neo Chemicals & Oxides

Rare Earth Technology in Wastewater Treatment

New England Water Environment Association

2020 Annual Conference

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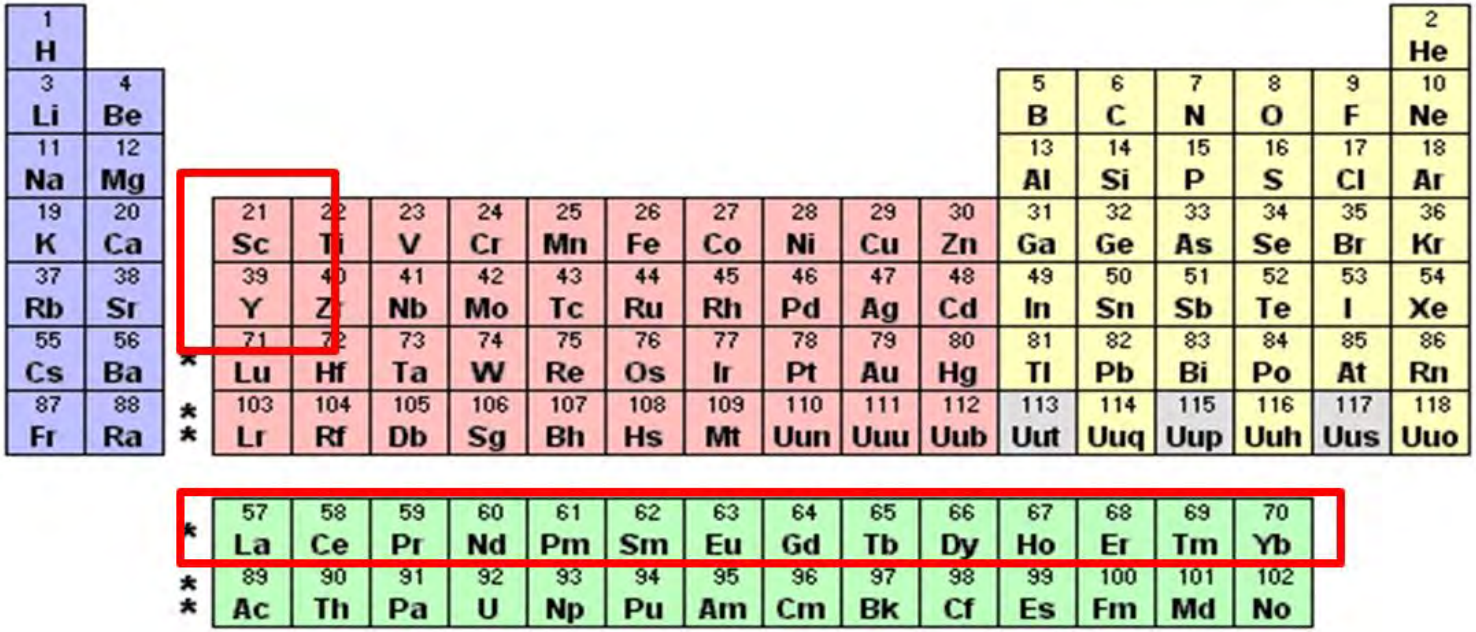
Session Overview

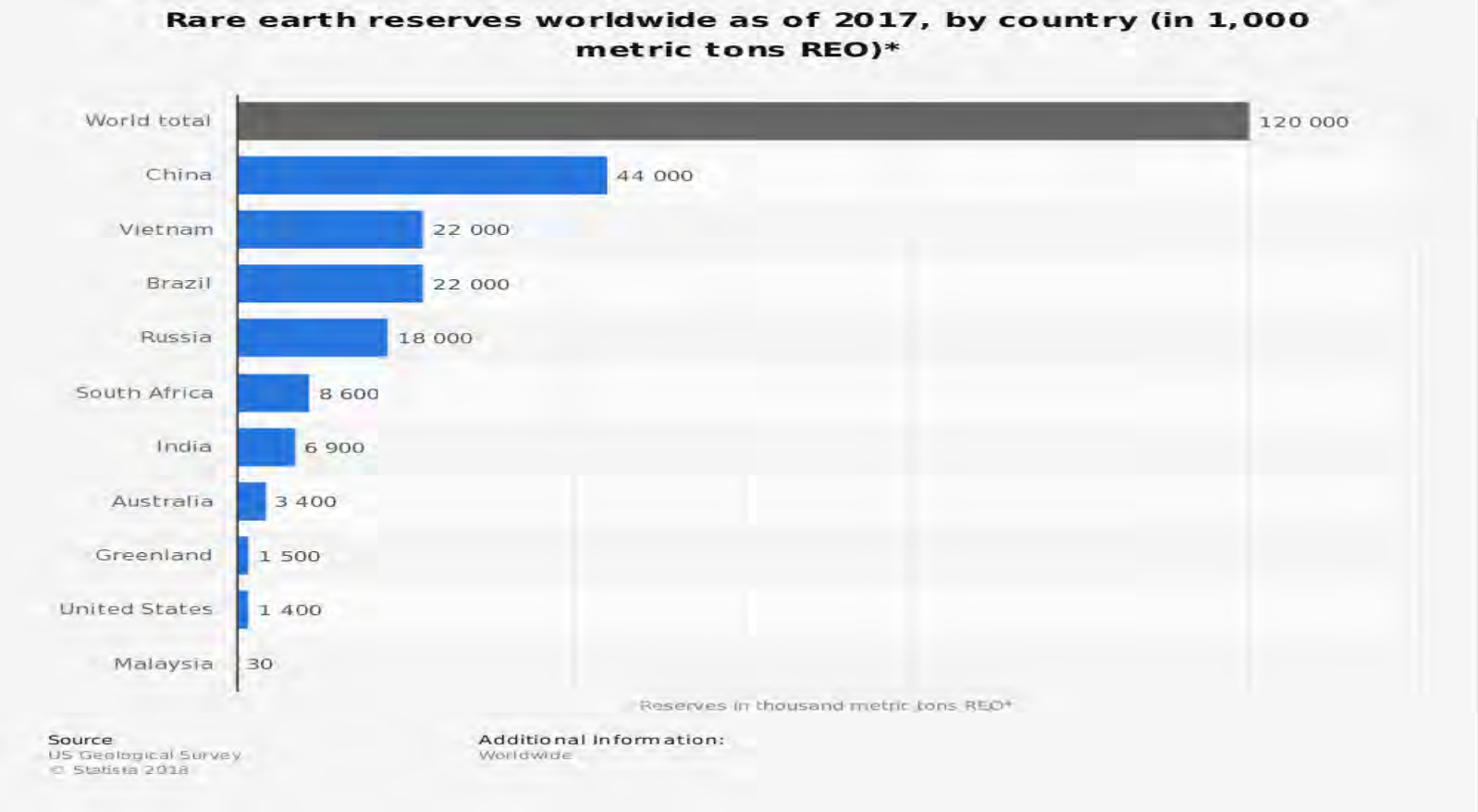
- Introduction to Rare Earth Metals and Uses
- Phosphorus breakdown
- Dosing and Chemistry Comparison to Al, Fe-based coagulants
- Case Study Applications
- Review, Discussion, Questions

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 Earth Elements are not very rare. Cerium is the 26th most abundant element, making up 66 ppm of the Earth's crust, half as much as chlorine and five times as much as lead.



