Implementing and Optimizing Chemical Phosphorus Removal

Alyssa Mayer, PE
Agenda

Drivers for Phosphorus Removal
Phosphorus Removal Mechanisms
Chemical Phosphorus Removal
  Principals
  Design Considerations
  Optimization of Chemical Feed with EBPR
Case Study: Upper Mill Creek
Case Study: Fairfield
Drivers for Phosphorus Removal
Eutrophication and Hypoxia

Under natural conditions, phosphorus (P) is a limiting nutrient, which restricts the growth of algae and/or aquatic plants.

**Eutrophication:**
Excess nutrients (either N or P, depending on the water body) lead to an overgrowth of aquatic plants (i.e. algae).

**Hypoxia:**
Low DO conditions in a water body (<2 mg/L \( \text{O}_2 \))
Leads to physiological stress/death of aquatic organisms.
Human activities have resulted in excessive loading of phosphorus into receiving water systems, promoting algae growth.

Impacts on water quality have led regulatory agencies to require phosphorus removal in some WWTPs.
Ohio Phosphorus Removal Feasibility Studies (Senate Bill 1)

Who: Publicly Owned Treatment Works (POTW) with design flow greater than 1 MGD with no phosphorus limit as of July 3, 2015

What: Conduct a study evaluating the technical and financial capability of the existing facility to meet an effluent TP limit of 1 mg/L through:

– Source reduction measures
– Operational changes
– Treatment process changes

Begin monitoring by Dec. 1, 2016
Submit study by Dec. 1, 2017
Phosphorus Removal Mechanisms
Phosphorus Historically leaves the WWTP in Two Ways

Effluent

Solids
Phosphorus Removal Mechanisms

Biological removal
   Enhanced Biological Phosphorus Removal (EBPR)

Chemical removal
   Addition of metal salts to promote precipitation

Physical removal
   Settling in a solids separation unit
   Filtration

Also...
Recovery
   Intentional formation of a P product for reuse
Wastewater Phosphorus Speciation & Removal Methods

Total Phosphorus

Ortho-Phosphate

Poly-phosphate

Organically Bound

Particulate Phosphorus

Biodegradable Soluble

Inert Soluble

Biological P Removal

Chemical P Removal

Solids Separation

Chemical Coagulation Adsorption

Cannot Remove
Impact of Phosphorus Speciation

Expected 0.075 mg/L Effluent TP Limit

An Effluent TP limit of 1mg/L is typically achievable through **EBPR** and/or **Chemical Removal**.
## Hierarchy of Treatment Priorities

<table>
<thead>
<tr>
<th>Nutrient Removal Process</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrification</td>
<td>- Meet required aerobic SRT</td>
</tr>
<tr>
<td></td>
<td>- Most effective option (breakpoint chlorination, stripping)</td>
</tr>
<tr>
<td>Denitrification</td>
<td>- TN, TIN or NOx-N limits</td>
</tr>
<tr>
<td></td>
<td>- Influent org-C for denitrification</td>
</tr>
<tr>
<td></td>
<td>- Most effective option (add-on processes w/ chemicals)</td>
</tr>
<tr>
<td>Phosphorus Removal</td>
<td>- EBPR</td>
</tr>
<tr>
<td></td>
<td>- Chem-P</td>
</tr>
</tbody>
</table>
Chemical Phosphorus Removal
Chem-P Application “Check List”

Solids Handling
- Intermittent dewatering
- Anaerobic digestion

Nitrogen Limits
- Aerobic volume
- TN/TIN/NOx-N

Secondary Clarifiers
- High blankets
- SLR

TP < 1.0
## Chem-P Removal
### Advantages and Disadvantages

#### Advantages
- Not biologically based performance
- Reduces sidestream impacts
- Particulate removal
- Low effluent TP
- Low capital costs

#### Disadvantages
- Higher solids production
- Impacts to digestion VSR
- Alkalinity consumption
- Potential overdosing
- Higher operational costs
Principles of Chemical Phosphorus Removal
Principles of Chemical Phosphorus Removal

