Agenda

• Chemical Phosphorus Removal Basics
• Phosphorus Species
• Performance
• Opportunities for Optimization
Phosphorus Species

- Total P
  - Dissolved P
    - Ortho P (Reactive P)
    - Inorganic Condensed P
    - Soluble Organic P
  - Particulate P
    - Particulate Reactive P
    - Particulate Acid Hyd P
    - Particulate Organic P
Fundamental Principle of Phosphorus Removal

There is no airborne (gaseous) form of phosphorus
Fundamental Principle of Phosphorus Removal

There is no airborne (gaseous) form of phosphorus

The exception
Convert to Particulate

Soluble P

Particulate P

Particulate P

Soluble P

SoIP

Liquid

Solid
Typical Chemical Treatment Opportunities

Primary → Secondary → Tertiary → Polish

Solids Processing
## Chemicals used for Phosphorus Precipitation

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Removal mechanism</th>
<th>Effect on pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Sulfate (Alum)</td>
<td>Al₂(SO₄)₃.14.3(H₂O) M.W. = 599.4</td>
<td>Metal hydroxides</td>
<td>removes alkalinity</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>FeCl₃ M.W. = 162.3</td>
<td>Metal hydroxides</td>
<td>removes alkalinity</td>
</tr>
<tr>
<td>Poly Aluminum Chloride</td>
<td>AlₙCl₃ₙ₋₃m(OH)ₘ M₁₂Cl₁₂(OH)₂₄</td>
<td>Metal hydroxides</td>
<td>none</td>
</tr>
<tr>
<td>Ferrous sulfate (pickle liquor)</td>
<td>Fe₂SO₄</td>
<td>Metal hydroxides</td>
<td>Removes alkalinity</td>
</tr>
<tr>
<td>Lime</td>
<td>CaO, Ca(OH)₂</td>
<td>Insoluble precipitate</td>
<td>Raises pH to above 10</td>
</tr>
</tbody>
</table>
Ferric Reaction with Phosphorus

The following illustrates a “stoichiometric reaction” of Fe+++ with P.

\[ \text{FeCl}_3 + \text{H}_3\text{PO}_4 = \text{FePO}_4 + 3\text{HCl} \]

1 mole of Fe reacts with 1 mole P.

\[ \Rightarrow 5.2 \text{ mg ferric per mg P} \]
\[ \Rightarrow 0.92 \text{ mg alkalinity per mg of ferric} \]
Alum Reaction with Phosphorus

The following illustrates a “stoichiometric reaction” of $\text{Al}^{+++}$ with $\text{P}$

$$\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 2\text{H}_3\text{PO}_4 \rightarrow$$

$$2\text{AlPO}_4 + 3\text{H}_2\text{SO}_4 + 18\text{H}_2\text{O}$$

2 mole of Al reacts with 2 mole P (or 1 mole Al per mole P)

$\Rightarrow$ 9.6 mg alum per mg P
$\Rightarrow$ 0.5 mg alkalinity per mg of Alum
Phosphorus Removal

Initial removal - Stoichiometric

Equilibrium control – need higher dose

Break ~ 1 mg/L
Molar Dose Ratio From Tests

- Slav Hermanowicz, Chemical Fundamentals of Phosphorus Precipitation,
  WERF Boundary Condition Workshop, Washington DC, 2006
Exact Molar Ratios Versus Effluent Soluble P will Vary with Applications

- 1.5 to 2.0 Molar ratios for 80-98 percent removal
- 5.0 to 7.0 Molar ratios for higher efficiency and to reach low minimal soluble P concentrations
- Ratios are higher with PAC
- Factors that influence ratios
  - pH
  - Mixing method
  - Wastewater characteristics
    - Colloids and solids effect P-metal hydroxide complexations
    - Organic substrates
    - Iron and aluminum can react with humic substances
Kinetics and Mixing of Phosphorus / Alum Reaction

Szabó et al. (2006) The Importance Of Slow Kinetic Reactions In Simultaneous Chemical P Removal, WEFTEC 2006
Photomicrographs of Phosphate Precipitants

What is REALLY Forming?
pH 7 --> pH 3
Fresh HFO
FePO$_4$ precipitant

After 4 days.
Aged HFO

HFO precipitants
After 2 years.
Hard!!

Scott Smith, Wilfrid Laurier University
Metal Hydroxide Removal of P Found for Ferric Addition

- Metal hydroxide formed
- Co precipitation of P into hydrous ferric oxides structure
  - $\text{Fe(OH)}_3, \text{Fe(OH)}_4^-$
- Surface complexation between P and metal hydroxide compounds
- Phosphorus and Iron share oxygen molecule:
  - $\text{FeOOH} + \text{HOPO}_3 = \text{FeOOPO}_3 + \text{H}_2\text{O}$
- Hydroxide formation can be simply represented:
  - $\text{FeCl}_3 + 3\text{H}_2\text{O} \Rightarrow \text{Fe(OH)}_3 + 3\text{HCl}$
  - $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 3 \text{H}_2\text{O} \Rightarrow 2\text{Al(OH)}_3(s) + 3\text{H}_2\text{SO}_4$
Closer Look at the Chemical Species
Phosphorus Speciation and Removal in Advanced Wastewater Treatment

L. Liu, D. S. Smith, D. Houweling
J.B. Neethling, H.D. Stensel
S. Murthy, Amit Pramanik and A. Z. Gu
Analytical Definitions of Phosphorus Species