Worldwide REE Reserves by Country



120mm tons in total reserves will supply market for up 800 years at current demand levels, approximately 140,000 tons per year

2016 Rare Earth Demand by Application

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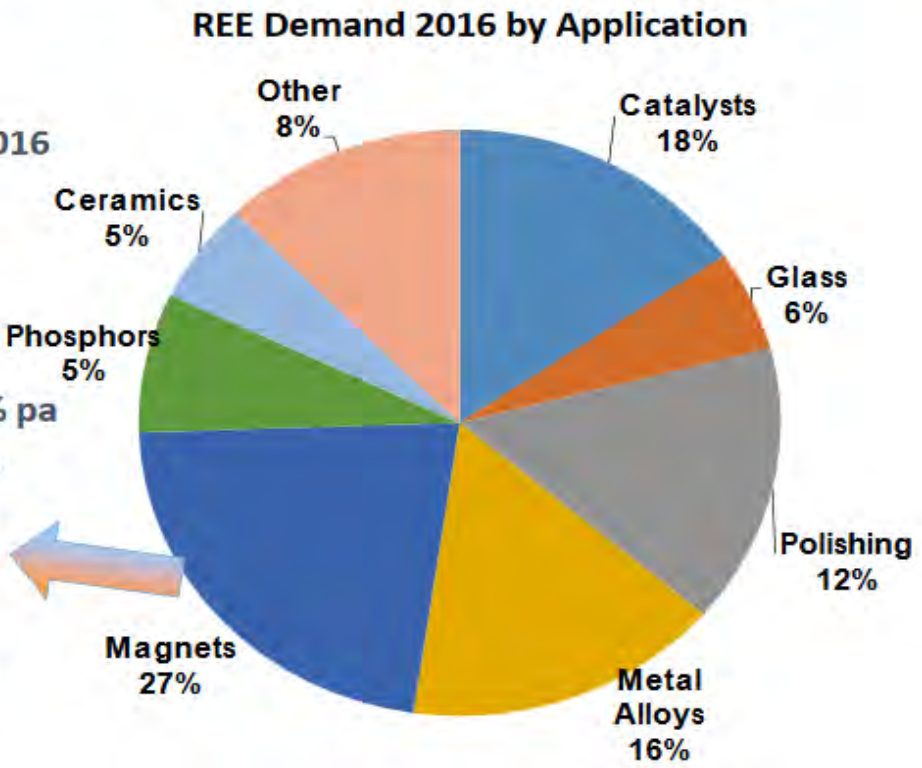
Rare Earth Demand Drivers

- US$3-5B Global market
- 159,500t Annual consumption 2016
- 6-8% Annual growth estimates
- 85-90% REE produced by China

- Permanent magnets dominate consumption and growth 6 - 12% pa
- Annual magnet market ~US$20B
- Major use for Nd, Pr, Dy and Tb
- 80% by value 20% by volume

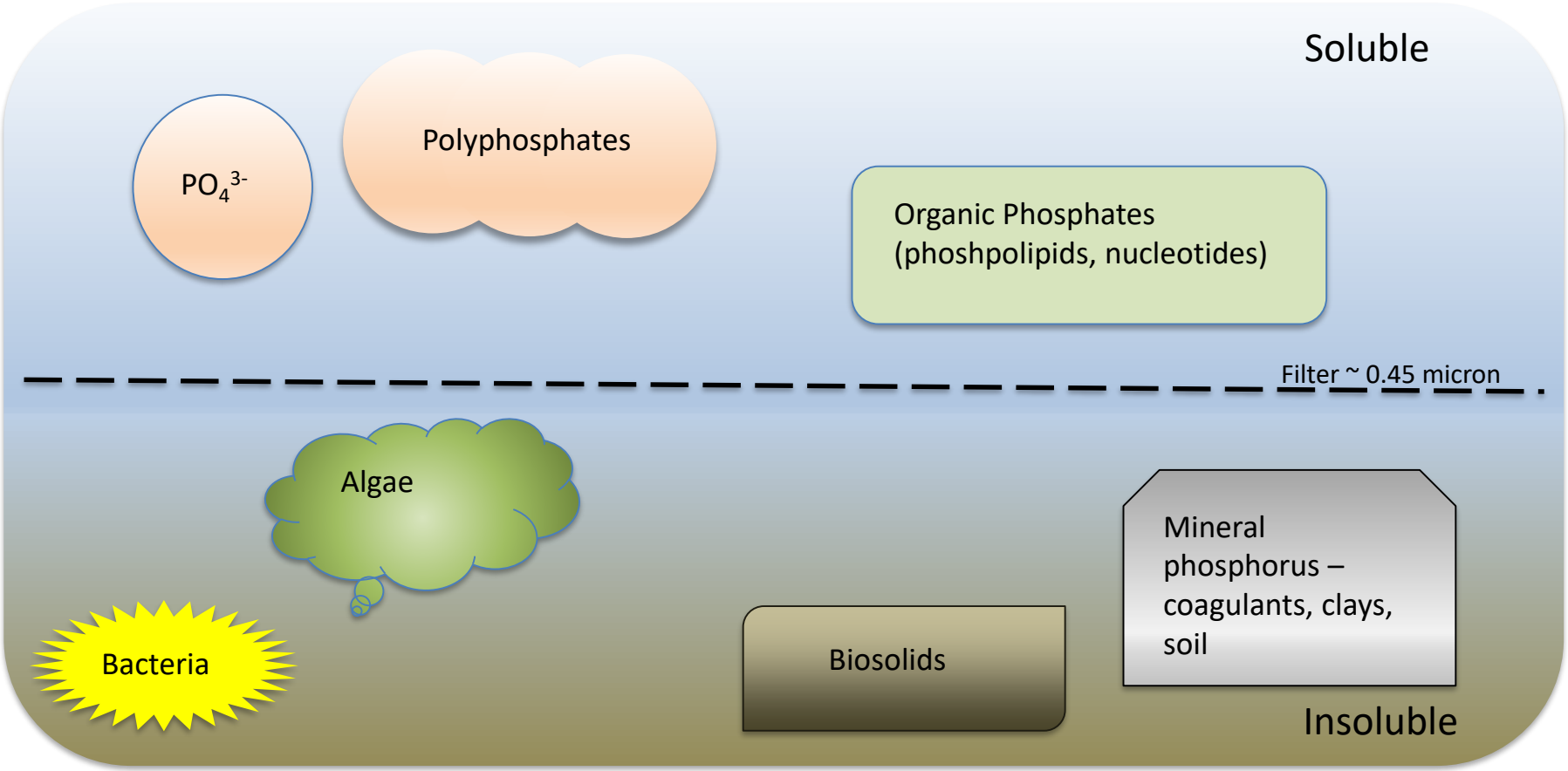
- Growth in other REs for special metal alloys and ceramics



Ce/La used in Catalysts, glass additives, polish and some metal alloys. Nd/Pr used in magnets. Phosphors being replaced by LED, Ceramics mostly as color pigments

