



Rare Earth Technology for Low Phosphorus Removal

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OWEA Technical Conference & Expo – June 2017

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Discussion Outline

- **Rare Earth Technology Introduction**
 - What are rare earths?
 - Rare earths vs. traditional P removal
 - Product Characteristics
- **Performance of Rare Earth Technology in Wastewater Treatment Facilities**
- **Summary of Benefits of Rare Earth Technology**
 - Ability to achieve low P levels
 - Sludge reduction
 - Improved Dewatering, Coagulation
 - Capital Costs Savings

What are Rare Earths?

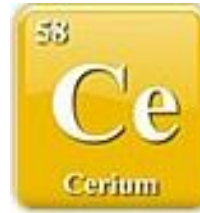
Periodic Table of the Elements

1 IA 1A																	18 VIIIA 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB Sc	4 IVB Ti	5 VB V	6 VIB Cr	7 VIIB Mn	8 VIII Fe	9 VIII Co	10 VIII Ni	11 IB Cu	12 IIB Zn	13 IIIA Al	14 IVA Si	15 VA P	16 VIA S	17 VIIA Cl	18 VIIIA Ar
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

- Alkali Metal
- Alkaline Earth
- Transition Metal
- Basic Metal
- Semimetal
- Nonmetal
- Halogen
- Noble Gas
- Lanthanide
- Actinide

Rare Earths in Water Treatment Markets



Recreation Water



Aquarium



Lake Remediation



Wastewater

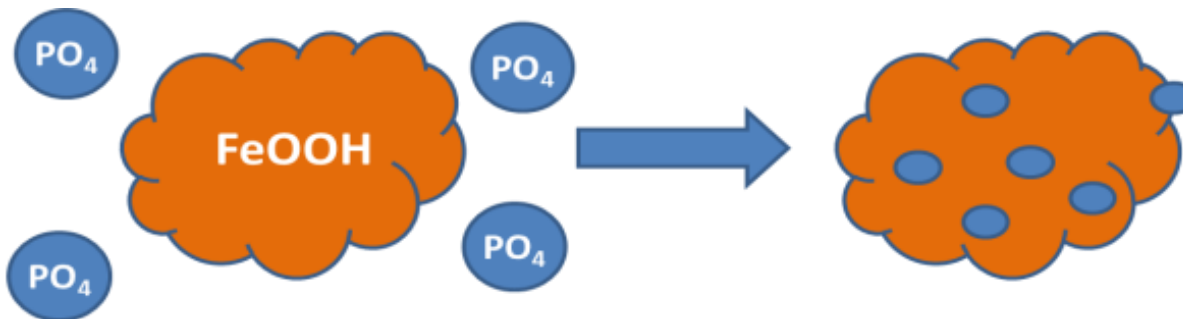


Phosphorus Removal Mechanism

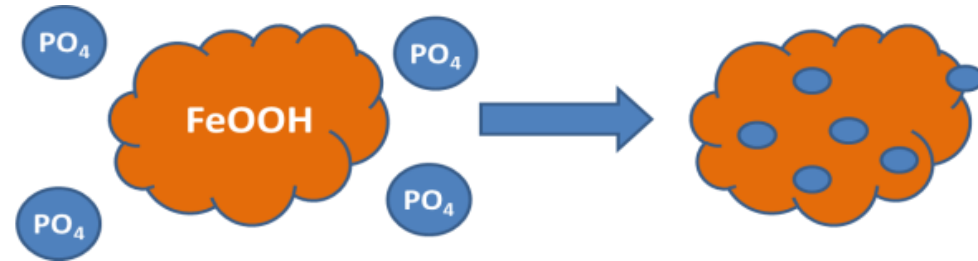
- Rare earth elements form strong, crystalline bonds with phosphorus
 - Forms insoluble rhabdophane precipitate



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



Why RE is different than traditional coagulants

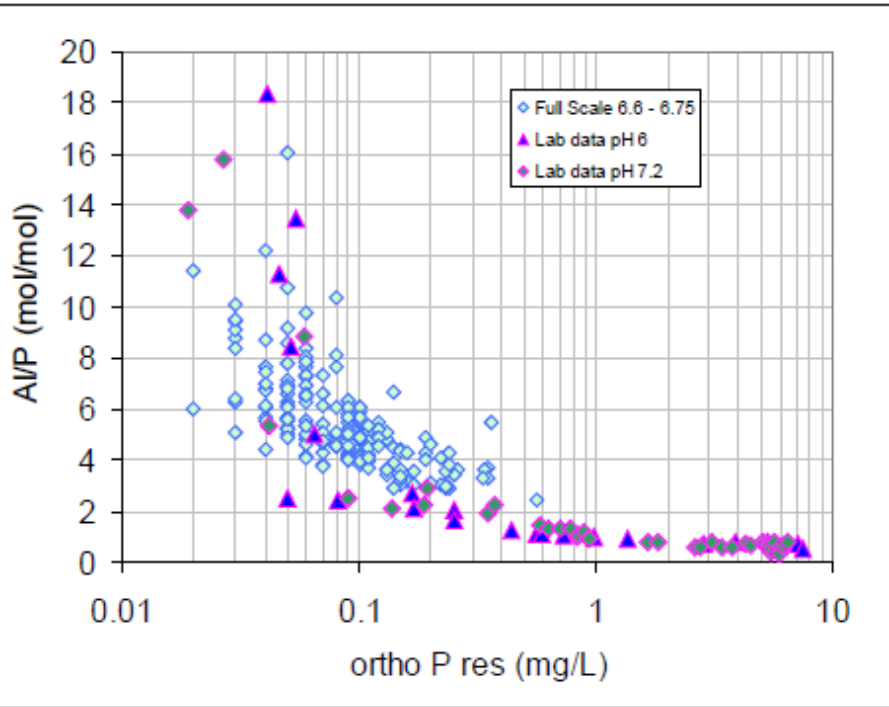


- Precipitate is CePO_4 / LaPO_4 (Rhabdophane)
- Forms ionic bonds
- Preferentially reacts with phosphorus
- Achieves 1:1 molar ratio of $\text{La/Ce}:\text{PO}_4 \rightarrow$
Reduced chemical sludge

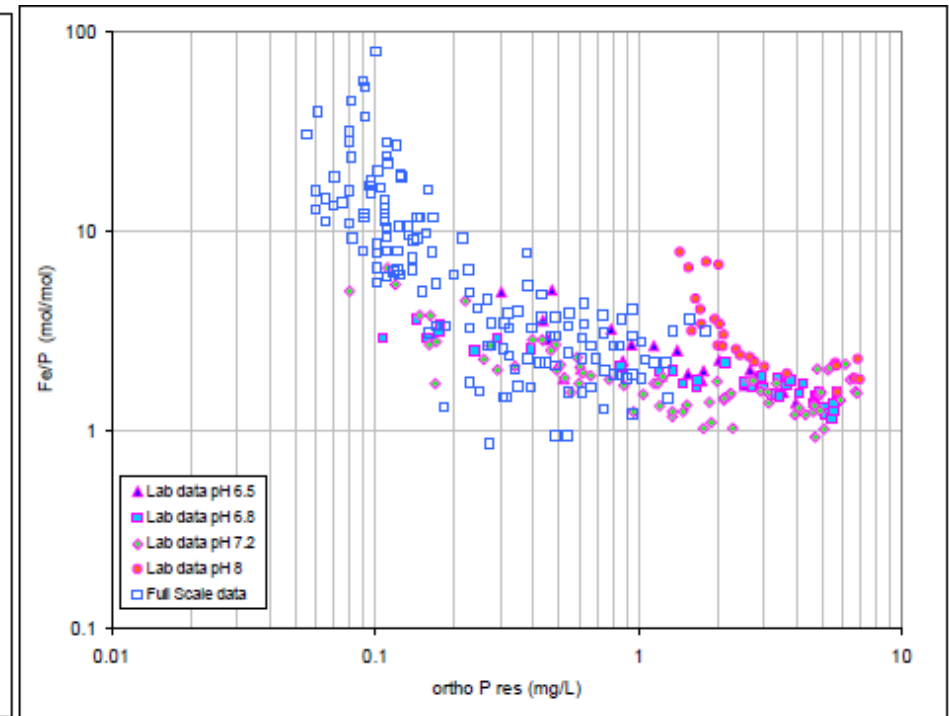
- Forms Fe/AlOOH and $\text{Fe/Al}(\text{OH})_3$ intermediates to adsorb P
- Phosphate adsorbs on the surface of the floc (surface chemistry)

