Rare Earth Technology for Low-Level Phosphorus Removal

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Coca Cola and other dark soft drinks contain Phosphoric Acid. Usually as the 3rd or 4th listed ingredient behind water, sugar, and color. Phosphoric acid is added for its flavor characteristics.
Phosphoric acid

Coca Cola has a phosphoric acid concentration of 170mg/L or 170 parts per million. Equivalent to roughly 2 moles of phosphate per liter.
Types of Phosphorus

- Soluble
  - Polyphosphates
  - Organic Phosphates (phospholipids, nucleotides)

- Insoluble
  - Bacteria
  - Algae
  - Biosolids
  - Mineral phosphorus – coagulants, clays, soil
Total Phosphorus (TP) measurement

- **PO$_4^{3-}$**
- **Polyphosphates**
- **Organic Phosphates** (phospholipids, nucleotides)
- **Algae**
- **Bacteria**
- **Mineral phosphorus** – coagulants, clays, soil
- **Biosolids**

- TP is a measure of all elemental phosphorus in an unfiltered sample
- TP = Includes all soluble + insoluble
- TP = Reactive + unreactive phosphorus
Ortho-Phosphorus OP

- OP = Soluble
- OP = Reactive
- Removed by chemical coagulation
Insoluble Phosphorus

- Insoluble phosphorus is removed by .45 um filtration
- Also called particulate phosphorus
- Insoluble phosphorus = Reactive + unreactive
- Removed in clarifier
Soluble Reactive Phosphorus – SRP

- SRP = soluble + reactive
- SRP =/= insoluble or unreactive phosphorus (organic phosphates)
- Removed by chemical coagulation
Soluble Non-reactive Phosphorus (sNRP)

- sNRP = soluble + non-reactive phosphorus
- Calculated from other P measurements (Soluble total P – SRP)
Difficulty of sNRP

Why is SNRP important if it is a small fraction of TP?
• Cannot be removed by filtration
• Cannot be removed by chemical coagulation
• Not available for biofiltration
• A high concentration (>0.3ppm) of sNRP can prevent a facility from ever reaching a permit level
Fond Du Lac SNRP complication

Average SNRP: 0.078 mg/L
Proposed Limit: 0.04 mg/L

FDL SNRP Trend

SNRP (mg/L)

0.3
0.25
0.2
0.15
0.1
0.05
0


SNRP  Proposed Limit  SNRP Average
Stages of Phosphorus Removal

- **Insoluble/particulate Phosphorus** (algae, bacteria, biosolids, soils)
- **Soluble Reactive Phosphorus (SRP)** removed by the coagulant
- **Soluble non-reactive phosphorus (sNRP)**

Chemical coagulant
Recommendations: Planning to meet an upcoming Phosphorus limit.

Measure Phosphorus (OP and TP) at:
- influent
- effluent
- chemical dosing point

once per week, for one to two months and repeat seasonally

Track the phosphorus species and loading
Repeat this data gathering process when trialing a new chemical.
Rare Earths

- Rare earth elements are located in the lanthanide series (plus Sc and Y) of the periodic table
- Most prominently known for high magnetic strength
- Unique reactivity with oxyanions, such as phosphate
Rare Earths in Water Treatment Markets

- Recreation Water
- Aquarium
- Lake Remediation
- Wastewater
**Phosphorus Removal Mechanism**

- Rare earth elements form strong, crystalline bonds with phosphorus
  - Forms insoluble rhabdophane precipitate

- Iron and aluminum based products form amorphous “cloud” in solution
  - Adsorbs phosphate onto metal hydroxide floc
Why RE is different than traditional coagulants

- Precipitate is CePO$_4$ / LaPO$_4$ (Rhabdophane)
- Forms ionic bonds
- Preferentially reacts with phosphorus
- Achieves a 1:1 molar ratio of Rare Earth:PO$_4$ → Reduced chemical sludge

- Forms Fe/AIOOH and Fe/Al(OH)$_3$ intermediates to adsorb P
- Phosphate adsorbs on the surface of the floc (surface chemistry)
Fe / Al Molar Dose Ratio

Molar Dose Ratio From Tests

Aluminum (Al)  Iron (Fe)

Molar ratio of Fe / Al based coagulants greatly increases as target phosphorus level decreases

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Coagulant Comparison – 2.5 mg/L

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)

Phosphorus Concentration (mg/L PO₄-P)

Molar Ratio (Ce,Fe,Al):P

0.0

0.5

1.0

1.5

2.0

2.5

0

2

4

6

8

10
Molar Ratios of Coagulants Versus Final Concentration P
1 mg/L PO₄²⁻-P Starting Concentration

- CeCl₃
- FeCl₃
- Fe₂(SO₄)₃ (as Fe)
- Alum (as Al)
- PAC (as Al)
- AlCl₃ (as Al)
- ACH (as Al)
Molecules in solution are flowing around and colliding with one another constantly in 3 dimensionals.
As the concentration of PO4 decreases, the probability of collision between PO4 and metal molecules decreases.
Rare Earth Technology used in Wastewater Industry