- Filterable/nonfilterable (soluble?)
  - Passing through filter paper
  - Could be colloidal (very small particles)
- Reactivity to analytical procedure
  - Measure for orthophosphate
- Pretreatment (acid hydrolisis, digestion, etc)
  - Convert larger molecules to be reactive (orthophosphate)
Phosphorus Species Categories

Total P

Dissolved P
- Ortho P (Reactive P)
- Inorganic Condensed P
- Soluble Organic P

Particulate P
- Particulate Reactive P
- Particulate Acid Hyd P
- Particulate Organic P
Particulate Chemical Precipitant Measures as Reactive P

Combined Secondary Effluent-Jar Testing Results

- P in = 0.31 mg/L

- Graph shows the relationship between Alum Dose (Al₂(SO₄)₃·14H₂O) and Effluent ortho-P (mg/L)
  - Filtered and unfiltered results are depicted

- Alum Dose range: 0 to 50 mg/L
- Effluent ortho-P range: 0 to 0.35 mg/L
Analytical Definition Based Phosphorus Fractions/Species

Method

Total P

Dissolved P
- Sol Reactive P (SRP)
- Sol Acid Hydrolyzable
- Sol Dig.

Particulate P
- PRP
- Part Acid H.
- Particle Digestible

Ortho P
- Inorganic Condensed P
- Sol Org

Colloidal P

Particulate Organic P

Chemical particulate P
Nonreactive Phosphorus

Total P

Dissolved P
- Sol Reactive P (SRP)
- Sol NonReactive P (SNRP)

Particulate P
- PRP

Particulate NonReactive P

Total Reactive P

Total NonReactive P
Analytical Definition Based Phosphorus Fractions/Species

- Total P
  - Dissolved P
    - Sol Reactive P (SRP)
    - Sol Non Reactive P (sNRP)
  - Particulate P
    - Ortho P
    - Acid Hydrolyzable P
    - Sol Org
    - Part Chemical P
    - Part Organic P
    - Colloidal P
Secondary Effluent TSS adds to Particulate NRP

Particulate Nonreactive Phosphorus, μg/L
TSS, mg/L

1.0% 1.5% 2.0% 2.5% 3.0%

160

1.5%

3%

5
Filtered Effluent TSS adds to Particulate NRP

- Particulate Nonreactive Phosphorus, ug/L
- TSS, mg/L

- 1.0%
- 1.5%
- 2.0%
- 2.5%
- 3.0%

35 ug/L
1 mg/L
Pilot Study Results Illustrated Challenges at Limits of Technology

- No Treatment Technology Available for SNRP
- Portion May Not Be Bioavailable / Biodegradable

Phosphorus [mg/L]

<table>
<thead>
<tr>
<th></th>
<th>DSBP</th>
<th>THS-1</th>
<th>ZW-500</th>
<th>DSD2</th>
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<tbody>
<tr>
<td>sRP</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>sNRP</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>pP</td>
<td></td>
<td></td>
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Neethling et al, 2007
Effluent P Fractions From Advanced Tertiary Treatment Processes

Lui, Gu, et al. (ongoing) Phosphorus Speciation and Removal in Advanced Wastewater Treatment, WERF Report
sAHP seems to remain after BNR, associated with biomolecules

Chemical addition converts sRP into pRP

Chemical sRP (PO$_4$) removal relies pRP removal
Plant P and N are similar as (BNR+sedimentation +Filtration): composition very different

DOP dominant soluble fraction; pAHP major particulate form

Multi stage barrier remove TP to lower level
Opportunities for Optimization
Opportunities for Improvement

- Improve understanding of chemical kinetics
  - Dose relationships
  - Reuse formed metal hydroxides
- Enhance solids separation
Molar Dose Ratio From Tests

![Graph showing molar dose ratio from tests with Al/P and Fe/P ratios plotted against ortho P res (mg/L). The graph includes data points for different pH levels and full scale data.]
**Single Step Chemical Addition Requires High Dose**

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Two Step Chemical Addition Reduce Dose

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<td>5</td>
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<td>5</td>
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<tr>
<td>P residual mg/L</td>
<td>0.1</td>
<td>1</td>
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<td>Alum/P dose mol/mol</td>
<td>5</td>
<td>1.5</td>
<td>5</td>
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<tr>
<td>Alum/P dose mg/mg</td>
<td>48</td>
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Reuse Chemical Sludge to Reduce Dose and Increase Reliability

• Return chemical sludge to upstream process
• Build solids inventory – operate in solids contact mode
Conventional Tertiary Chemical P Removal
“ReUse” Chemical Sludge Upstream
Contact Clarification in Tertiary
Coeur d’Alene: Microfiltration and Solids Recycle
Implications for Design and Operation – Coeur d’Alene Pilot

No Solids Inventory

Loss of Alum feed
Implications for Design and Operation – Coeur d’Alene Pilot

With Solids Inventory
Summary and Conclusion - I

- Chemical reactions for phosphorus removal with ferric or alum is a primarily a surface complexation reaction
- Good mixing and contact time is needed to maximize chemical efficiency
- Preformed Metal Hydroxides retain the ability to react and remove phosphate
Summary and Conclusion - II

• Target phosphorus species for effective removal:
  – Precipitate Reactive Phosphorus – Phosphate
    • Increased dose can improve removal
  – Filter particulate fractions
    • High efficiency filters
  – Soluble Non- Reactive P remains difficult to remove

• Reuse metal hydroxides to reduce chemical use