Molar Dose Ratio of Traditional Coagulants

Aluminum



Iron



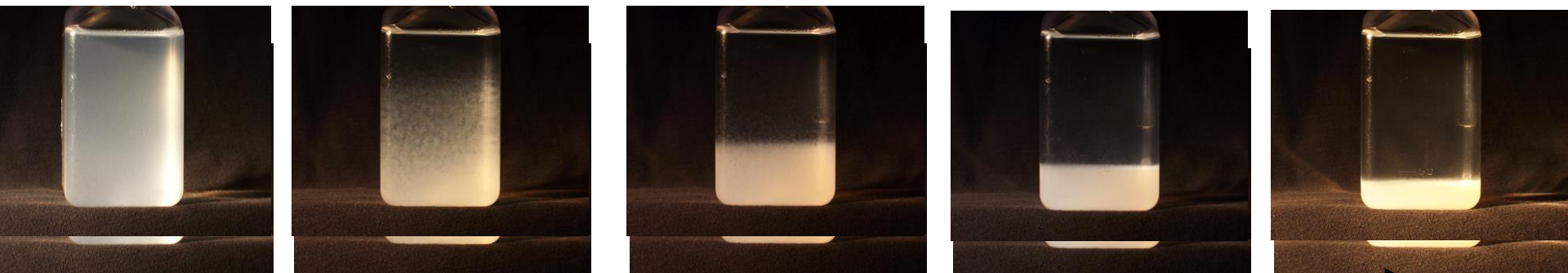
Phosphorus Removal Demonstration

- Rare earth chloride quickly reacts to form a dense precipitate which readily settles out of solution

Ferric Chloride



Rare Earth Chloride

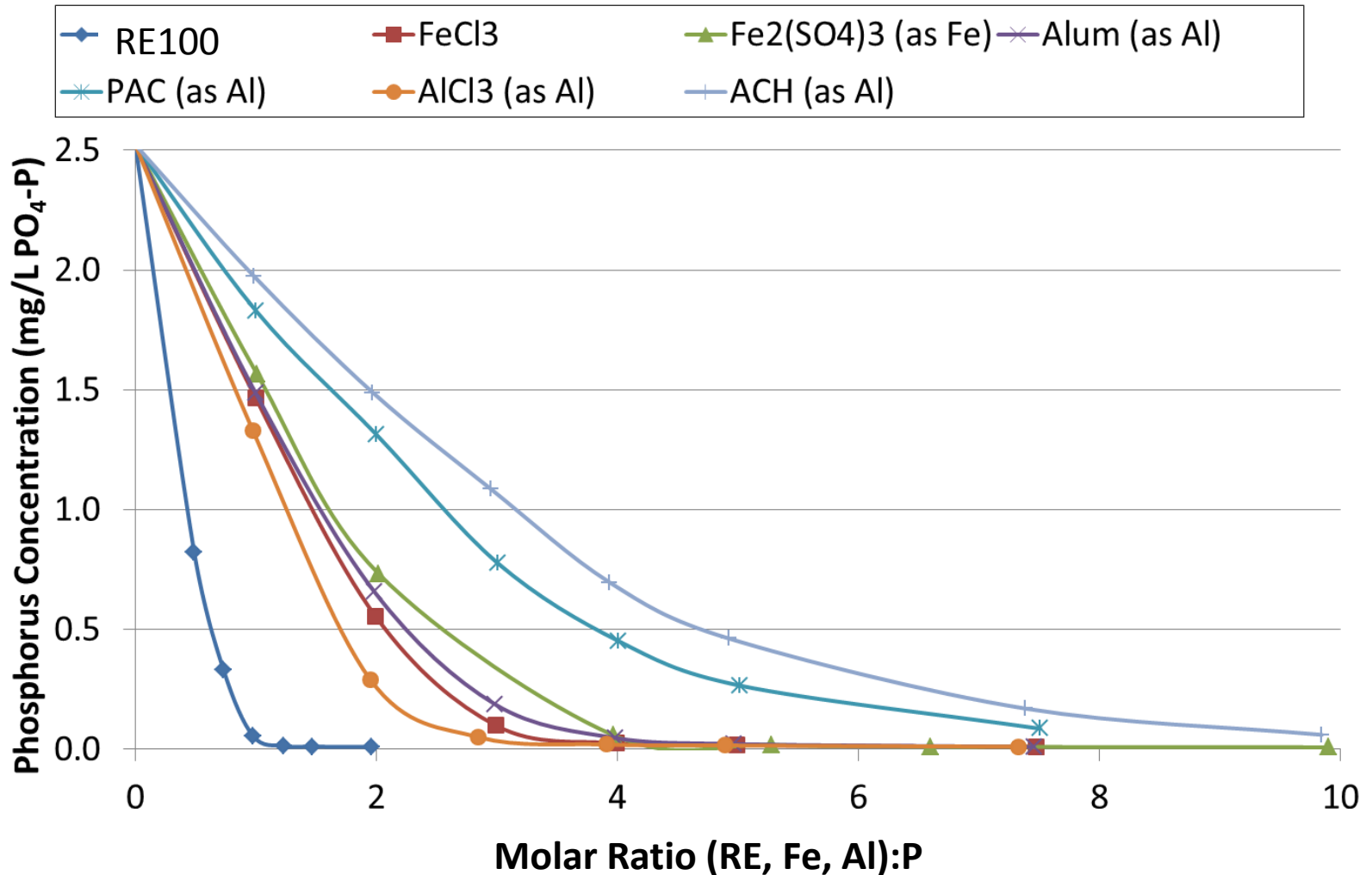


0 Min

15 Min

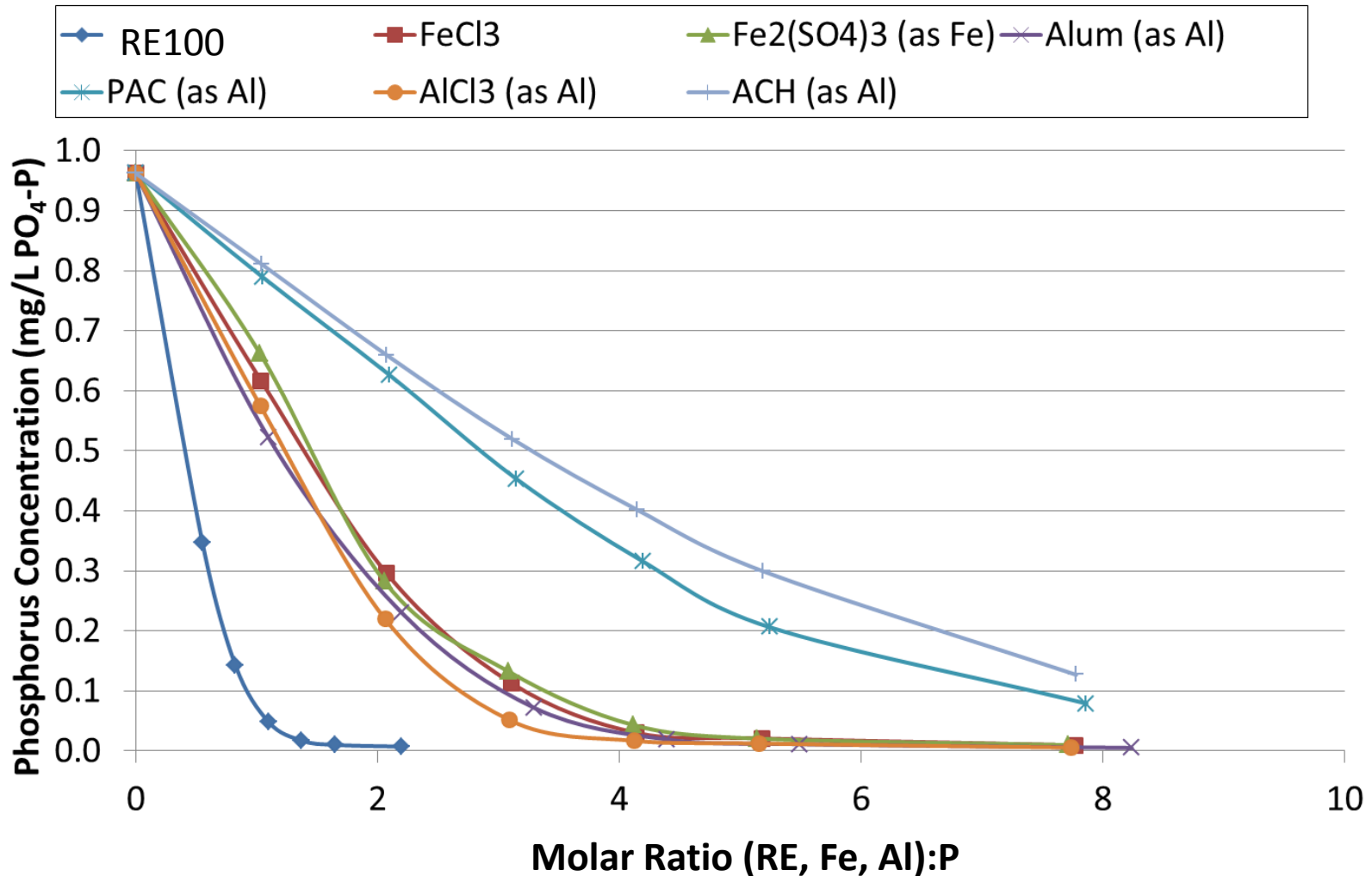
Coagulant Comparison – 2.5 mg/L

Molar Ratios of Coagulants Versus Final Concentration P
2.5 mg/L PO₄-P Starting Concentration



Coagulant Comparison – 1 mg/L

Molar Ratios of Coagulants Versus Final Concentration P
1 mg/L PO₄-P Starting Concentration



- Introduced in 2013
- Has been used in over 50 facilities in over 10 states, including Virginia, Pennsylvania, New York, Vermont, Ohio, Illinois, Wisconsin, Indiana, Texas, Washington
- Proven effective for meeting low phosphorus permit levels
- Additional benefits include sludge reduction & dewatering of biosolids