- Introduced in 2013 as SorbX
- Has been used in over 50 facilities in over 20 states, including Wisconsin, Virginia, Pennsylvania, New York, Minnesota, Vermont, Ohio, Illinois, Wisconsin, Indiana, Texas, Washington, Idaho, Georgia, Florida, Utah, California
- Proven effective for meeting low phosphorus permit levels
- Additional benefits include sludge reduction & dewatering of biosolids, and struvite prevention
Product Characteristics

• Rare earth chloride solution
  – Rare earth Active Ingredient: CeCl$_3$ / LaCl$_3$

• Non-hazardous rating

• Compatible with existing equipment
  – 275 gallon totes / 3500 gallon tankers
Freezing Temp  -40°C

- Outside storage @ -30°F in Northeast US during Winter 2015
Using Rare Earth to Meet Low-Level Phosphorus
Eric Roundy, Jim Gallman, and Ken Vose
March 22, 2018
Snake River Watershed - Idaho

- Watershed TP limits of 0.07 mg/L TP
- Point dischargers limited to 0.1-0.35 mg/L TP in effluent
- EBPR system reliable to levels below 2.0 mg/L
Phosphate profile

Star Sewer & Water District

Reactive Phosphorus

The lines correlate between the measures for soluble, soluble reactive, and total phosphorus.

This indicates that the filtration is working to remove particulate phosphorus and the remaining P is soluble and reactive which is ideal for chemical phosphorus removal.
Coagulant effects on membrane

**Star Sewer & Water District**

**Membrane Impacts**

After continuous use with RE300, membrane flux was fouled less than 10% between cleaning cycles.

After continuous use with alum, membrane flux was fouled by 60% between cleaning cycles.
Starting with similar volumes, the sample treated with RE300 generated considerably less sludge than the alum test.
# Cost Analysis

## Star Sewer & Water District

### Cost Comparison

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<td><strong>Construction Subtotal</strong></td>
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<td>Soft Costs (Engineering &amp; CMS; 22%)</td>
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<td><strong>Total Project Cost</strong></td>
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<td>Annual Chemicals</td>
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<td><strong>Total 20-Year Life Cycle Cost</strong></td>
<td>$6,370,000</td>
<td>$6,540,000</td>
<td>$4,780,000</td>
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Options 1 and 2 compare RE300 and alum within 2% total 20 year life cycle cost when used with tertiary filtration.

Options 3 and 4 show RE300 can save 10% over alum in the 20 year life cycle cost and avoid the installation of tertiary filtration.
RE300 Dose vs Effluent TP concentration
Conclusions

- Dosing RE 300 into the MBR system can effectively achieve the effluent limits
- Online dosing control can reduce chemical usage
- Biological treatment did not appear to be significantly affected by RE 300
- RE 300 also does not appear to inorganically foul the flat sheet membranes
- Effluent toxicity does not appear to be a concern
Borough of Albion, PA WWTF

- 0.8 MGD municipal WWTF located in Pennsylvania
- Difficulty meeting phosphorus & aluminum permit levels
  - Total P limit of 1.0 mg/L
  - Total Al limit of 1.1 mg/L
- Attempts to meet the permit by increasing the dosage rate of ferric or PAC were unsuccessful.
- RE100 has allowed Albion to achieve compliance for phosphorus and aluminum discharge permits since Sept 2014

- Aluminum levels before & after RE100
Borough of Albion, PA WWTF

- Total Phosphorus levels before & after RE100
Improved Clarification

Before RE100 addition

After RE100 addition
Improved Clarification

Albion PA  “In 30 years of working here, I have never seen the clarifier look this clear!”
Improved Dewatering of Biosolids

- Albion PA WWTF: “We have doubled our belt filter press throughput, compared to iron and aluminum.”
RE100 Benefits - Borough of Albion, PA WWTF

- RE100 has allowed Albion to meet its meet phosphorus and aluminum discharge permits & remain in compliance since Sept 2014

- Improved coagulation & settling in clarifiers

- Significant decrease in sludge volume
  - 68% savings on the sludge disposal costs/ year
  - $70,000/year annual savings

- Improved performance on belt filter press
  - Prior to RE, ran belt filter press 5 days/week
  - With RE, run only 1 day/week
  - Energy savings (estimated to be $7K/year)

- Started dosing RE100 at the headworks (3 GPD)
Key Benefits of Rare Earth Technology

✓ Less coagulant volume required to reach low phosphorus limits
✓ Significant reduction in chemical sludge volumes through targeted chemical reaction
✓ Improved coagulation – noticeable improvement in water clarity
✓ Improved dewatering of biosolids
✓ Non-hazardous – safer to work with than iron based products
✓ Non corrosive – less maintenance costs
✓ No need for pH adjustment – Low pH of iron and aluminum based products can require addition of pH control chemicals
✓ Will not stain or discolor facility structures or equipment
✓ Compatible with existing equipment