Classical approach – precipitation of MePO$_4$

$$\text{Me}^{3+} + \text{PO}_4^{3-} \leftrightarrow \text{MePO}_4^{(S)}$$

No longer thought to be primary mechanism in WW treatment

Updated theory – Surface Complexation Model (SCM)

PO$_4$-P adsorption to metal oxides/hydroxides dominant mechanism for chemical P removal

Potential for direct precipitation at high Me and P concentrations, and low pH conditions
Chem-P Removal Mechanism

1. Dose chemical
2. Rapid mix to disperse chemical
3. Hydrous metal oxide (HMO) particles form
4. PO$_4$ binds to HMO particles
5. HMO floc form
6. HMO floc trap additional PO$_4$
7. PO$_4$ surface adsorption to HMO floc
8. Solids settle in clarifier
## Common Chem-P Removal Chemicals

- Typically, Al or Fe metals

<table>
<thead>
<tr>
<th>Aluminum Based</th>
<th>Iron Based</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum sulfate ( \text{Al}_2(\text{SO}_4)_3\cdot14\text{H}_2\text{O} )</td>
<td>Ferric chloride</td>
</tr>
<tr>
<td>Sodium aluminate ( \text{Na}_2\text{Al}_2\text{O}_4 )</td>
<td>Ferrous chloride</td>
</tr>
<tr>
<td>Poly-aluminum chloride (PACL, PAX) ( \text{Al}_n\text{Cl}(3n-m)(\text{OH})_m )</td>
<td>Ferrous sulfate</td>
</tr>
</tbody>
</table>
What are all of these values?

Stoichiometric Example

\[ 1\text{FeCl}_3 + 1\text{PO}_4^{3-} \leftrightarrow 1\text{FePO}_4(S) + 3\text{Cl}^- \]

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Dose as FeCl$_3$</th>
<th>Dose as Fe$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dosing Ratio</td>
<td>FeCl$_3$ : P</td>
<td>Fe : P</td>
</tr>
<tr>
<td>Mole Ratio</td>
<td>1 : 1</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Weight Ratio</td>
<td>5.2 : 1</td>
<td>1.8 : 1</td>
</tr>
<tr>
<td>Solution Specific Weight</td>
<td></td>
<td>11.4 lb solution / gal</td>
</tr>
<tr>
<td>Strength</td>
<td>35% as FeCl$_3$</td>
<td>12% as Fe$^{3+}$</td>
</tr>
<tr>
<td>Density</td>
<td>4.0 lb as FeCl$_3$ / gal</td>
<td>1.4 lb as Fe$^{3+}$ / gal</td>
</tr>
<tr>
<td>Volumetric Dosage</td>
<td>1.3 gallon solution / lb P removed</td>
<td></td>
</tr>
</tbody>
</table>

Be consistent as either chemical or metal !!!!!
Typical Chemical Properties

- **Alum**: 8% Active Metal, 48% Chemical Strength, 44% Water
- **Sodium Aluminate**: 13% Active Metal, 38% Chemical Strength, 50% Water
- **PACI**: 9% Active Metal, 32% Chemical Strength, 59% Water
- **Ferric Chloride**: 12% Active Metal, 35% Chemical Strength, 53% Water
- **Ferrous Chloride**: 11% Active Metal, 25% Chemical Strength, 64% Water
- **Ferrous Sulfate**: 5% Active Metal, 25% Chemical Strength, 70% Water
Design Considerations
Typical Chem-P Dosing Requirements

Chemical Usage (gallons of chemical/lb TP removed)

<table>
<thead>
<tr>
<th>Effluent TP Goal</th>
<th>Stoichiometric</th>
<th>1.0 mg/l P</th>
<th>0.5 mg/l P</th>
<th>0.1 mg/l P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1.5</td>
<td>3.0</td>
<td>8.0</td>
</tr>
<tr>
<td><strong>Alum</strong></td>
<td><strong>Ferric</strong></td>
<td><strong>Alum</strong></td>
<td><strong>Ferric</strong></td>
<td><strong>Alum</strong></td>
</tr>
<tr>
<td><strong>+50%</strong></td>
<td><strong>+50%</strong></td>
<td><strong>+150%</strong></td>
<td><strong>+500%</strong></td>
<td></td>
</tr>
</tbody>
</table>
Factors that Increase Dosing Requirement

- Presence of organic material
  - Interference with HMO binding sites
- Elevated pH
  - Ideal range 5.5 – 7.0
- High soluble P concentrations
  - More TP to remove
- Mixing intensity
  - Too much – Shear HMO floc and reduces settling
  - Too little – Inadequate dispersion of chemical
Jar Testing

Compare multiple types of coagulant to identify the best fit for specific wastewater.