Product Characteristics

- Rare earth chloride solution
- Active Ingredient: CeCl_3 / LaCl_3

	RE 100	RE 300
% active ingredient (w/w)	33%	40.5%
Density (lbs/gal)	11.9	13.2
pH	3 - 4	
Freezing Point	-40°C	

- 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

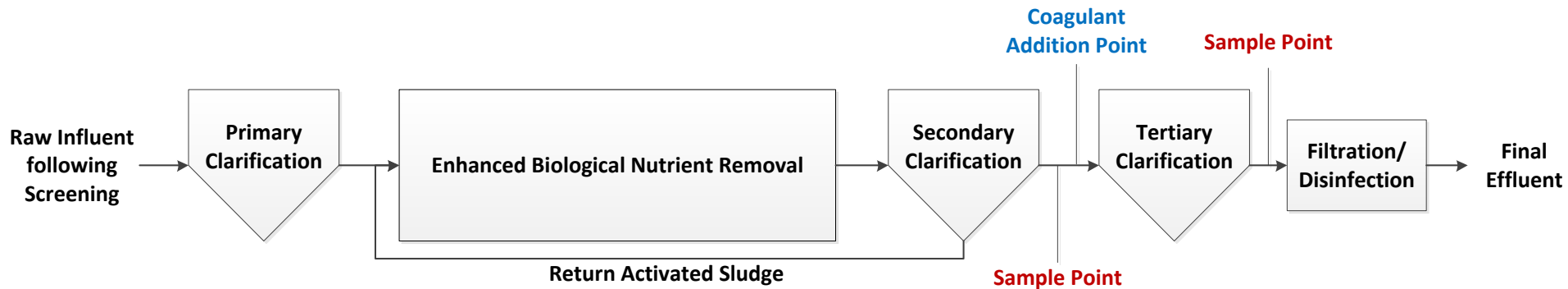


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 - Sludge reduction
 - Improved Dewatering, Coagulation
 - Capital Costs Savings

Noman Cole VA WWTF

- 45 MGD municipal WRF located in Chesapeake Bay region
- Total phosphorus limit of 0.18 mg/L P
 - Target of 0.10 mg/L P
- Interested in seeking new coagulant with lower consumption rate, less chemical solids produced, and less staining of UV

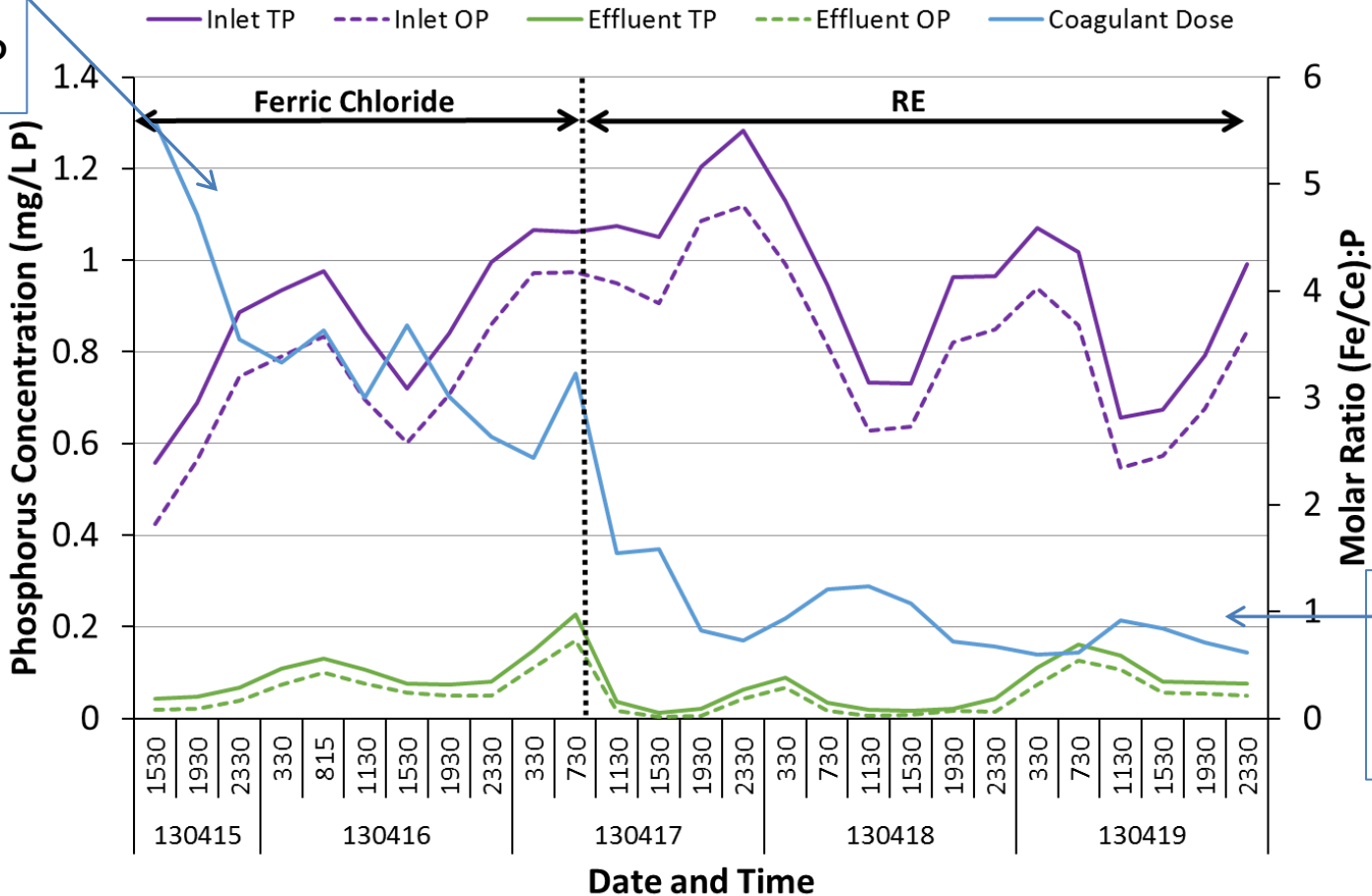


Noman Cole VA WWTF

Rare Earth technology maintained phosphorus below limit with a dosage rate 3x less than FeCl_3

Ferric
34 ppm_v
3.5:1 Fe/P

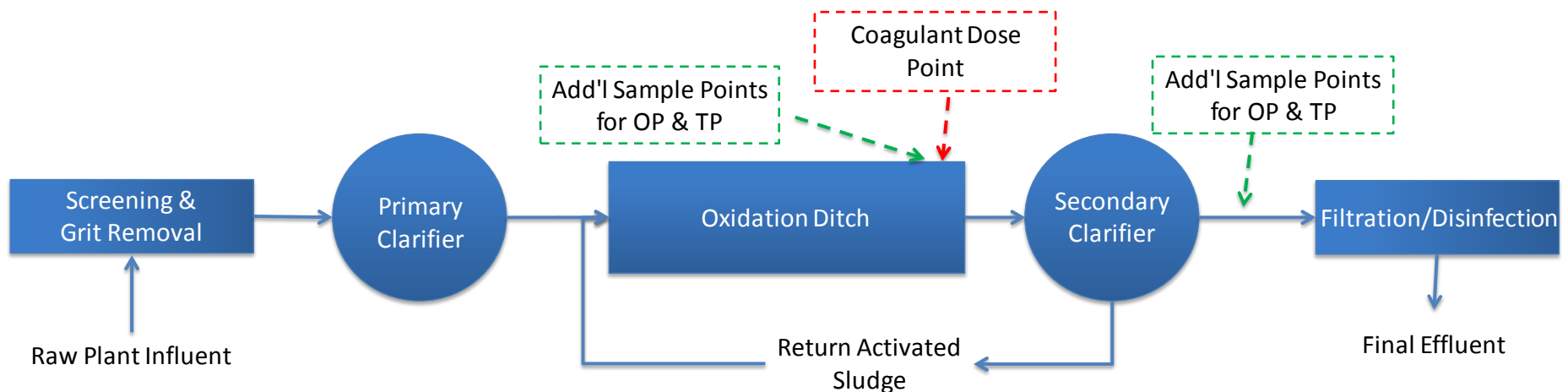
45 MGD WWTP - Tertiary Clarifier Treatment