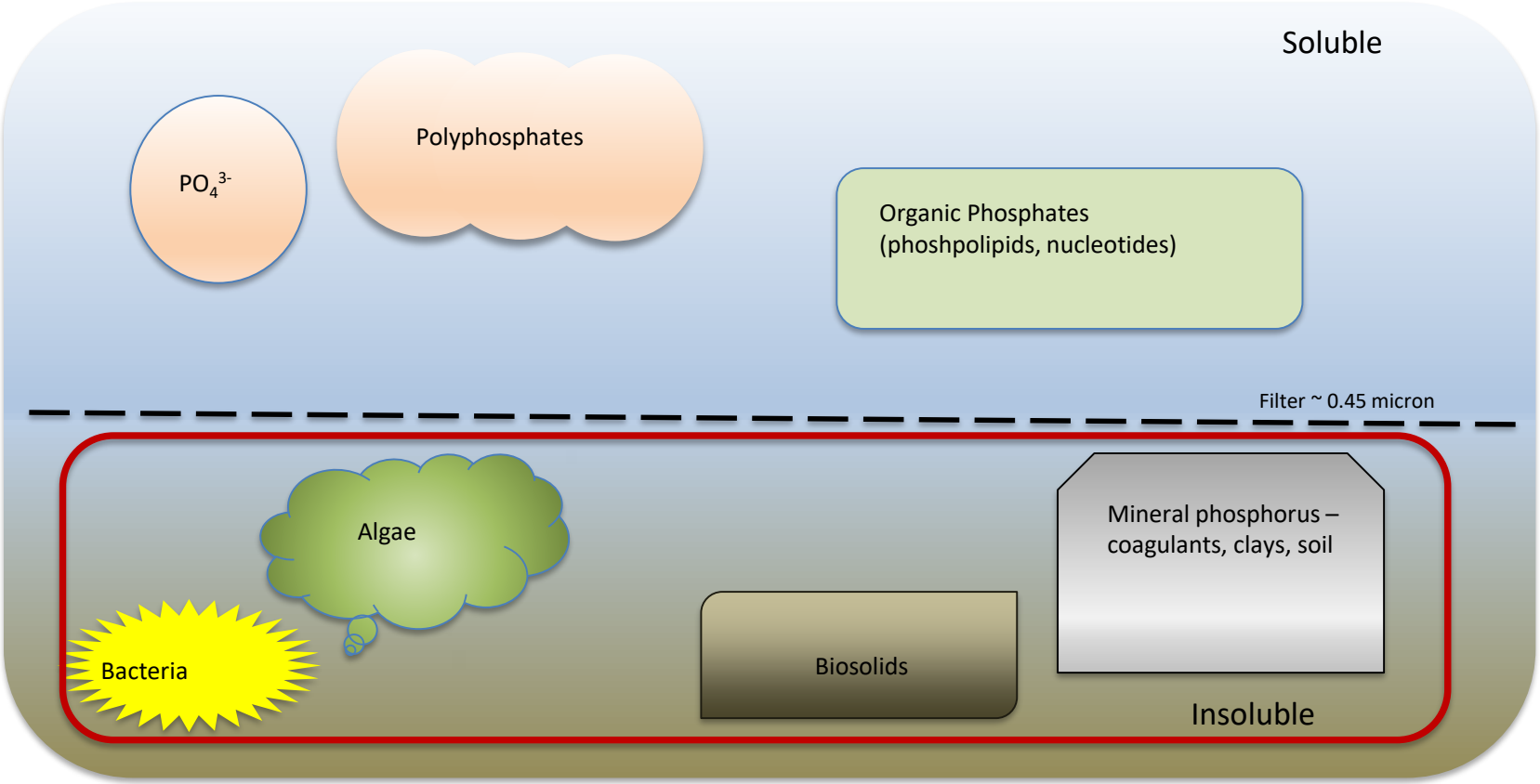
- Phosphorus breakdown

Total Phosphorus (TP) measurement



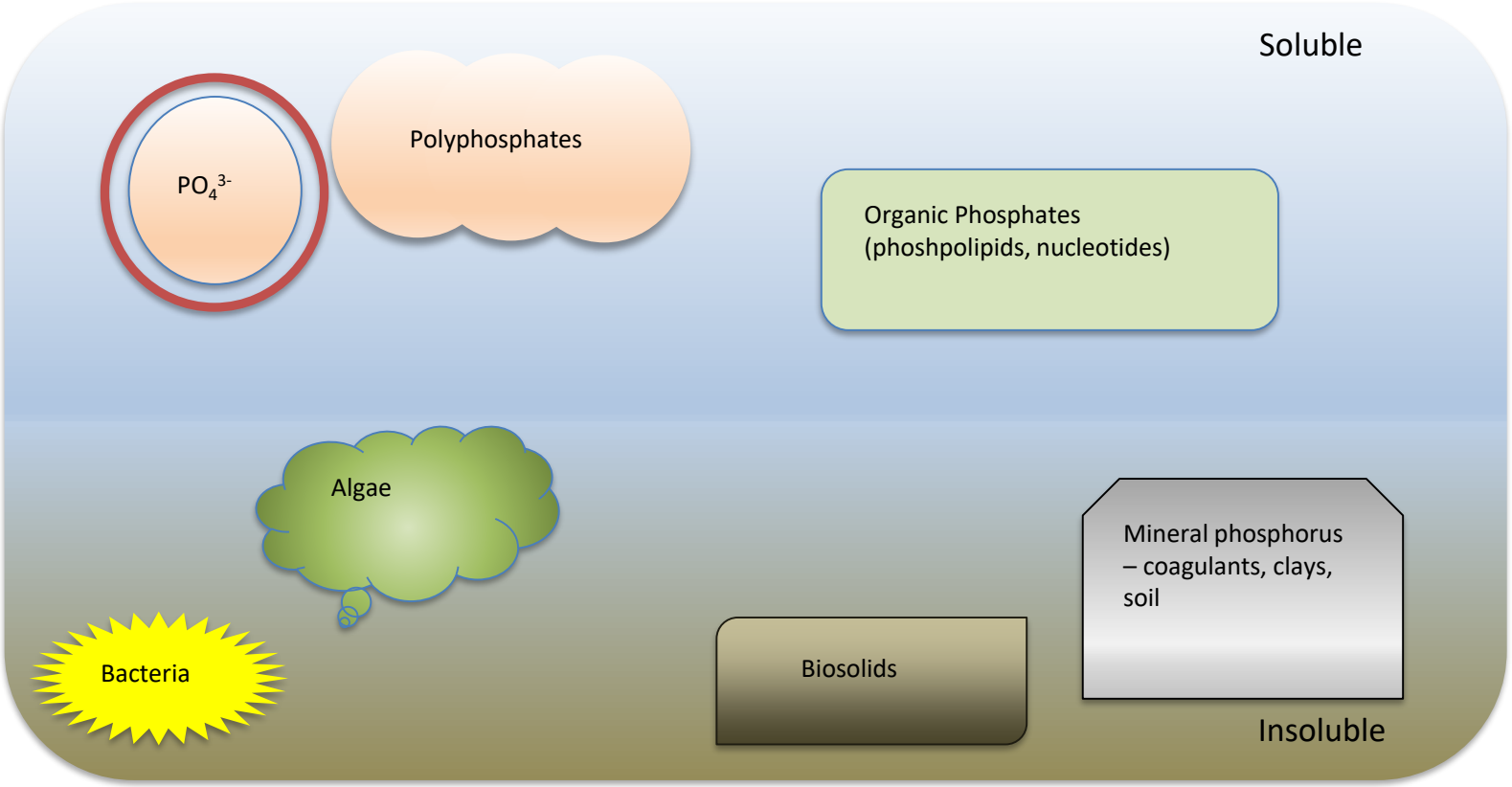
- TP is a measure of all elemental phosphorus in an unfiltered sample
- TP = Includes all soluble + insoluble
- TP = Reactive + unreactive phosphorus

Insoluble Phosphorus



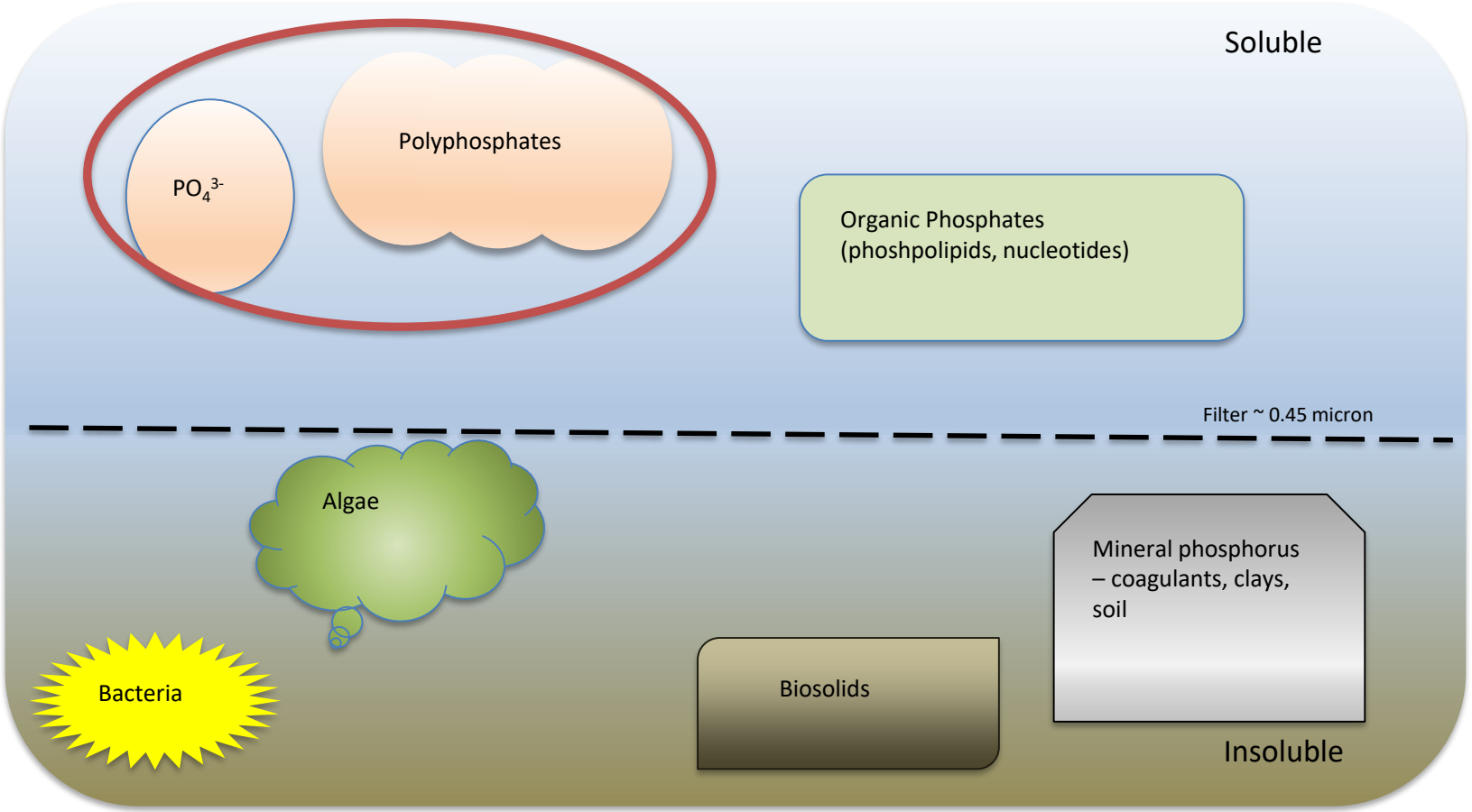
- Insoluble phosphorus is removed by .45 um filtration
- Also called particulate phosphorus
- Insoluble phosphorus = Reactive + unreactive
- Removed in clarifier