Verify site-specific dosing to obtain a more accurate estimate of chemical costs.
Multi-Point Chemical Addition

- Primary clarifiers (dose at Q)
- Secondary clarifiers (dose at Q + RAS)
- Filters (final polishing)
- Recycle streams (dose concentrated load)
## Chem-P Removal Design Considerations

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials of Construction</td>
<td>Most are corrosive (low pH) FRP, plastic and lined steel</td>
</tr>
<tr>
<td>Storage Crystallization</td>
<td>May require heated tanks, heat tracing or in building</td>
</tr>
<tr>
<td></td>
<td>• 35% ferric ~ -42°F</td>
</tr>
<tr>
<td></td>
<td>• 42% ferric ~ 20°F</td>
</tr>
<tr>
<td></td>
<td>• 8% alum ~ 32°F</td>
</tr>
<tr>
<td>Mixing</td>
<td>G-value &gt; 200 s⁻¹</td>
</tr>
<tr>
<td>Pacing</td>
<td>• Peristaltic or diaphragm metering pumps</td>
</tr>
<tr>
<td></td>
<td>• Flow pacing may overdose (I/I or variable P-conc)</td>
</tr>
<tr>
<td></td>
<td>• TP pacing at higher cost</td>
</tr>
</tbody>
</table>
Chemical Costs for P Removal Increase Dramatically as Effluent Limit Decreases

Chemical P Removal Cost vs. Al:P Molar Ratio

Chemical Costs to Remove PO4-P below 0.1 mg/L

Optimizing EBPR Results in Decreased Chemical Costs

Chemical Costs to Remove PO4-P below 1 mg/L
Enhanced Biological Phosphorus Removal
Specific bacteria (known as Poly phosphate Accumulating Organisms (PAOs)) can sequester high levels of phosphorus by storing it inside their cell as poly-phosphate (poly-P) when cycled through anaerobic and aerobic conditions.

An EBPR process is designed to select for these bacteria and waste them while poly-P content is high (resulting in net removal of phosphorus).
Required Conditions for Enhanced Biological Phosphorus Removal (EBPR)
Anaerobic Zone Sizing

**Anaerobic Zone**
- Selects for PAOs
- HRT 1 – 3 hours
Aeration Control and Prevention of Secondary Phosphorus Release

Aeration Control
• Sufficient aerobic HRT necessary to allow for complete removal of PO4-P
• DO control to match diurnal loading fluctuations

Sludge Blanket Depth Control
• Anaerobic conditions in sludge blankets can result in P release in the clarifiers

Influent

Effluent

Clarifier

PO4-P (mg/L)

INF  ANA  AER1  AER2  AER3  AER4  EFF  RAS
Influent Characteristics

- Influent TP fractions
- Influent Carbon: Phosphorus Ratio
- Volatile Fatty Acid (VFAs) required

Influent Ratios favorable for EBPR
- $\text{BOD:TP} > 25$
- $\text{rBCOD:TP} > 16$
Solid Removal

- Solids removal drives ability to achieve low TP limits
- Tertiary filtration typically not necessary to meet Effluent TP of 1 mg/L; but recommended for limits below 0.5 mg/L

Non-EBPR biomass is approximately 1.5% to 2% phosphorus

PAO biomass can be as high as 8%-12% phosphorus
Chemical Trim

Facilities with EBPR processes should include provisions to remove P by chemical addition.