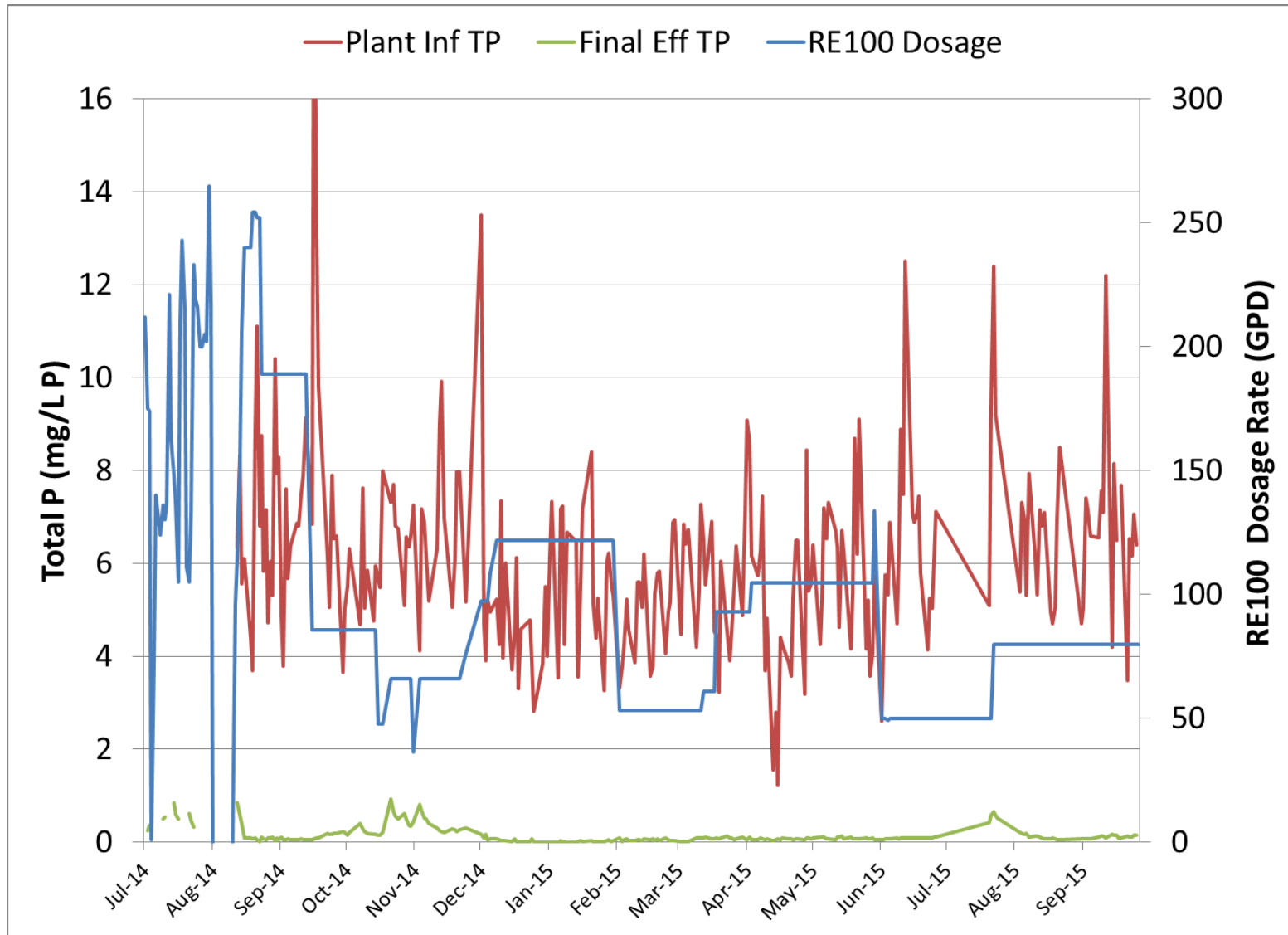
RE Dose
11 ppm_v
0.7:1 RE/P

City of Hartford WI WWTF

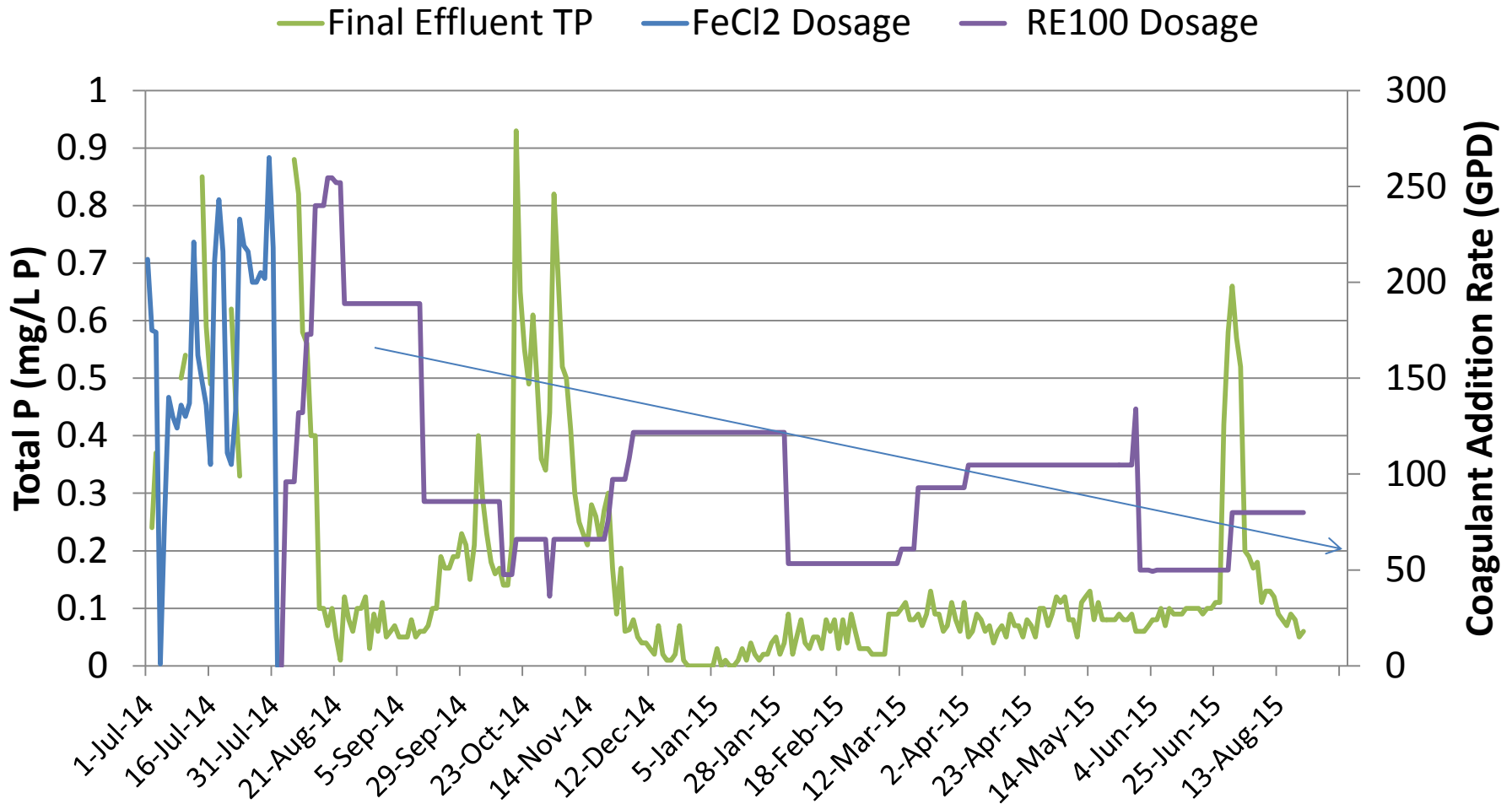
- 3.4 MGD municipal WWTF located in Wisconsin
 - Activated Sludge, Extended Aeration / Tertiary Filtration
- Current limit 1.0 mg/L-P / Upcoming limit of 0.075 mg/L-P
 - Final Compliance Report submitted July 2016
- Previously used ferrous chloride (FeCl_2) for chemical P removal
 - 200 GPD achieved ~0.8 mg/L (~ 100 ppmv)
 - Lowest TP level achieved with FeCl_2 was 0.3 mg/L



Hartford achieved < 0.075 mg/L effluent



Hartford Plant Effluent TP vs. Dose



- RE 100 dose in 2016 was 69 GPD to achieve < 0.075 mg/L-P (36 ppmv)
- → 0.97:1 Molar Ratio (Rare Earth:Phosphorus)

CSWEA 88th Annual Meeting (May 18-20, 2015)

Hartford WI Permit Compliance Schedule

Hartford WPCF Preliminary Facilities Planning

Process

Equipment Cost

- | | |
|---------------------------------|---------------|
| ▪ Ultrafiltration | ▪ \$4,567,000 |
| ▪ Disk Filtration (cloth) | ▪ \$974,000 |
| ▪ Disk Filtration (membrane) | ▪ \$1,026,000 |
| ▪ Ballasted Sedimentation | ▪ \$1,153,000 |
| ▪ Continuous Backwash Filter | ▪ \$1,950,000 |
| ▪ Rare Earth Product/Biological | ▪ \$0 |

**Use Anthracite Filters Concrete Superstructure
No new Building**

Rare Earth Technology Benefits – Hartford WI WWTP



- Able to reach ultra low phosphorus level without capital costs
- Significant reduction in sludge volume (~ 40%)
 - FeCl_2 Sludge Volume = 6 MG/year (dose rate to meet 1 mg/L-P)
 - RE Sludge Volume = 3.7 MG/year (dose rate to meet 0.075 mg/L-P)
- Thicker MLSS concentration