Ortho-Phosphorus OP



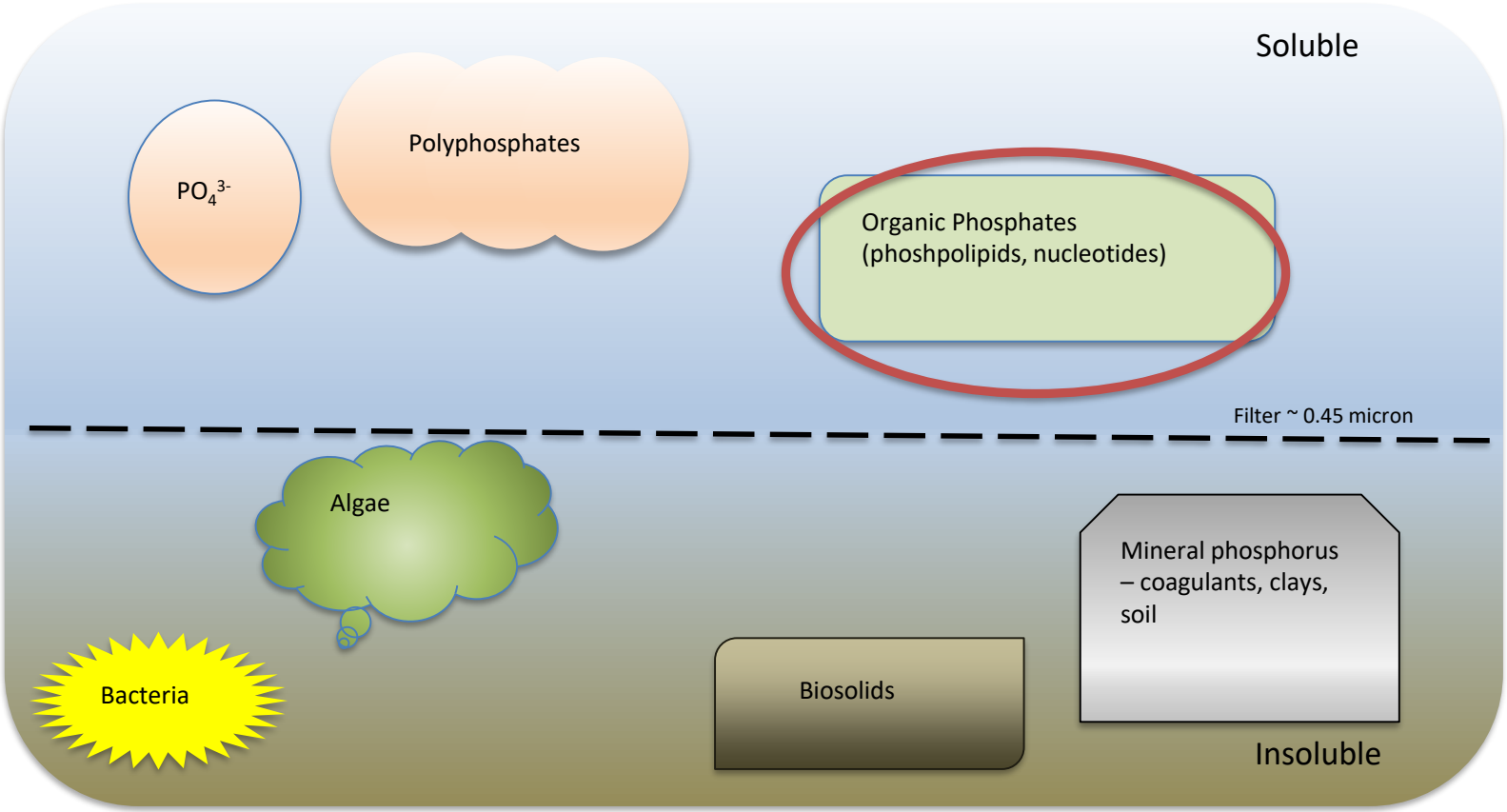
- OP = Soluble
- OP = Reactive
- Removed by chemical coagulation

Soluble Reactive Phosphorus – SRP



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

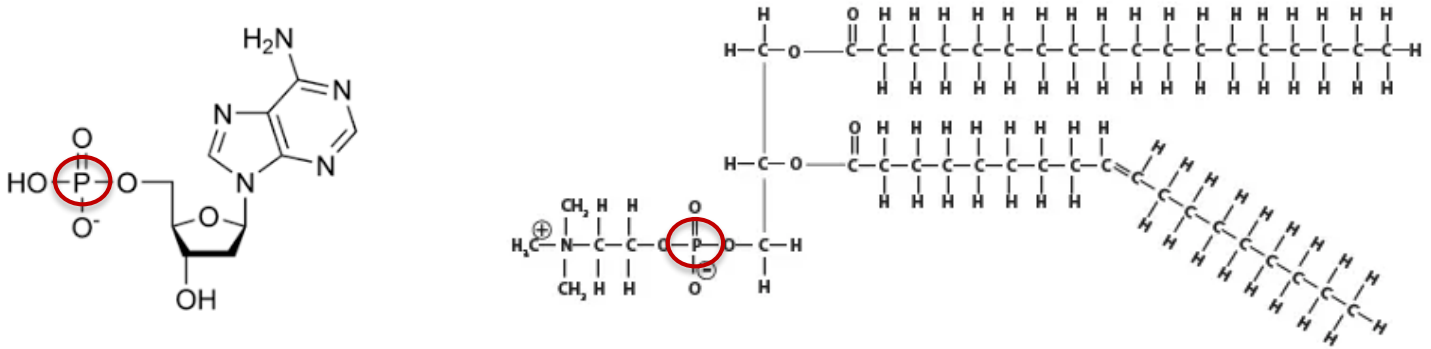
Soluble Non-reactive Phosphorus (sNRP)



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

Why is sNRP important?

- Cannot be removed by filtration
- Cannot be removed by chemical coagulation
- Not available for biofiltration.
- A high concentration (>0.3 ppm) of sNRP can prevent a facility from ever reaching a permit level.