Achievable effluent concentrations:
- Typically 0.5 mgP/L (without tertiary filtration)
- Can be lower with optimized addition and solids separation

Warning: Overfeeding chemical can shut down PAOs
Case Study –
Upper Mill Creek
Plant Overview

Capacity: 16 mgd

Two Oxidation Ditch Trains

Biological Nitrogen and Phosphorus Removal with Chemical Trim

Current effluent nutrient limits:

1 mg/L NH3-N (summer), 3 mg/L (winter)
5 mg/L NOx-N
1 mg/L TP

- Historical Plant Data Review
- Industrial Discharger Data Review
- Detailed Sampling and Bench Scale Testing
- Process Model Development
Historical Data Revealed Variable Influent Phosphorus Loading and Marginal Carbon

[Graph showing fluctuating data points with trends for Influent TP Concentration (mg/L) and Influent BOD:TP Ratio.]
Sampling and Modeling Revealed Operational Optimization Opportunities

Overfeeding Chemical Results in shut down on PAOs

DO sag under high loading period results in P release
Summary of Recommendations

**Influences**

- Variable influent P from industries
- Variable influent P from sidestreams
- Periods of low COD:TP
- DO sags in Ox. Ditches during high demand
- Over/under with sodium aluminate

**Optimization Suggestions**

- Work with SIUs to reduce phosphorus discharges
- Increased process control sampling
- Higher capacity sodium aluminate feed
- Move sampling location for sodium aluminate prior to feed
Case Study – Fairfield
### Plant Overview

<table>
<thead>
<tr>
<th>Unit Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permitted Capacity</td>
<td>10 mgd</td>
</tr>
<tr>
<td>Primary Clarifiers</td>
<td>Yes</td>
</tr>
<tr>
<td>Treatment</td>
<td>CAS</td>
</tr>
<tr>
<td>Stabilization</td>
<td>Anaerobic Digestion</td>
</tr>
<tr>
<td>Dewatering</td>
<td>Belt Press</td>
</tr>
</tbody>
</table>

- Currently no TP limit (eff TP 2 – 3 mg/l)
- Proactively evaluating improvements for 1 mg/l TP
2014 Bio-P Evaluation Summary

BioWin Model developed to evaluate phosphorus removal options:

Both EBPR and Chemical Addition were considered viable options to meet an effluent TP of 1 mg/L

**EBPR**
- Higher Capital Cost
  - New Anaerobic Tank
  - New Pump Station
- Significant contribution of filtrate P due to digestion requires chemical trim
- Anaerobic selector results in improved settling, addressing a current capacity limitation

**Chemical Addition**
- Higher operating cost
  - Sodium Aluminate
  - Increased sludge production
2015 Full Scale Chemical P Removal Pilot

Fairfield conducted chem-P study with Sodium Aluminate
Feed locations: Raw Influent, Belt Press Filtrate
Sample locations: Influent, Effluent, Filtrate (Pre- & Post-chem add.)
Sample type: Unfiltered and 0.45-micro filtered
Chem-P Pilot Results

No Chem | Filtrate Only | Filtrate + Influent

<table>
<thead>
<tr>
<th>Days</th>
<th>0</th>
<th>7</th>
<th>14</th>
<th>21</th>
<th>28</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Phosphorus (mg/l)</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Influent | Effluent
Chem-P Pilot Results

<table>
<thead>
<tr>
<th>Location</th>
<th>Dosage (lb Al(^{3+}) / lb TP removed)</th>
<th>Overall Chemical Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>0.87</td>
<td>100%</td>
</tr>
<tr>
<td>Filtrate</td>
<td>2.74</td>
<td>32%</td>
</tr>
<tr>
<td>Influent</td>
<td>1.65</td>
<td>52%</td>
</tr>
<tr>
<td>Total</td>
<td>1.85</td>
<td>47%</td>
</tr>
</tbody>
</table>

- Filtrate efficiency lower than typical (inadequate reaction time)
- Influent efficiency higher than typical (filtrate underestimation)
Summary

Chemical phosphorus precipitation can reduce effluent phosphorus concentrations below 1 mg/L.

Dosage could be optimized across the two feed points.

But significant capital and operating costs.
Questions?