FeCl_2	RE 100
1800-2000 mg/L	2600 – 2800 mg/L

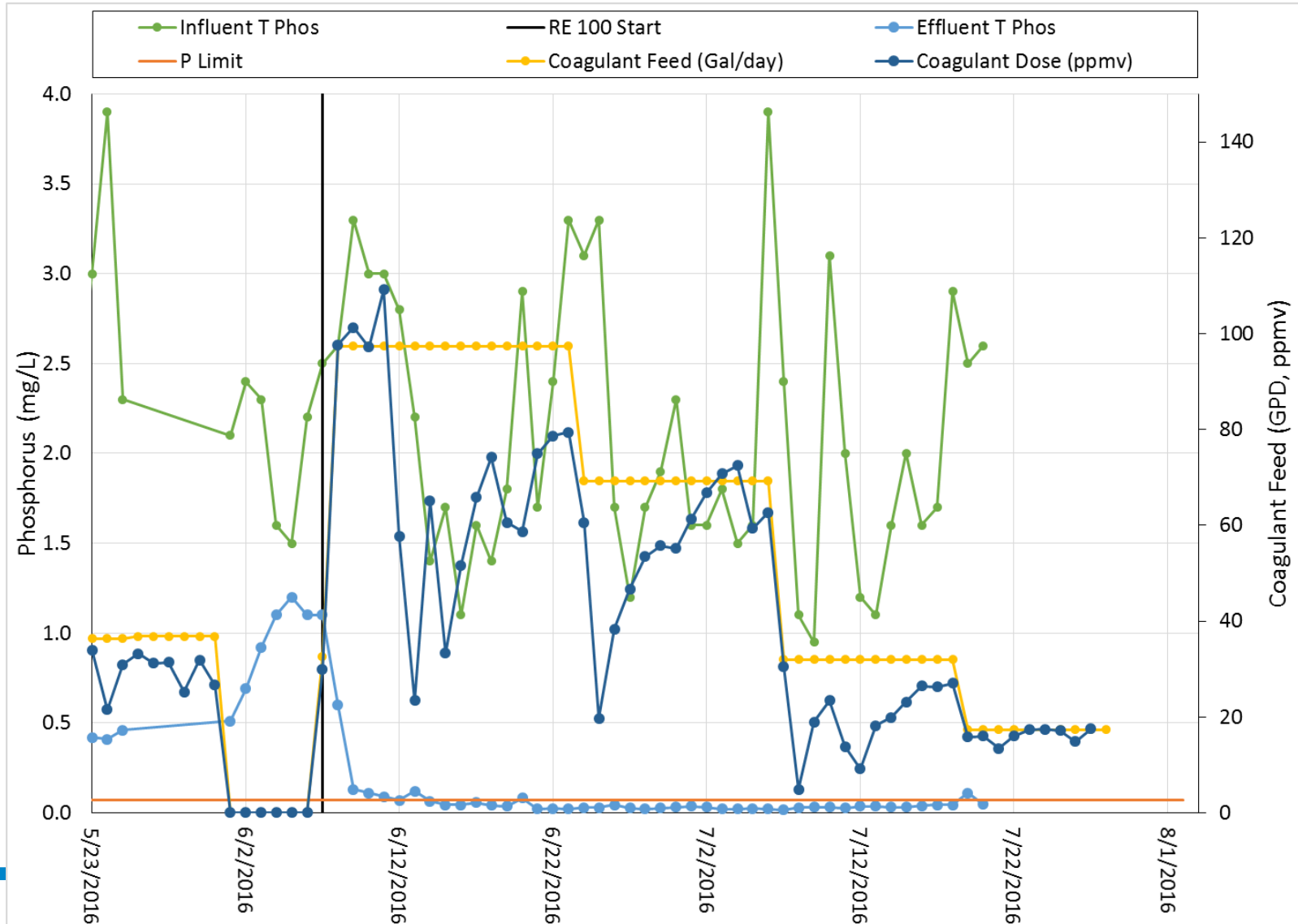
- Lower SVI
- Non-potable water has no smell
- Plant runs more smoothly
 - RE creates a buffer in the process to withstand large spikes in influent P

City of Virginia MN WWTF

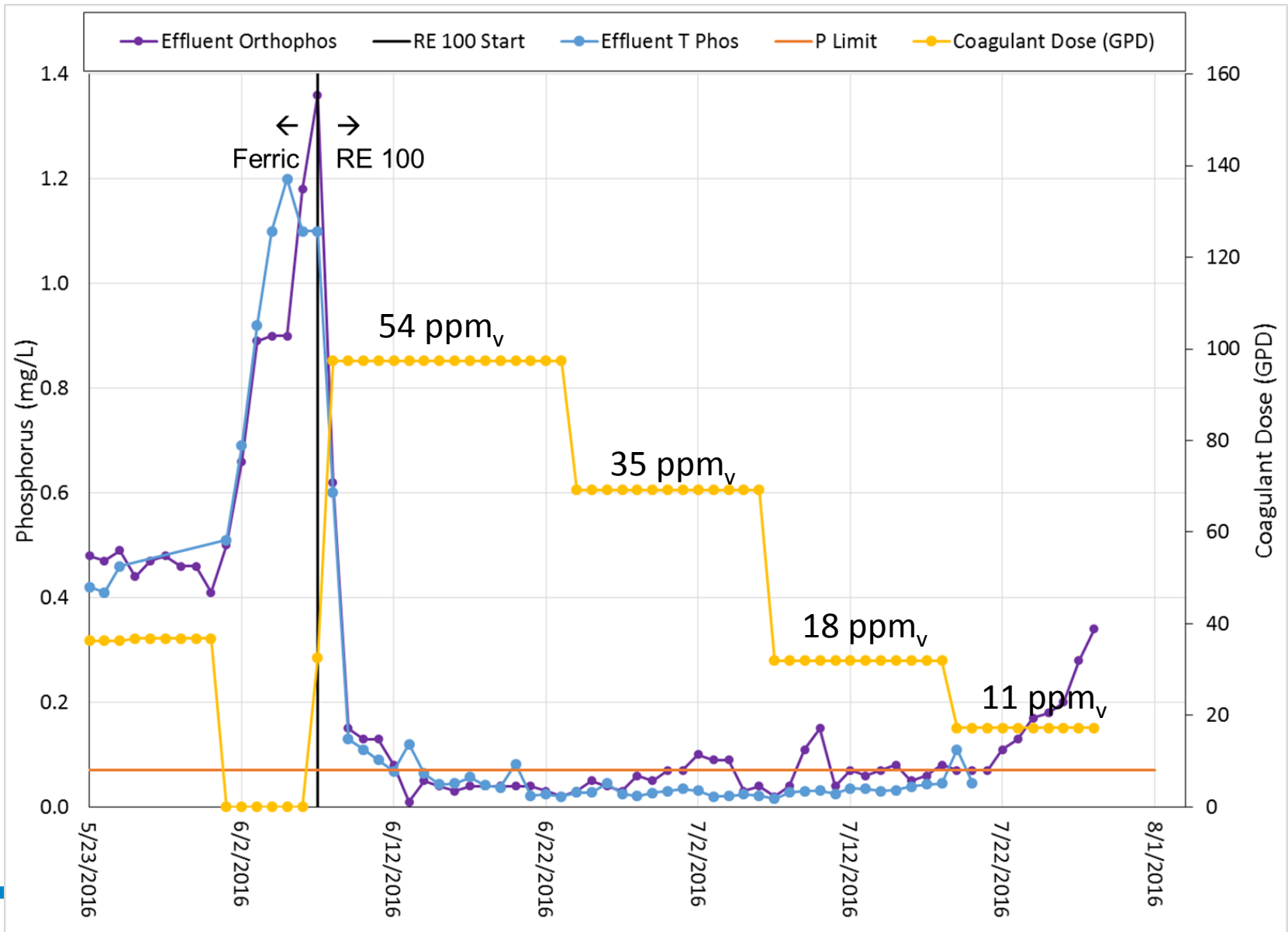
- 2.7 MGD Municipal WWTF located in Minnesota
 - Activated Sludge Aeration Basins / Secondary Clarification / Filtration
 - Anaerobically digester; belt filter press
- Minnesota Pollution Control Agency (MPCA)
 - Current phosphorus limit of 0.8 mg/L-P (CalMonAvg)
 - 0.5 mg/L 12 month rolling avg
 - New permit of 0.07 mg/L-P (CalMonAvg) – Mar 2023
 - Mgmt Plan with Annual Progress
 - Alternatives Identification Plan (Jan 2017)
- Currently use ferric chloride to meet permit
- Trialed Ferric + PAC in 2015
- Trialed RE 100 in Summer 2016