- Dosing and Chemistry Comparison to Al, Fe-based coagulants

Fast Coagulation Properties

- Molecular weight of rare earth vs. traditional chemical coagulants is much higher

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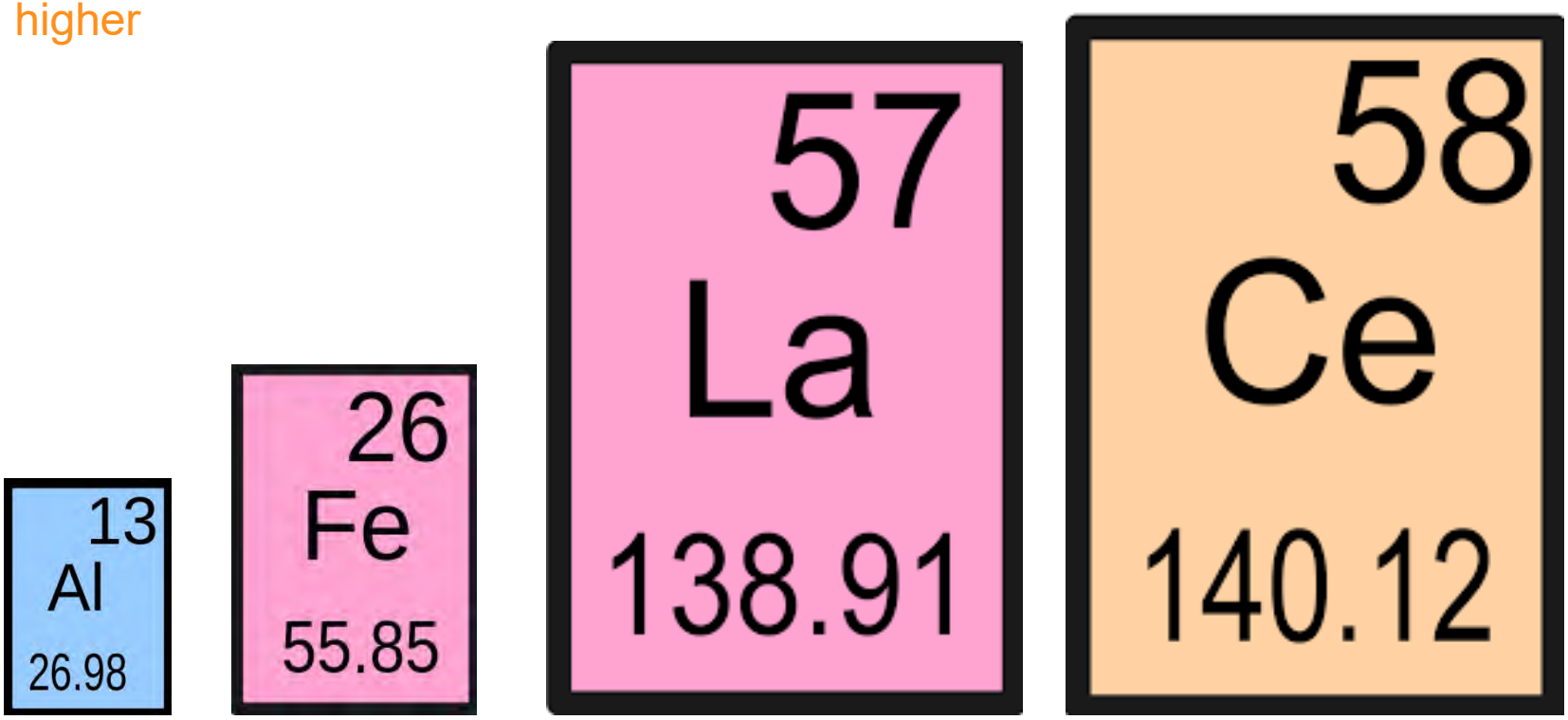


- Forms denser precipitate which settles well in clarifier

Phosphorus Removal Mechanism

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

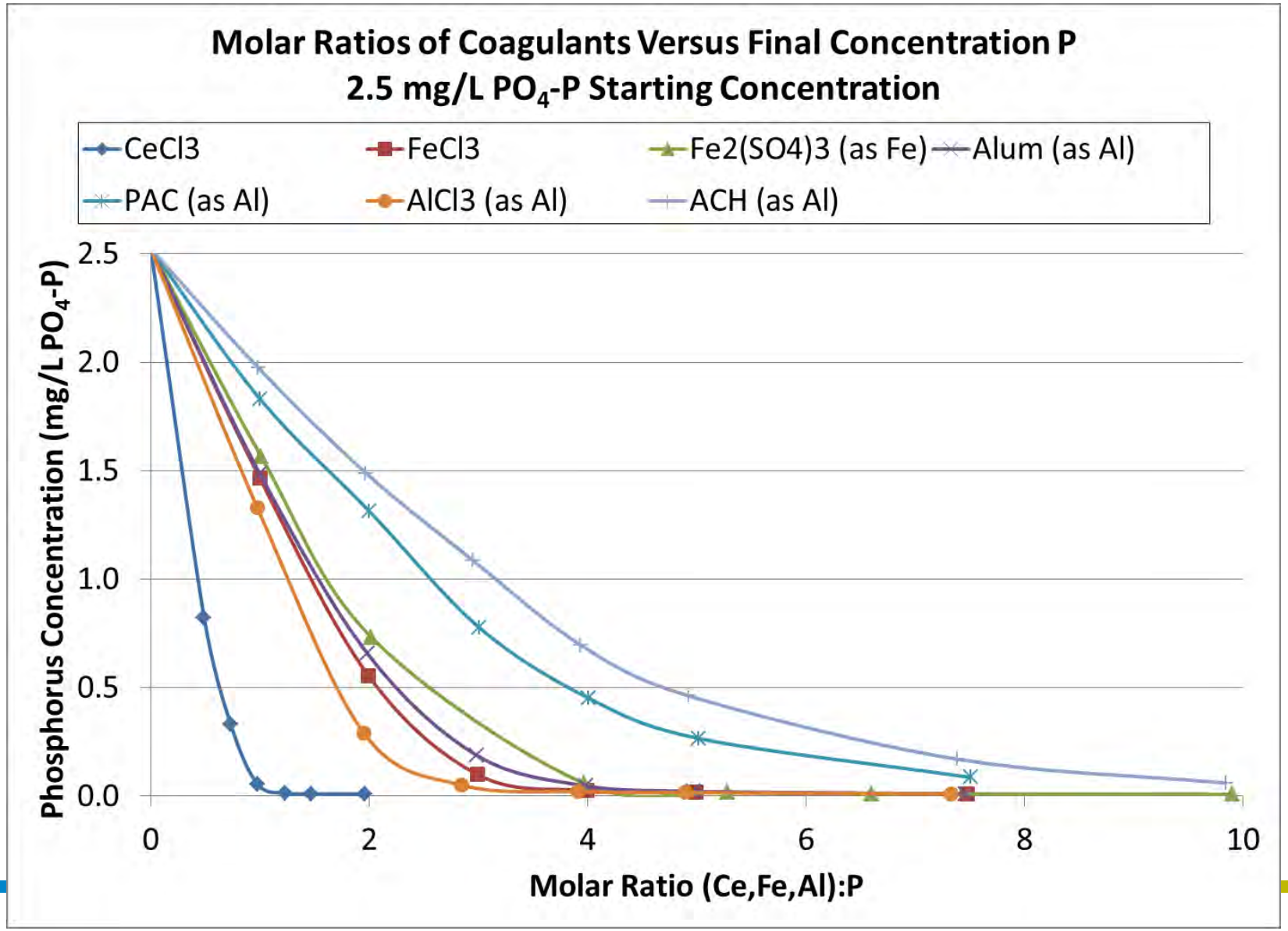
- Iron and aluminum based products form amorphous “cloud” in solution
  - Adsorbs phosphate onto metal hydroxide floc

