Selecting the Optimal Coagulant to Achieve Low-Level Phosphorus and Metal Limits at the Upper Blackstone Wastewater Treatment Facility

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Upper Blackstone Wastewater Treatment Facility

- Serves 250,000 people in central Massachusetts, including the City of Worcester
- Discharges into the Blackstone River which ultimately flows to the Narragansett Bay
- Designed for 45 mgd ADF and 160 mgd peak hour; 30 mgd current ADF
- Regional biosolids facility
Upper Blackstone’s NPDES Permit Limits

<table>
<thead>
<tr>
<th>Constituent</th>
<th>2012 Permit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Nitrogen (mg/L)</td>
<td>5.0</td>
</tr>
<tr>
<td>Total Phosphorus (mg/L) – 60-day rolling average</td>
<td></td>
</tr>
<tr>
<td>Apr-Oct</td>
<td>0.10</td>
</tr>
<tr>
<td>Nov-Mar</td>
<td>1.0</td>
</tr>
<tr>
<td>Aluminum (µg/L)</td>
<td>87</td>
</tr>
<tr>
<td>Cadmium (µg/L)</td>
<td></td>
</tr>
<tr>
<td>Avg Monthly</td>
<td>0.2</td>
</tr>
<tr>
<td>Max Day</td>
<td>1.5</td>
</tr>
<tr>
<td>Copper (µg/L)</td>
<td></td>
</tr>
<tr>
<td>Avg Monthly</td>
<td>7.2</td>
</tr>
<tr>
<td>Max Day</td>
<td>10.2</td>
</tr>
<tr>
<td>Zinc (µg/L)</td>
<td>91.3</td>
</tr>
<tr>
<td>Lead and Nickel (µg/L)</td>
<td>Report</td>
</tr>
</tbody>
</table>

- **Stringent nutrient limits due to Blackstone River (impaired) and Narragansett Bay (hypoxia)**
- **Currently operating under interim limits**
  - TN of 6 mg/L
  - TP of 0.45 mg/L
- **Meet metals limits but not TP limit**
- **Challenging combination of TP and metals limits**
Upper Blackstone’s Adaptive Management Approach

Current Process Configuration:

- No chemical addition or tertiary process for TP removal
- Requires additional process to achieve TP limit

Proposed Process Configuration for TP:

- Requires coagulant addition and add-on process to achieve < 0.1 mg/L TP
EBPR Performance

- 50th Percentile = 0.20 mg/L
- 90th Percentile = 0.49 mg/L
- 50th Percentile = 0.54 mg/L
- 90th Percentile = 1.00 mg/L

Apr to Oct 2010-2012
Apr to Oct 2013-2016
Steps Toward Achieving 2012 TP Permit Limit

- Interim Measures
- Nutrient Facilities Plan
- **Bench-Scale Testing**
- Pilot-Scale Testing
- Full Scale Implementation of Tertiary Phosphorus Removal Technology
Bench Scale Testing Protocol

- Blueleaf, Inc. conducted a series of jar tests on secondary effluent
  - If TP<0.2 mg/L, spiked with anaerobic zone mixed liquor to achieve 0.2 mg/L TP
- Six coagulants tested at varying Me:TP-removed ratios and pH levels
  - 13 jar tests for each coagulant
- Coagulated samples filtered through 1.5 µm filter and analyzed for TP
- Effluent TP objective = 0.08 mg/L
  - 80% of permitted TP value
- Response surface charts created using results
- Sulfide-based polymer tested at 1 coagulant dose with varying polymer doses
Response Surface Testing Approach

- Evaluates the effect of two independent variables on a dependent variable, when two independent variables interact.

Center point tested with 5 replicate jars to evaluate variability

Each of the 8 perimeter points represent one jar test (a particular coagulant dose and pH level)

![Diagram showing Molar Ratio (Metal:TP) vs. pH with data points and center point marked.](image-url)
Chemicals
Aluminum-Based Coagulants

- Coprecipitates/adsorbs phosphorus with Al-hydroxide floc with phosphates
  - Surface chemistry
- Gelatinous floc may not easily settle (less dense than floc formed with iron)
- Unwanted aluminum introduced to wastewater (NPDES Permit)
- Considered PACI and ACH since doesn’t suppress pH as much (as alum)
- Considered ACH due to higher Al content by weight

**Alum (Aluminum Sulfate)**
- $\text{Al}^{3+}$
- $\approx 4.4\% \text{ Al}$

**PACI (Polyaluminum Chloride)**
- $\text{Al}^{3+}$
- $\approx 5.6\% \text{ Al}$

**ACH (Aluminum Chloride Hydrate)**
- $\text{Al}^{7+}$
- $\approx 12.4\% \text{ Al}$
Iron-based Coagulants

- Coprecipitates/adsorbs phosphorus with Fe-hydroxide floc with phosphates that settle
  - Surface-chemistry
- Iron-based floc are more dense than aluminum-based floc, can settle more easily
- Can cause reddish brown staining on equipment
- Considered ferric sulfate since should have lower copper

Ferric Chloride
Fe$^{3+}$
≈13.5% Fe

Ferric Sulfate
Fe$^{3+}$
≈13.1% Fe
Cerium-Based Coagulant

- Cerium (rare earth metal) forms a crystalline solid precipitate with phosphorus
  - Forms strong ionic bonds
- Effective at lower molar ratios (as low as 1:1)
- Reduced chemical usage and sludge
  - Proven at pilot studies in Mid-West
- Distributed by NeoChemicals and Oxides
  - Formerly named SorbX-100
MetClear™ 2405