City of Virginia MN – RE 100 Trial Results

- Despite Influent P variability, effluent TP remains below 0.07 mg/L

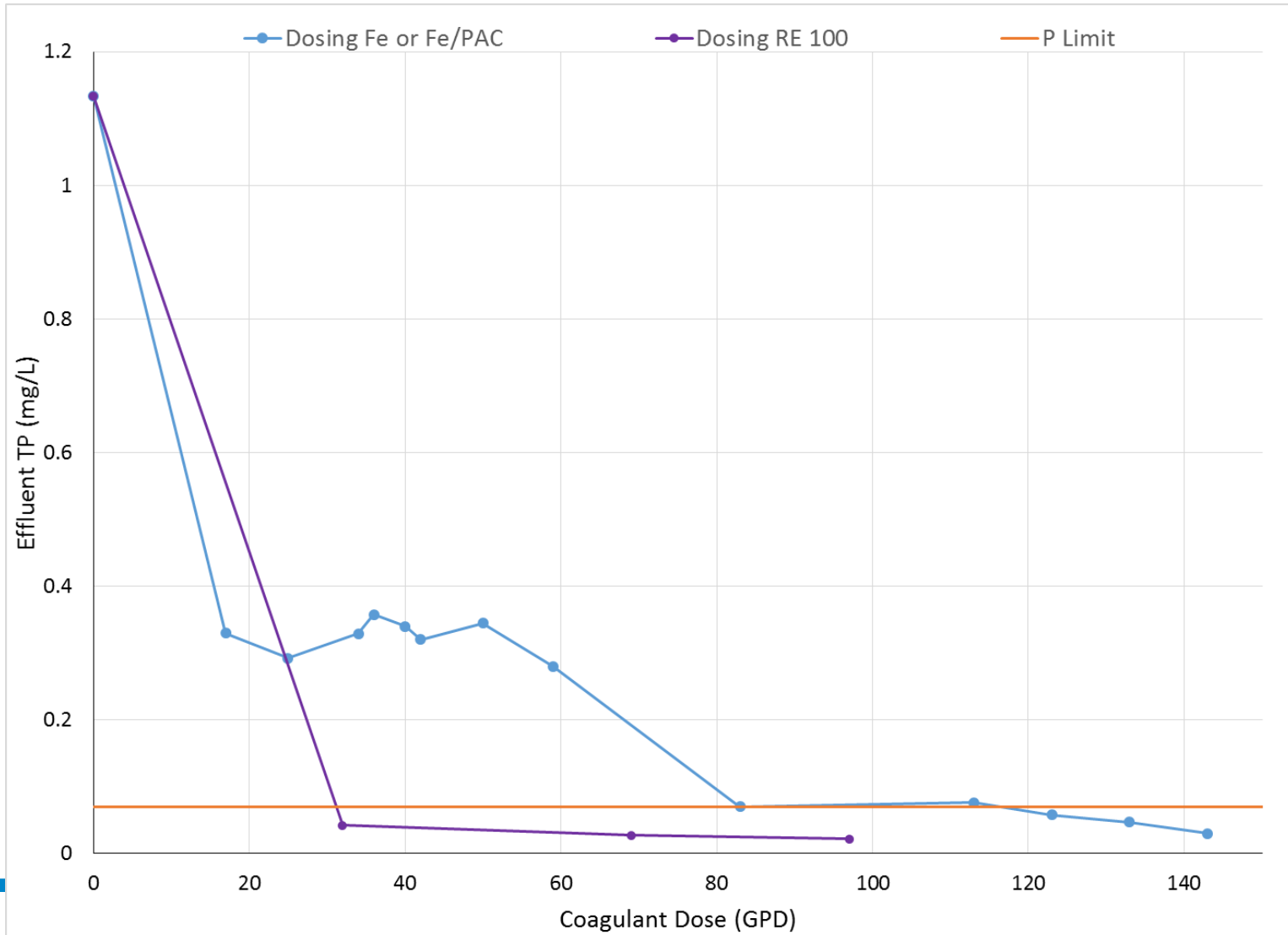


City of Virginia MN – RE 100 Trial Results



City of Virginia MN – RE 100 Trial Results

- RE 100 dose of 32 GPD achieved <0.07 mg/L-P



Virginia MN WWTF - Dewatering Biosolids



- Belt Filter Press results with RE 100
 - ~977 more gallons removed per hour (vs. Ferric)
 - 7,783 more gallons removed per month (vs. Ferric)
 - Ferric + PAC trial – Biosolids production increased by 5000 gpd
- Performance improvement occurred after one month of feeding RE-100. Additional improvement may be evident over longer periods of time.
 - “Perhaps the greatest benefit of RE 100 to biosolids dewatering at the Virginia MN Wastewater Treatment Facility was the avoidance of issues seen with Polyaluminum Chloride during the 2015 Pilot Study that led to over-thickening of biosolids in the anaerobic digester and a dramatic decrease to dewatering efficiency. The fact that RE 100 increased dewatering efficiency at all while achieving effluent total phosphorus results below 0.07 mg/L demonstrates its superiority over other chemicals on the market today.” Brad Bennett, People Services

Ferric + PAC

45 ppm PAC + 70 ppm Ferric

38 days of results

Linear relationships

Freezes @ approx. 32°F

Add'l infrastructure
/renovation needed

May need add'l digester

Met limit

Did not
bind filters

Improved
treatment
overall

RE 100

30 ppm RE 100

54 days of results

Built up quickly in RAS

Maintained low results @
30 GPD feed rate

Freezes @ -40°C

Can use existing
infrastructure

Improved bio-solids
dewatering performance

RE 100 Benefits – City of Virginia, MN WWTF



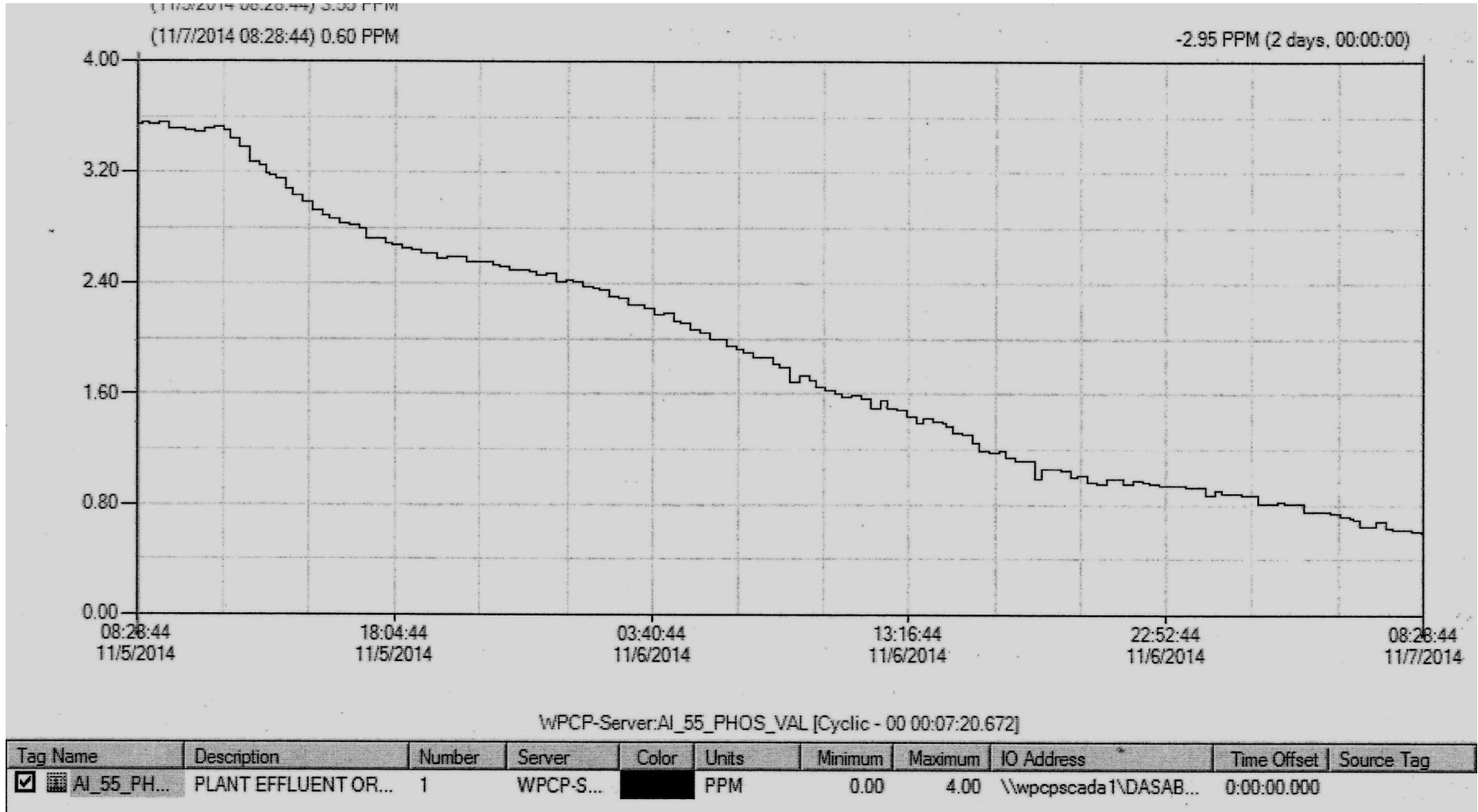
- Achieved < 0.07 mg/L-P in final effluent
- Avoidance of capital costs (vs. FeCl_3 + PAC)
 - Add'l infrastructure/renovation required for PAC due to freezing point
 - Decreased sludge volumes eliminate need for add'l digester
- Decrease in sludge volume
 - Will better quantify sludge reduction for 2nd trial on-going in 2017
- Improved dewatering of biosolids
- Decrease in chloride levels vs. FeCl_3

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
- ✓ Eliminates need for settling aids, polymers/flocculants
- ✓ 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