Why RE is different than traditional coagulants

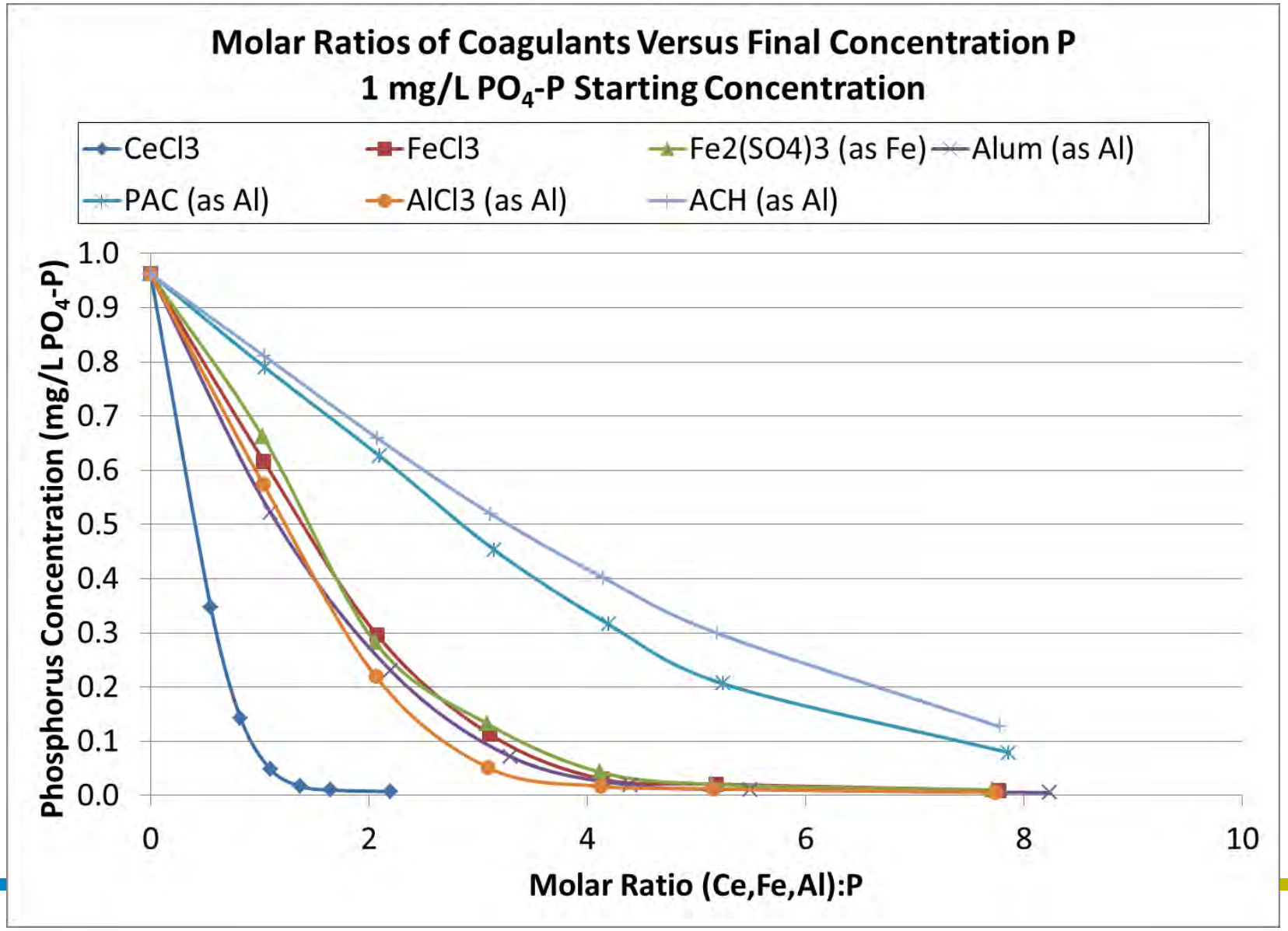
- Precipitate is $CePO_4$ / $LaPO_4$ (Rhabdophane)
- Forms ionic bonds
- Preferentially reacts with phosphorus
- Achieves a nearly 1:1 molar ratio of Rare Earth:PO_4 → Reduced chemical sludge

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

Coagulant Comparison – 2.5 mg/L



Coagulant Comparison – 1 mg/L



Solids Handling

- Less coagulant volume required to reach phosphorus limits.
  - 30 to 70% reduction based on traditional coagulants
- Improved dewatering of biosolids – less water molecules
  - Increase Belt Filter Press 15-17% to 21-25%
  - Centrifuge: 21-23% to 25-29%
- Creates a Denser Sludge
  - Increase percent solids in sludge holding tank

pH

- pH scale is a measure of acid and base concentration. It ranges from 1 to 14 with 7 considered neutral.
- The pH scale is logarithmic which means that every integer change results in a 10x higher acid or base concentration.
- Rare earth chloride is stable in a solution of 3 to 4 pH.
- Other coagulants often have a pH of 1.5 to 2.2.
- Rare earth chloride is 100 times less acidic than other coagulants due to the logarithmic nature of the pH scale.

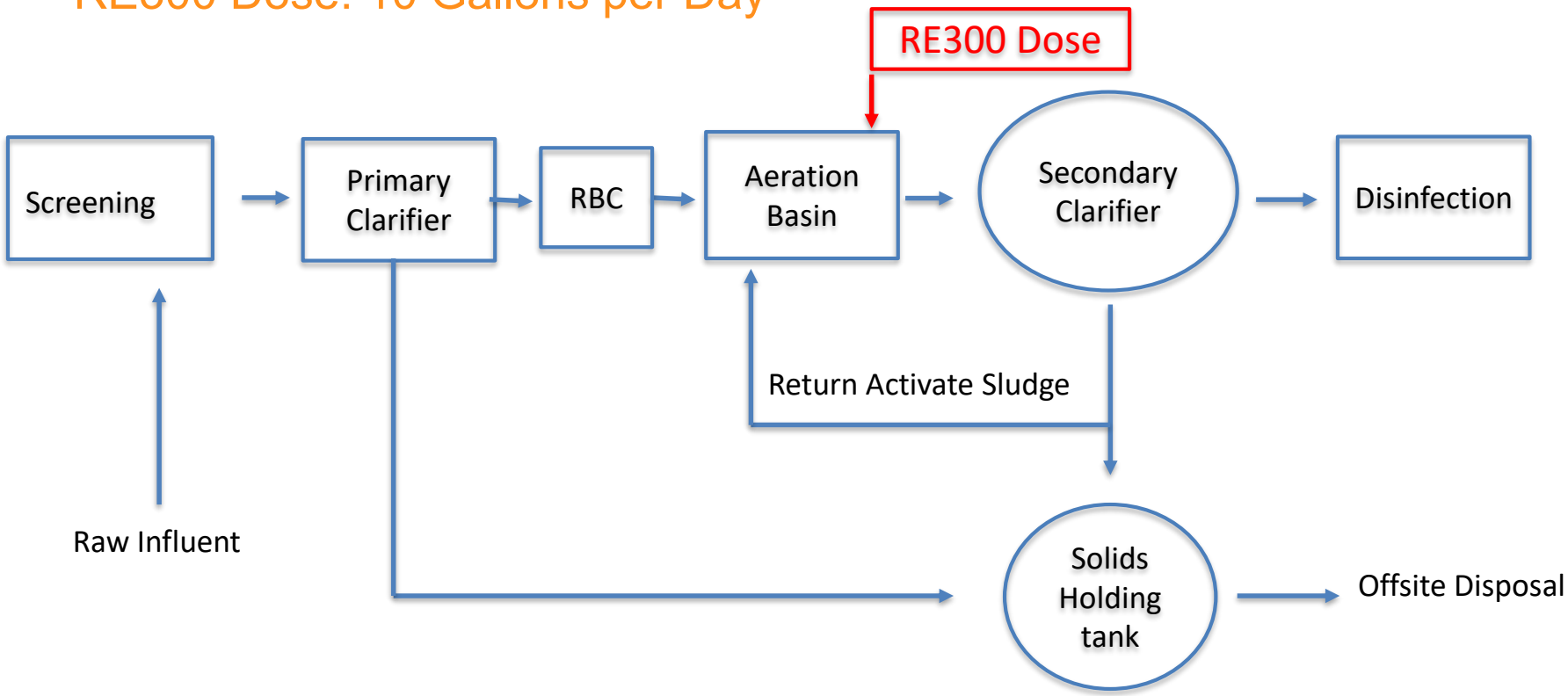
Alkalinity

- Alkalinity is the ability of a solution to resist pH changes when an acid is added.
- Rare earth chloride is 100 times less acidic than other coagulants.
- Rare earth chloride replaces other coagulants with a dose volume 25% or less.
- These two mechanisms combine to result in a reduction of acid addition of 300-500 times.
- Rare earth chloride reduces chemical alkalinity consumption by several hundred times leaving more alkalinity for denitrification.

