th>
<th>RECl₃ Dosage (ppmᵥ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.83</td>
<td>7</td>
</tr>
<tr>
<td>20</td>
<td>0.80</td>
<td>7</td>
</tr>
<tr>
<td>40</td>
<td>0.85</td>
<td>7</td>
</tr>
</tbody>
</table>
Effluent Toxicity Testing

- Sample tested: Secondary clarifier effluent
- Phosphorus Level: Spiked to 2 mg/L PO$_4$-P using NaH$_2$PO$_4$
- Treated with CeCl$_3$ at volumetric dose rate of 50 ppm$_v$
- Filtered and unfiltered samples submitted for acute whole effluent toxicity testing

<table>
<thead>
<tr>
<th></th>
<th>Water Flea</th>
<th>Fathead Minnow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Filtered</td>
<td>Unfiltered</td>
</tr>
<tr>
<td>NOEC Value</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>LC$_{50}$ Value</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
<tr>
<td>TU$_a$ Value</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
</tr>
</tbody>
</table>
Samples Tested:
- Secondary clarifier effluent (spiked to 2 mg/L PO$_4$-P)
- Centrifuge centrate (117 mg/L PO$_4$-P)

Treated with CeCl$_3$ at dose rates of:
- 50 ppm$_v$ for secondary clarifier effluent
- 3,000 ppm$_v$ for centrifuge centrate

Unfiltered samples submitted for extraction testing via CalWET procedures
<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Secondary Clarifier Effluent</th>
<th>Centrifuge Centrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>0.91 mg/L</td>
<td>1.5 mg/L</td>
</tr>
<tr>
<td>Inorganics: Sb, As, Ba, Be, Cd, Total Cr, Hex. Cr, Co, Cu, Pb, Hg, Mo, Ni, Se, Ag, Tl, V, Zn</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Pesticides</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Polychlorinated Biphenyls</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Herbicides</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Volatiles</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Bases/Neutrals/Acids (Semi-volatiles)</td>
<td>BDL</td>
<td>BDL</td>
</tr>
</tbody>
</table>
Field Trials – Equipment Set-up
• 45 MGD municipal WWTP in Mid-Atlantic US
• Total phosphorus limit of 0.18 mg/L P
  – Target of 0.10 mg/L P
• Interested in seeking new coagulant with lower consumption rate, less chemical solids produced, and less staining of UV
• CeCl$_3$ maintained phosphorus below limit with dosage rate 3x less than FeCl$_3$
• Ferric usage: 34 ppm$_v$ = molar ratio 3.4:1 Fe/P
• CeCl$_3$ usage: 11 ppm$_v$ = molar ratio 0.7:1 Ce/P
- 2 MGD municipal WWTF located in Wisconsin
- Total P limit of 1.0 mg/L
  - New limit of 0.075 mg/L being enacted
- Used ferrous chloride (FeCl$_2$) for chemical P removal
- Was unable to meet new TP limits with iron coagulant
Hartford achieved < 0.03 mg/L effluent

- CeCl$_3$ maintaining ave. effluent TP < 0.03 mg/L with dose rate of 120 GPD
- Historical ferrous usage required 125-250 and only reduced TP to ave. of 0.5 mg/L
Hartford, WI Dose Response Curve

CeCl₃ Dosage 0.075 mg/L

Lower dose rate to reach 0.075 mg/L after 3-4 months of CeCl₃ use

Initial dose rate to reach 0.075 mg/L
• 6-8 MGD municipal WWTF located in Wisconsin
• Total P limit of 1.0 mg/L
  – Future permit as low as 0.04 mg/L TP
• Used aluminum sulfate (Al₂(SO₄)₃) for chemical P removal
• Unable to meet new TP limits with alum
Mixed Liquor sample - settling

<table>
<thead>
<tr>
<th>Initial</th>
<th>1 min</th>
<th>2 min</th>
<th>4 min</th>
<th>5 min</th>
<th>10 min</th>
</tr>
</thead>
</table>

Rapid Coagulation Performance
Plant Effluent – from 3.6 mg/L-PO4 to 0.6 mg/L-PO4 in 48 hours
• Achieved average of 0.15 mg/L TP in effluent for month of December with average of 50 ppm \( \text{v} \) \( \text{RECl}_3 \) dose
• Maintained average effluent TP at 0.6 mg/L with 200 GPD of \( \text{RECl}_3 \) compared to historical dose of about 700 GPD total chemical dose
• Average final sludge total solids increased from 25% to 29%

![Graph showing Fond du Lac, WI Analysis of Waste Sludge]
Observed Benefits of Rare Earth Technology

✓ Able to achieve very low TP discharge limits without capital equipment
✓ Reduced sludge volumes compared to competitive coagulants
✓ Faster coagulation and noticeable impact than competitive coagulants
✓ Less coagulant volume required to reach low phosphorus limits
✓ Improved water clarity due to good coagulation properties
✓ Will not stain or discolor facility structures or equipment
✓ Compatible with existing dosing and filtration equipment
✓ Rated non-hazardous for DOT regulations
• City of Hartford, WI WWTP - Dave Piquett
• City of Fond du Lac WPCP - Jeremy Cramer, Autumn Fisher & team
• Mulcahy Shaw Water
• Ruekert & Mielke, Inc. - Dave Arnott
• Strand Associates - Jane Carlson, Troy Larson
Questions?

Pam Cornish
PCornish@molycorp.com
734-216-2089

Joseph Carlston
JCarlston@molycorp.com