Rare Earth Technology Benefits – Fond du Lac WWTP

Fast Coagulation properties



Plant Effluent – from 3.6 mg/L-PO₄ to 0.6 mg/L-PO₄ in 48 hours

Fast Coagulation properties

- Mixed Liquor sample - settling



Initial

1 min

2 min

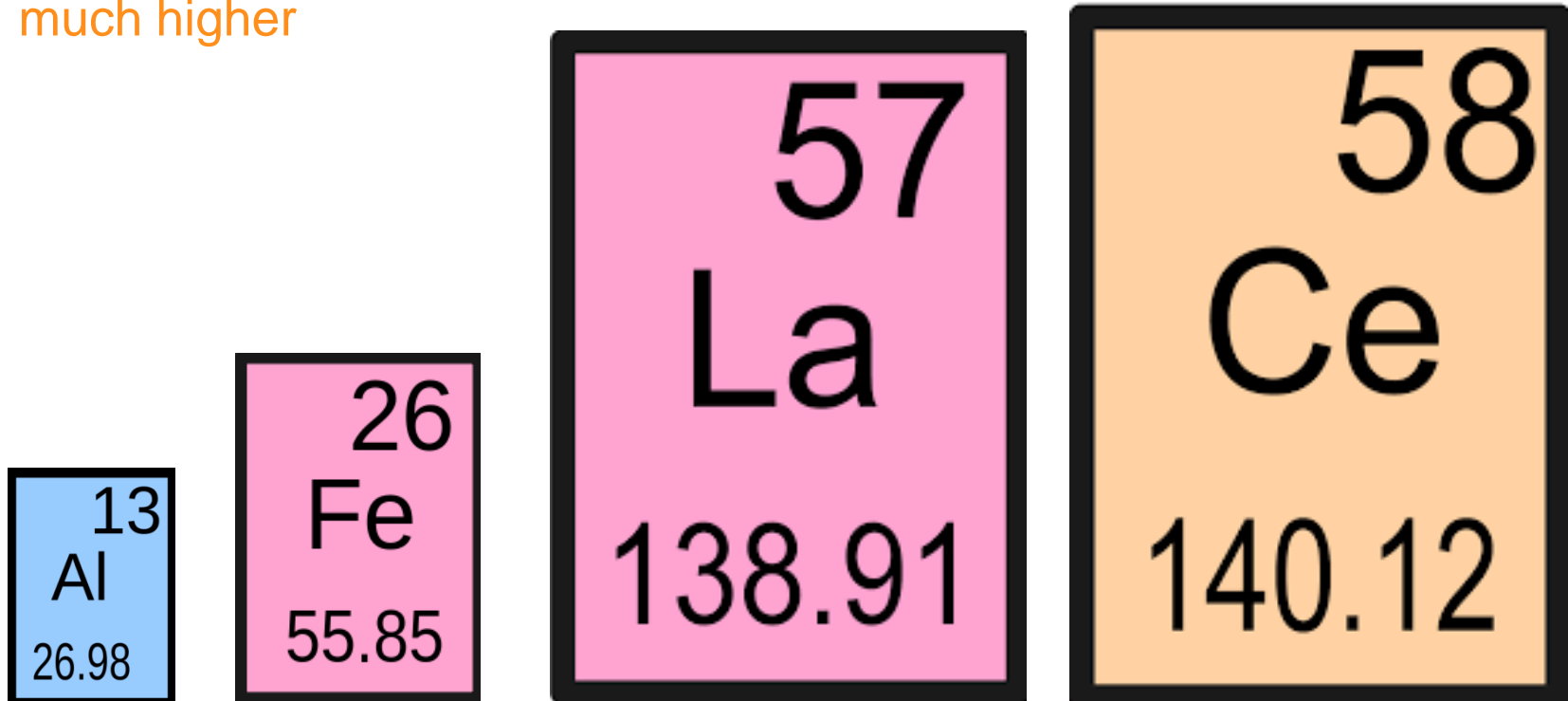
4 min

5 min

10 min

Fast Coagulation Properties

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



- Forms denser precipitate which settles well in clarifier

Rare Earth Technology Benefits – Fond du Lac WWTP

- Improved dewatering of biosolids

- Cake %TS

Before RE 100	After RE 100
25 – 26%	28 – 29%

- Prevention of struvite formation



- Plant runs more smoothly

- RE 100 provided a buffer in the process to manage spikes of industrial feed containing high levels of phosphorus

Rare Earth Technology Benefits – Albion PA

Improved water clarification



Before RE100 addition



After RE100 addition

Improved Clarification

Before RE 100 addition



After RE 100 addition



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

Improved Dewatering of Biosolids



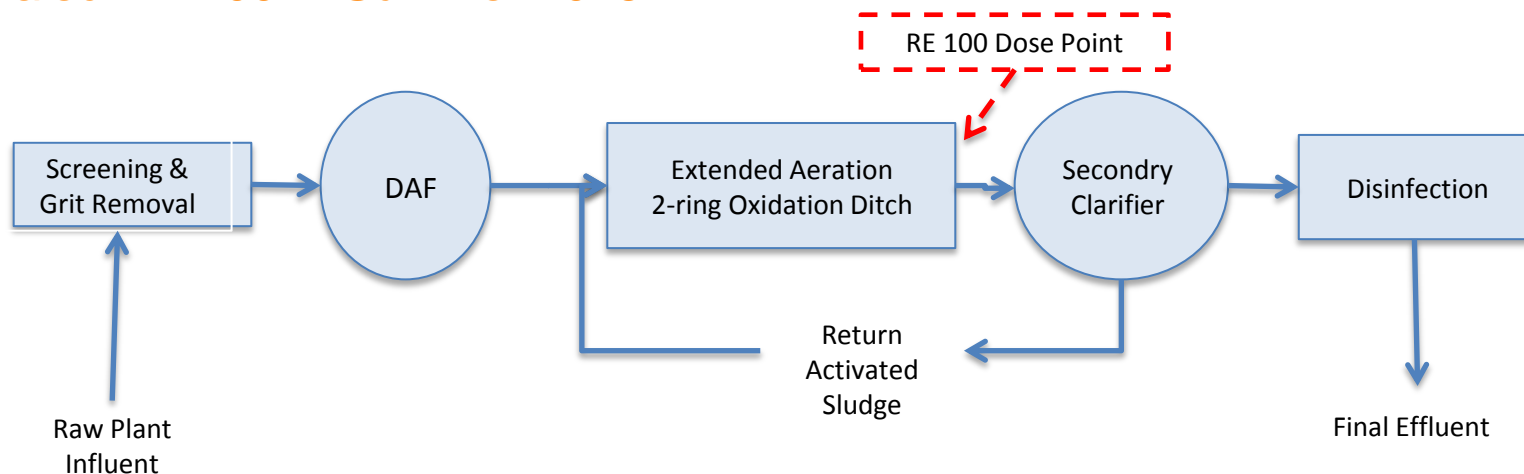
- Albion PA WWTF: “We have doubled our belt filter press throughput, compared to iron and aluminum.”

Rare Earth Benefits - Borough of Albion, PA WWTF

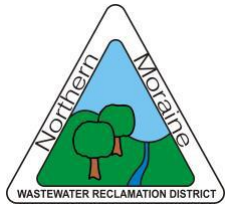
- Improved coagulation & settling in clarifiers
- Significant decrease in sludge volume
 - 68% savings on the sludge disposal costs/ year
= \$70,000/year annual savings
- Improved performance on belt filter press
 - Prior to RE100, ran belt filter press 5 days/week
 - With RE100, run only 1 day/week
 - → 80% decrease in energy savings (estimated to be \$7K/year)
- Less maintenance, more steady overall operations

Northern Moraine Water Reclamation District, Illinois (NMWRD)

- 2 MGD municipal WWTF located in Illinois (Design Max 5 MGD)
- Effluent discharges to Fox River
 - Illinois Environmental Protection Agency's list of impaired waterways
- No current phosphorus permit & not equipped for chemical dosing
 - New limit of **1.0 mg/L-P**
 - Plans & Specifications due May 2017 / Full compliance May 2019
- Trialed RE 100 in Summer 2015



RE 100 Dose Rates @ NMWRD



- 9 GPD achieve < 1.0 mg/L-P (8 ppm_v)
- 12 GPD achieved < 0.5 mg/L-P (11 ppm_v)