- Sulfide-based polymer removes heavy metals
- Anionic polymer with sulfide functional groups
  - Solubility of metal sulfide precipitates are much less than metal hydroxide precipitates
  - Metal sulfide precipitates are amphoteric (unlike metal hydroxide precipitates)
- Manufactured by GE
- Typically used for industrial pretreatment applications
  - Low flow, high metals concentrations
- Useful tool to mitigate elevated metals
Results
Alum
(Aluminum Sulfate)

- Achieved TP objective at all molar ratios
  - 9-28 mg/L as Alum
- Most effective at pH <7.0
  - Can be mitigated by higher alum doses
- Molar Ratio=5:1
- Projected annual chemical cost: $34,000/year
PACI
(Polyaluminum Chloride)

- Achieved TP objective at molar ratios >5.5:1
  - 15-46 mg/L as PACI
- Highly Dependent on pH
  - Ineffective at pH > 7.7
- Molar Ratio=10:1
  - Higher molar ratio than alum requirement
- Projected annual chemical cost: $336,000/year
  - Much more expensive than alum
ACH (Aluminum Chloride Hydrate)

- Achieved TP objective at molar ratios >15:1
  - 19 mg/L as ACH
- Ineffective at high pH
  - Ineffective at pH > 7.5
- Molar Ratio=15:1
  - Higher than Alum and PACl
- Projected annual chemical cost: $445,000/year
  - Higher than Alum and PACl
Ferric Chloride

- Achieved TP objective at all molar ratios tested
  - 5-15 mg/L as Ferric Chloride
- Little effect from pH
- Molar Ratio=5:1
  - Similar to Alum
- Projected annual chemical cost: $49,000/year
  - Slightly higher than Alum cost
- Achieved TP objective at molar ratios 10:1
  - 13-19 mg/L as Ferric Sulfate
- More effective at higher pH values
  - Can be mitigated with increased iron doses up to a point
- Molar Ratio=10:1
  - Higher than Ferric Chloride
- Projected annual chemical cost: $159,000/year
  - Much higher than Ferric Chloride cost
RE-100 (Cerium Chloride)

- Achieved TP objective at molar ratios >2:1
  - 3 mg/L SorbX-100
- Ineffective at pH >8.3
- Molar Ratio=2:1
  - The lowest molar ratio of all coagulants
- Projected annual chemical cost: $286,000/year
  - Greater than Alum and iron-based coagulants, but less than PACl and ACH
Coagulation Summary

**Alum**
- Achieved TP objective at all molar ratios
- Effective without pH adjustment
- Estimated Molar Ratio- 5:1 (9 mg/L)
- $34,000/year
  - Least expensive coagulant

**Ferric Chloride**
- Achieved TP objective at all molar ratios
- Little dependence upon pH
- Estimated Molar Ratio- 5:1 (5 mg/L)
- $49,000/year
  - Second least expensive coagulant

**RE-100**
- Achieved TP objective at much lower molar ratios
- Ineffective at pH > 8.3
  - Should not impact UB operations
- Estimated Molar Ratio- 2:1 (3 mg/L)
- $286,000/year
  - Higher cost could be offset by savings attributed to low residuals/solids handling

Coagulants to move forward to sulfide-based polymer testing
Resultant Metal Concentrations

- **Alum** increases **Aluminum**
  - $17 \mu g/L$ vs. $45 \mu g/L$

- No impact on **Cadmium**
  - $0.32 \mu g/L$ vs. $0.26 \mu g/L$

- **FeCl₃** increases **Copper**
  - $3.8 \mu g/L$ vs. $5.0 \mu g/L$
MetClear™ 2405 with Alum

Alum dose = 42 mg/L

Cadmium Reduction: 27%-47%
Independent of Polymer Dose

% Metal Reduction

Polymer Dose

0.25 mg/L  0.50 mg/L  0.75 mg/L  1.00 mg/L
MetClear™ 2405 with Ferric Chloride
Ferric Chloride dose = 24 mg/L

Nickel Reduction: 3%-15%

<table>
<thead>
<tr>
<th>Polymer Dose</th>
<th>Cu Reduction</th>
<th>Cd Reduction</th>
<th>Pb Reduction</th>
<th>Al Reduction</th>
<th>Zn Reduction</th>
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<tbody>
<tr>
<td>0.25 mg/L</td>
<td>52% - 65%</td>
<td>33% - 46%</td>
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<tr>
<td>0.50 mg/L</td>
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<td>0.75 mg/L</td>
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<tr>
<td>1.00 mg/L</td>
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MetClear™ 2405 with RE-100

RE-100 dose = 16 mg/L

Cadmium Reduction: 33%-46%
Key Conclusions

- No pH adjustment required with alum, ferric chloride, and SorbX
- Alum and ferric chloride were the least expensive coagulants
- RE-100 achieved TP goals at the lowest molar ratios, but with higher costs
  - Higher chemical costs could be offset by savings from residuals handling
- MetClear™ 2405 was able to reduce heavy metal concentrations
  - Copper by >50%
  - Cadmium by 30%
  - Nickel (10-20%) from Ferric Chloride and RE-100 samples
  - Aluminum (10-30%) from RE-100 samples
  - Little to no impact on Lead and Zinc Concentrations
Steps Toward Achieving 2012 TP Permit Limit

- Interim Measures
- Nutrient Facilities Plan
- Bench-Scale Testing
- Pilot-Scale Testing
- Full Scale Implementation of Tertiary Phosphorus Removal Technology

Materials:
- Alum
- Ferric Chloride
- RE-100

MetClear™ 2405
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Questions? Contact us!

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