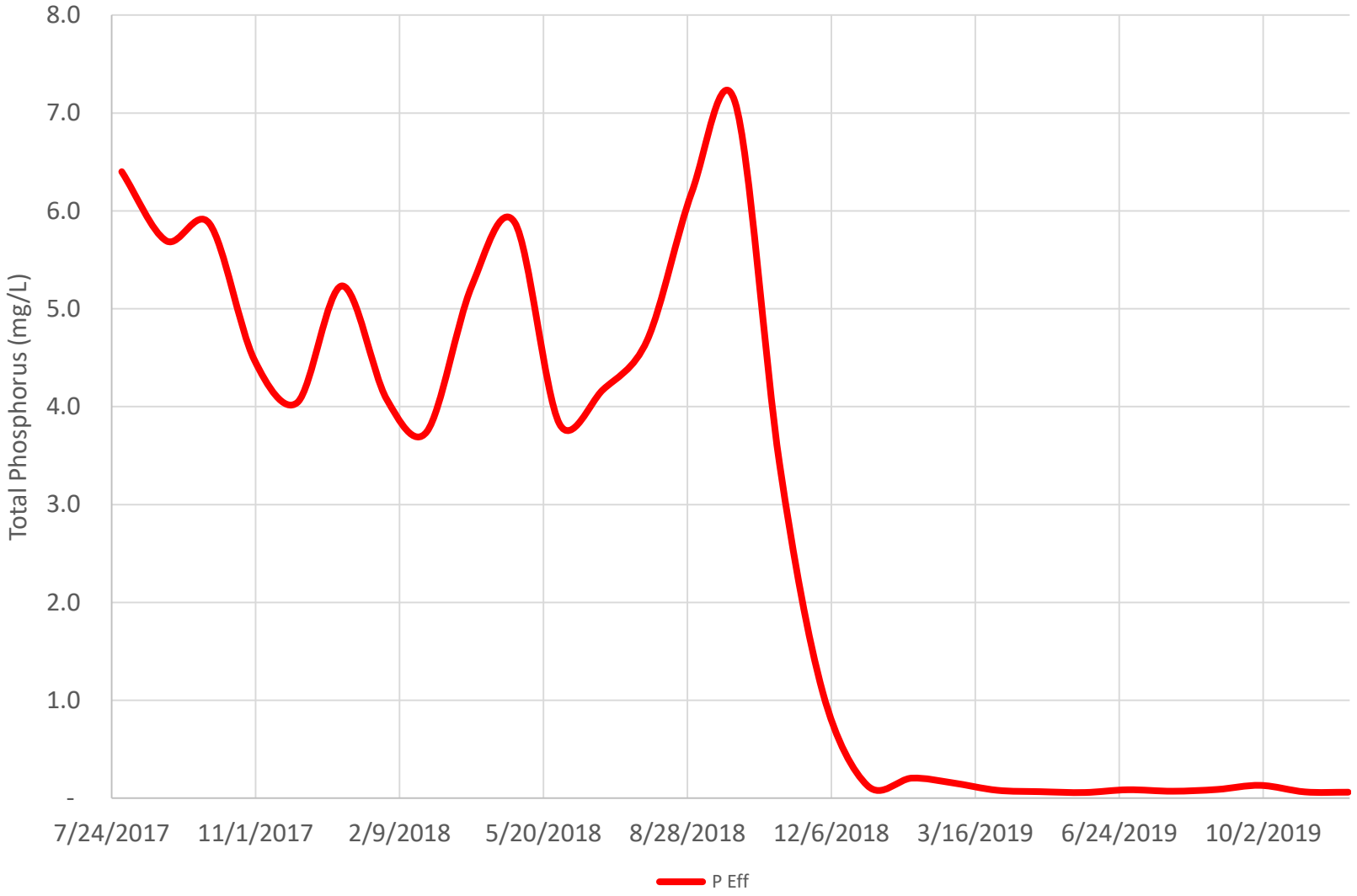
- Case Study Applications

Shullsburg, WI WWTP

- Flow: Approximately 0.200 MGD
- Total Phosphorus Limit: 0.075 mg/L
  - Implemented October 2019
- RE300 Dose: 10 Gallons per Day

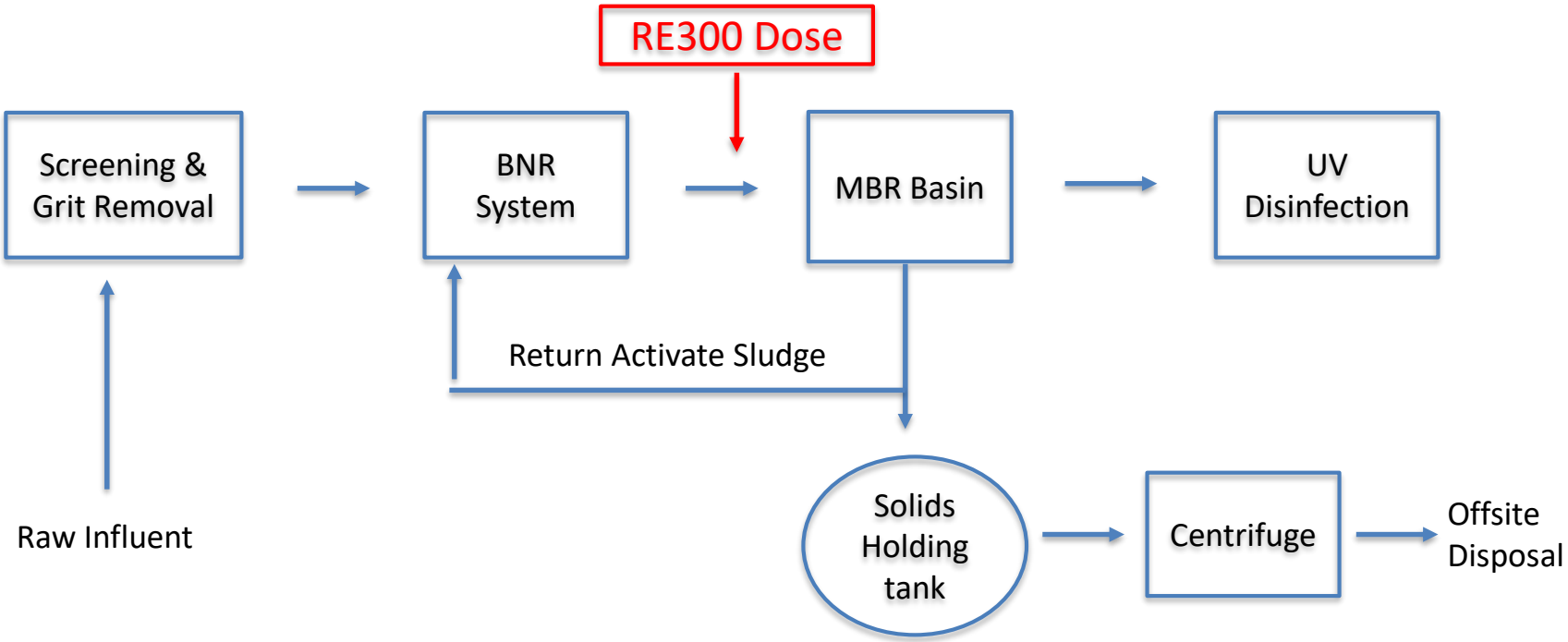


Shullsburg, WI – Total Phosphorus Effluent



MBR Facility - Georgia

- Flow: Approximately 0.450 MGD
- Total Phosphorus Limit: 0.13 mg/L – Weekly Average