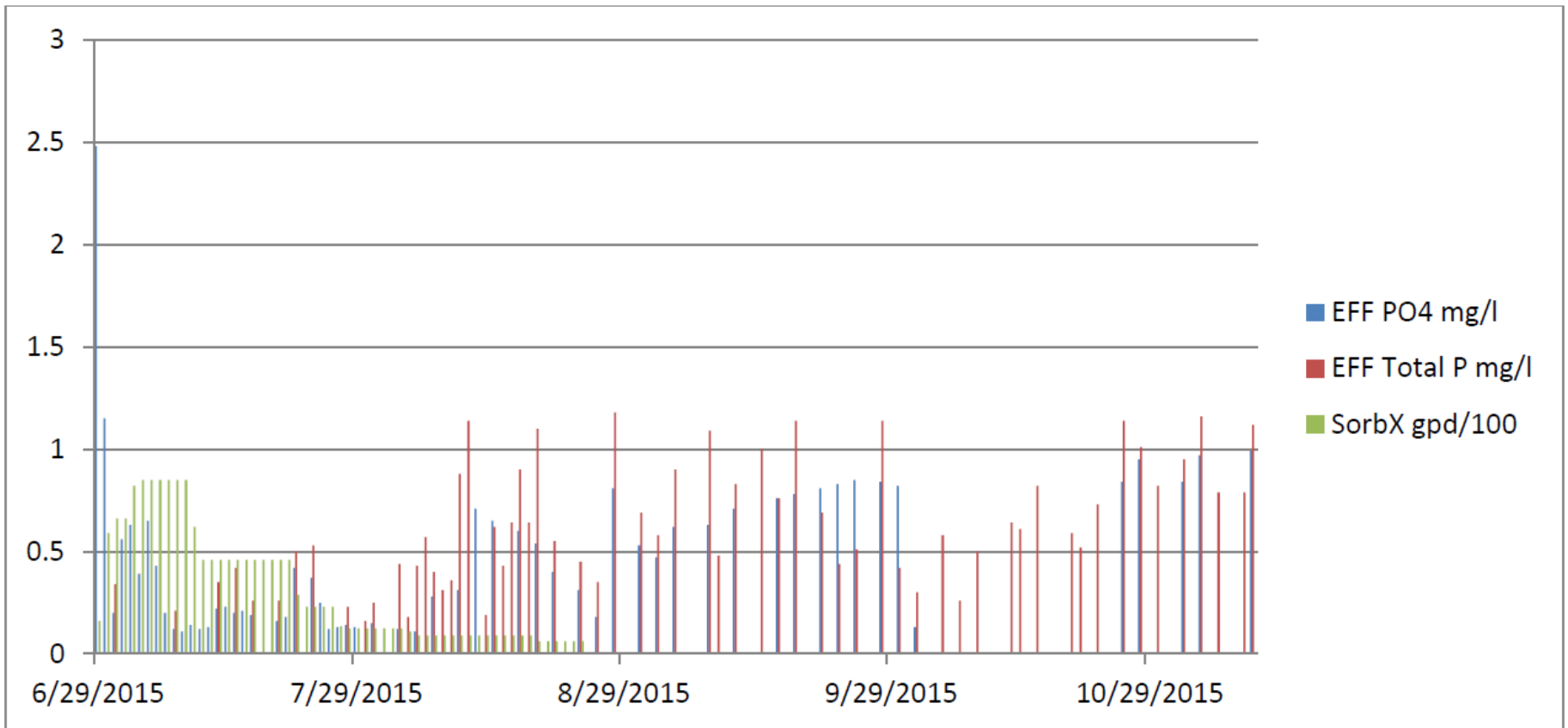
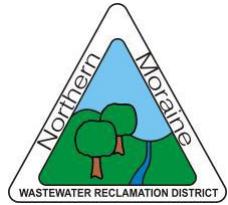


Figure 2. NMWRD Pilot Test Data, SorbX-100 Dosages 6.29.15 to 8.29.15 vs. Effluent P concentrations.

NMWRD – RE 100 Trial Results



RE100 continued to suppress phosphorus levels for 2+ months after turning off dose

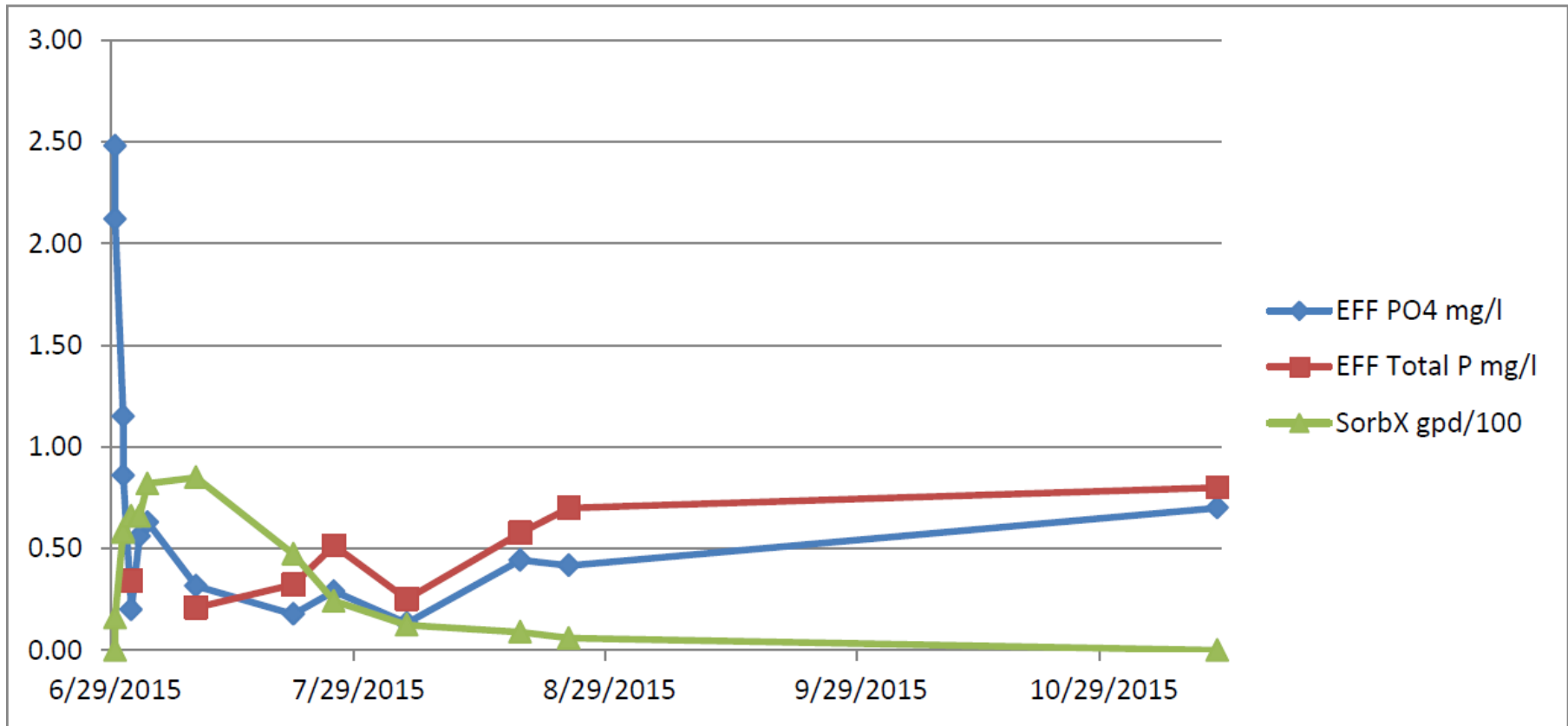
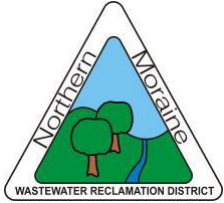


Figure 3. NMWRD Pilot Test Data, SorbX-100 Averages P and PO4 mg/l at each dosing rate.

NMWRD – RE100 Trial Results



- Plant Flow = 1.1 MGD
- Influent P = 6.2 mg/L (3.8 – 12.4 mg/L)
 - High P peaks due to side stream impacts from digester decant and dewatering centrifuge concentrations of around 15.7 mg/l TP
- RE100 dose rate
 - 9 GPD achieve < 1.0 mg/L-P (8 ppm_v)
 - 12 GPD achieved < 0.5 mg/L-P (11 ppm_v)

Reduction in Capital Costs

Costs for chemical addition facilities needed to meet limits of 0.5 to 1.0 mg/L

Description	FeCl ₃ *	SorbX-100
	Chemical Feed Building and System	
Construction Subtotal	\$358,015	\$100,000
General Conditions	\$44,750	\$12,500
Contingency @ 25%	\$100,690	\$25,000
Construction total	\$503,455	\$137,500
Design Engineering @ 7.5%	\$37,760	\$10,312
Construction Engineering @ 7.5%	\$37,760	\$10,312
Total Capital Costs	\$578,975	\$158,124

* Source: Trotter and Associates 2014 Facility Plan Update

RE 100 Benefits – NMWRD WWTF

- RE100 quickly achieved target in effluent
- RE100 continued to suppress phosphorus levels for several months after dosing was turned off
- Reduced capital costs to meet 0.5 – 1.0 mg/L-P
 - No need for large chemical storage tanks, buildings and ancillary equipment
 - No need for tertiary filtration
- Preferred a non-hazardous product

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Plant Trial Recommendations

- Understand phosphorus levels throughout plant
 - TP & OP
- Know the phosphorus speciation in the plant
 - sNRP is important to know if phosphorus permit is < 0.5 mg/L-P
- Minimum trial period is 3 months
 - Unable to quantify overall benefits in less time
- Plant needs the ability to measure phosphorus
 - At a minimum, have ability to measure OP

Conclusions

Observed Benefits of Rare Earth Technology

- ✓ Able to achieve very low TP discharge limits without capital equipment
- ✓ Significant reduction in sludge volumes
- ✓ Faster coagulation and noticeable water clarification
- ✓ Less coagulant volume required to reach low phosphorus limits
- ✓ Reduction in maintenance costs vs. ferric-based coagulants
- ✓ Will not stain or discolor facility structures or equipment
- ✓ Compatible with existing dosing and filtration equipment
- ✓ Rated non-hazardous for DOT regulations

■ Questions?

- Pam Cornish
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- 734-216-2089