Alyssa Mayer, PE
amayer@hazenandsawyer.com
513-469-5135 (direct)
Bullpen
## Chemical Properties of Common Coagulants

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Alum</th>
<th>PACI</th>
<th>ACH</th>
<th>Sodium Aluminate</th>
<th>Ferric Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical solution strength</td>
<td>48%</td>
<td>32%</td>
<td>45%</td>
<td>38%</td>
<td>35%</td>
</tr>
<tr>
<td>Solution strength as % Al³⁺ or Fe³⁺</td>
<td>4.4%</td>
<td>9.0%</td>
<td>13.9%</td>
<td>12.5%</td>
<td>12%</td>
</tr>
<tr>
<td>Typical solution density, lb/gal</td>
<td>11.1</td>
<td>10.8</td>
<td>11.1</td>
<td>12.7</td>
<td>11.4</td>
</tr>
<tr>
<td>lb Me³⁺/gal solution</td>
<td>0.49</td>
<td>0.97</td>
<td>1.55</td>
<td>1.59</td>
<td>1.37</td>
</tr>
<tr>
<td>Alkalinity consumed, g CaCO₃/ g chemical</td>
<td>0.51</td>
<td>0.52</td>
<td>0.29</td>
<td>(-) 0.61</td>
<td>0.92</td>
</tr>
<tr>
<td>Alkalinity consumed, g CaCO₃/ g Me³⁺</td>
<td>5.6</td>
<td>1.9</td>
<td>0.93</td>
<td>(-) 1.9</td>
<td>2.7</td>
</tr>
</tbody>
</table>
Steps to Evaluate Feasibility
Phosphorus Monitoring

Historical Data Review (Carbon, Phosphorus Loading, if available)

Wastewater Sampling
  Influent Characterization
  Effluent
  Sidestreams
Look for Optimization Strategies with Existing Infrastructure

Influent source control (industry)
Create anaerobic zones within existing tanks?
P release in storage tanks?
Major sidestream loads that could be reduced?

Can your facility meeting 1mg/l right now, without major capital upgrades? – IF YES, then DONE
Evaluate Improvements to Reduce P

EPBR – Anaerobic Zone Addition

- HRT ~1-3 hours
- Create within existing tanks?
- Build new tanks?

Chemical P Removal

- Identify the best chemical for your facility
- Rule of Thumb feed rates (ie Ferric 1.3 gal/lb P removed)
- Chemical storage / feed
Bench Scale Testing – The Next Level

Chemical Phosphorus Removal Jar Tests

Microscopic Analysis

Biological Phosphorus Release and Uptake Testing
If You Want to Go Further with Evaluation-Process Modeling

Model can be used to evaluate:

- Feasibility of Enhanced Biological Phosphorus Removal (EBPR)
- Energy optimization opportunities
- Impacts of chemical phosphorus removal on entire plant
Determine Costs for Alternatives

Capital
1. New tankage and equipment
2. Chemical storage and feed equipment

O&M (expressed as monthly cost for OEPA form)
1. Chemicals
2. Energy
3. O&M changes
Funding Available for Nutrient Removal Projects

• Funds cover the project portion related to nutrient reduction
• Priority is given to the Lake Erie Watershed or other OEPA-identified watersheds with excessive nutrients
• Nominations may be submitted through the end of 2017
• A Nutrient Reduction Project Addendum must be submitted with WPCLF application
Phosphorus Recovery and Reuse

- Phosphorus is a non-renewable resource
- Natural P-ore diminishing due to growth in last 65 years.
- Price of fertilizer has skyrocketed in past 5 years

(Jasinski, 2006; European Fertilizer Manufacturers Association, 2000)
Limit NO$_3$ and DO Recycle to Maintain Anaerobic Zone

Aeration Control
• Prevent Over-Aeration

Influent

An aerobic zone with a purple shaded area indicating low DO or NO$_3$-N.

Aeration Control

Effluent

Clarifier

Recycles
Maintain control of internal recycles and RAS to prevent excessive oxygen or nitrate entering the anaerobic zone.

Available Carbon for PAOzs Reduced by OHOs

Size of Anaerobic Zone Effectively Reduced

Low DO INFLUENT

RAS

High DO or NO$_3$-N
Increased Load from Sidestreams

**Impact of Sidestreams**
- Digestion or Anaerobic storage results in phosphorus release
- High TP, Low BOD
- Can contribute up to 50% phosphorus load back onto process