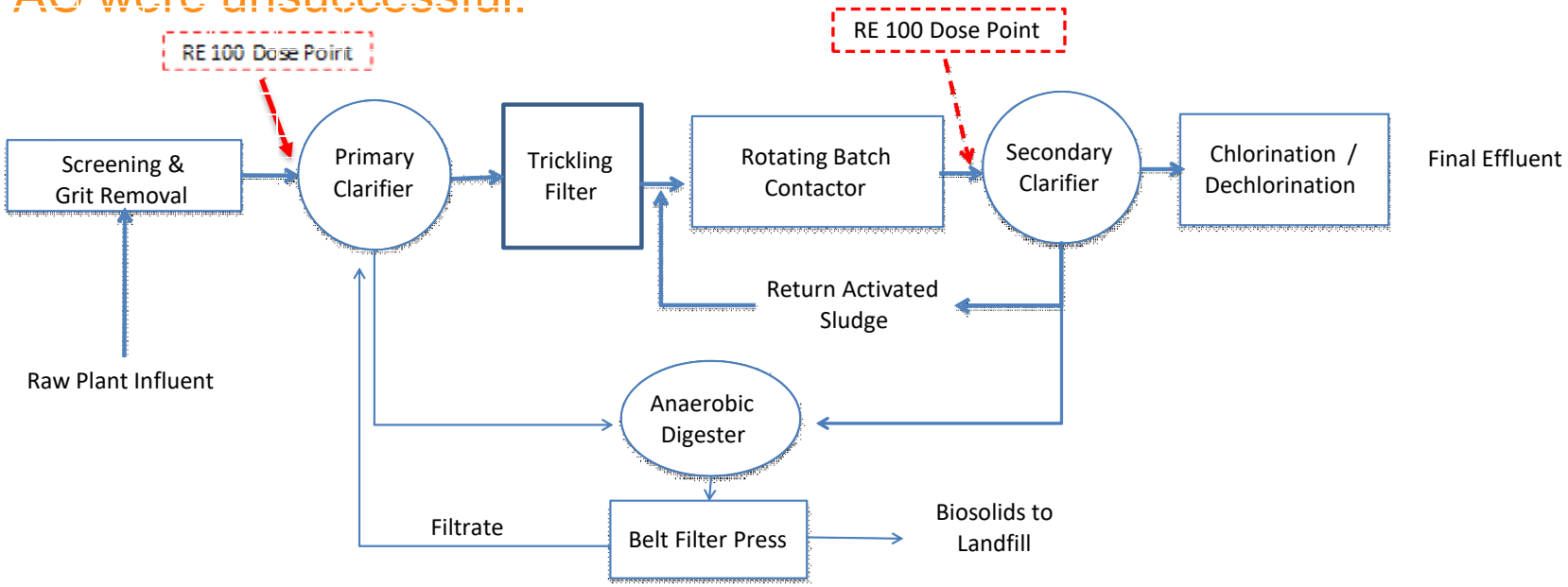


MBR Facility – Georgia - Results

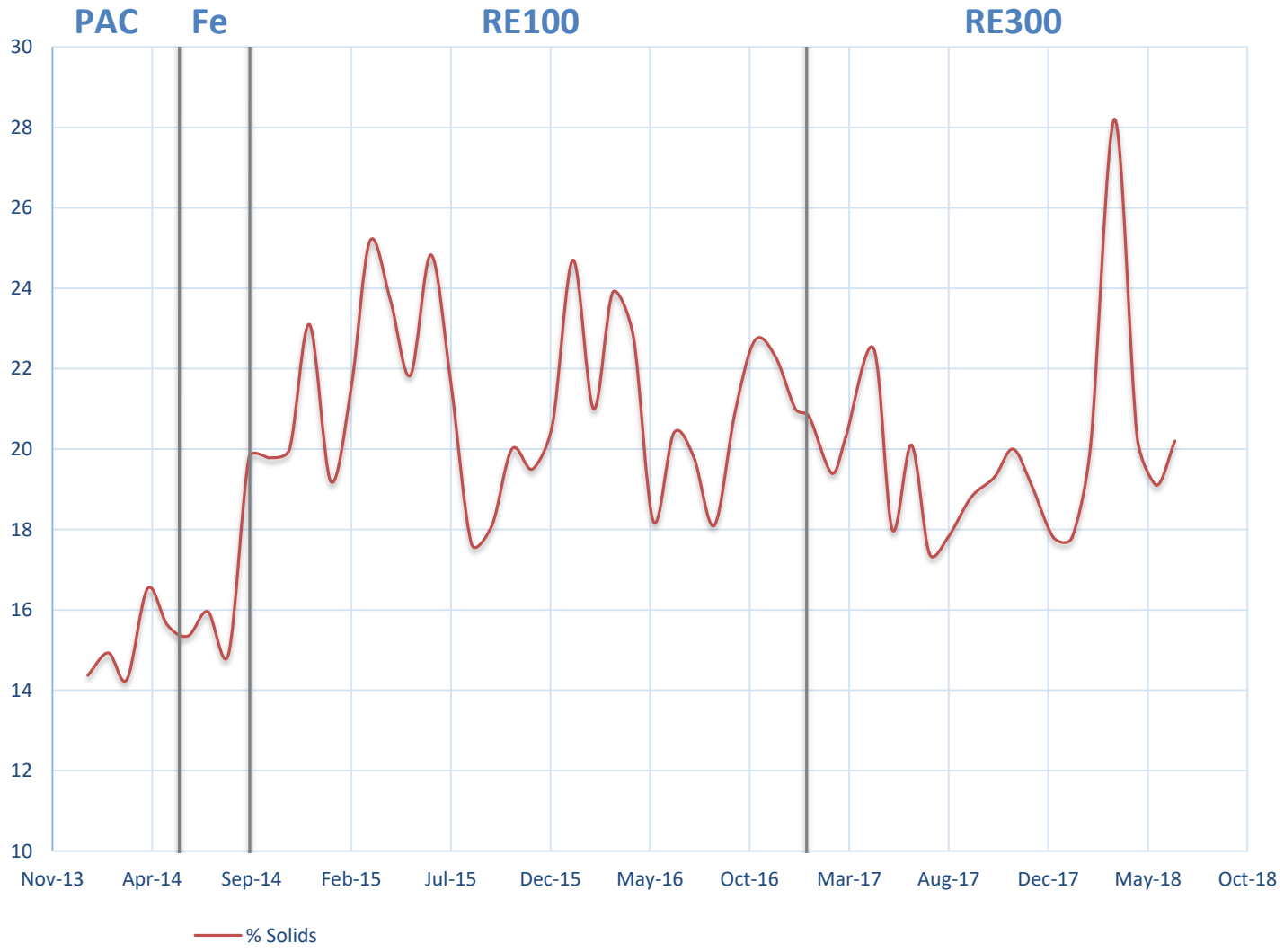
- 2018 Chemical Usage
  - Alum (48%) – 206 GPD
  - Sodium Hydroxide (25%) – 313 GPD
- 2019 Chemical Usage – Started Dosing July 2019.
  - RE300 – 20 GPD
  - Sodium Hydroxide (25%) – 40 GPD
- Total Chemical Cost is 50% versus 2018.
- Solids Handling – Centrifuge
  - 2018 Percent Solids – 17.81%
  - Current Percent Solids – 21.35%

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 mg/L-P
  - Total Al limit 1.1 mg/L was going to be reduced
- Attempts to meet the permit by increasing the dosage rate of ferric or PAC were unsuccessful.



Borough of Albion, PA WWTF – Percent Solids



Struvite

- Struvite is a mineral that forms at a 1:1:1 combination of phosphate, magnesium, and ammonia, and growth is accelerated at pH of 8 or higher
- Plant is targeting 100 mg/L as phosphate limit for struvite formation. During winter months they use RE to reduce phosphate below this level.
- Without sufficient phosphate in solution, struvite does not have the ingredients needed to grow.

Struvite Control – Centreville VA

Struvite build up on pump impeller after just 15 days

Struvite growth in pipe. ID decreased from ~4” to 2”

Struvite manually removed from centrifuge

1 year results – RE to prevent struvite

After 1 year of struvite prevention with RE, the pump and pipe show no signs of struvite growth compared to just 18 days of use shown previously. The centrifuge did show struvite growth, but it was characterized as minor, soft, and was washed off with a hose.

Key Benefits of Rare Earth Technology

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- ✓ 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
- ✓ Low corrosivity – less maintenance costs
- ✓ Reduced 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

Questions?

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