Chemical Precipitation as Primary or Polishing Process for Phosphorus Removal

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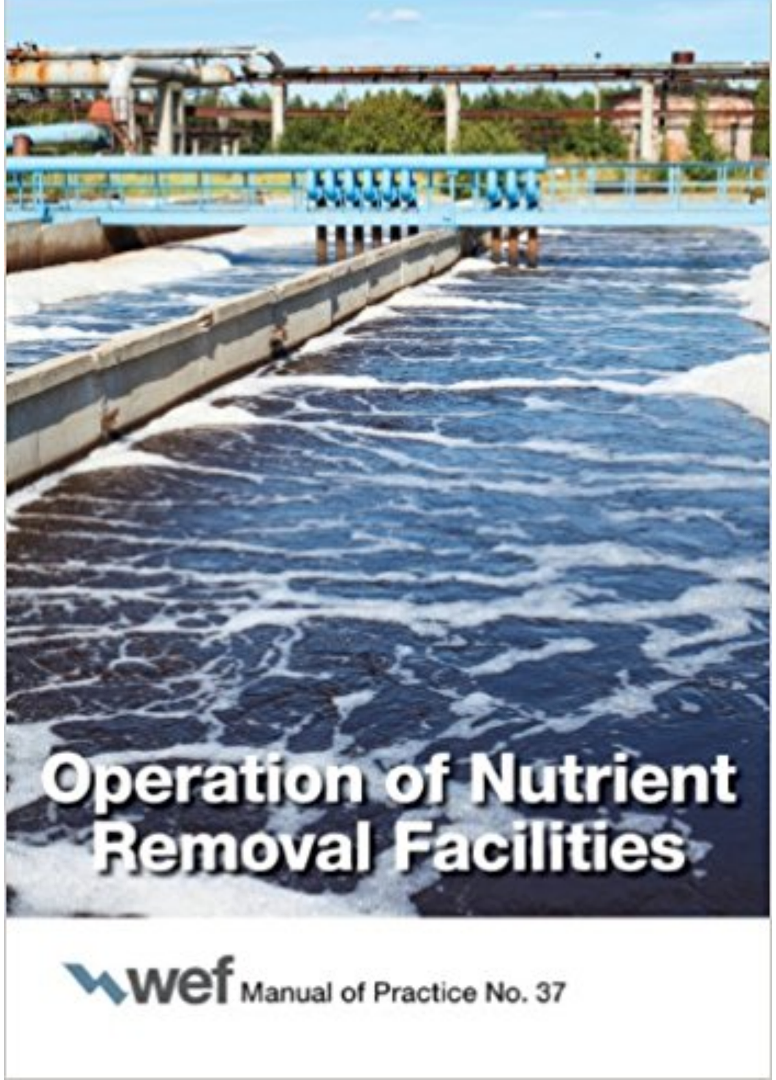

Operation of Nutrient
Removal Facilities
wef Manual of Practice No. 37

Why Chemical P Removal?

- Often method of choice for small plants
- Retrofit to bio-P may be not practical
- Bio-P is subject to upsets – back-up
- Utilized as polishing step

Chemical addition is an integral part of any phosphorus removal facility either as a primary, polishing or back-up process

Overview

Chemical addition is an integral part of any phosphorus removal facility either as a primary, polishing or back-up process

1. Basics of chemical precipitation
2. Chemicals for P removal
3. Summary dose formulas
4. Role of solids separation
5. Point of addition considerations
6. Response time and start-up
7. Sludge generation and inerts accumulation
8. Pros and Cons of chemical P removal

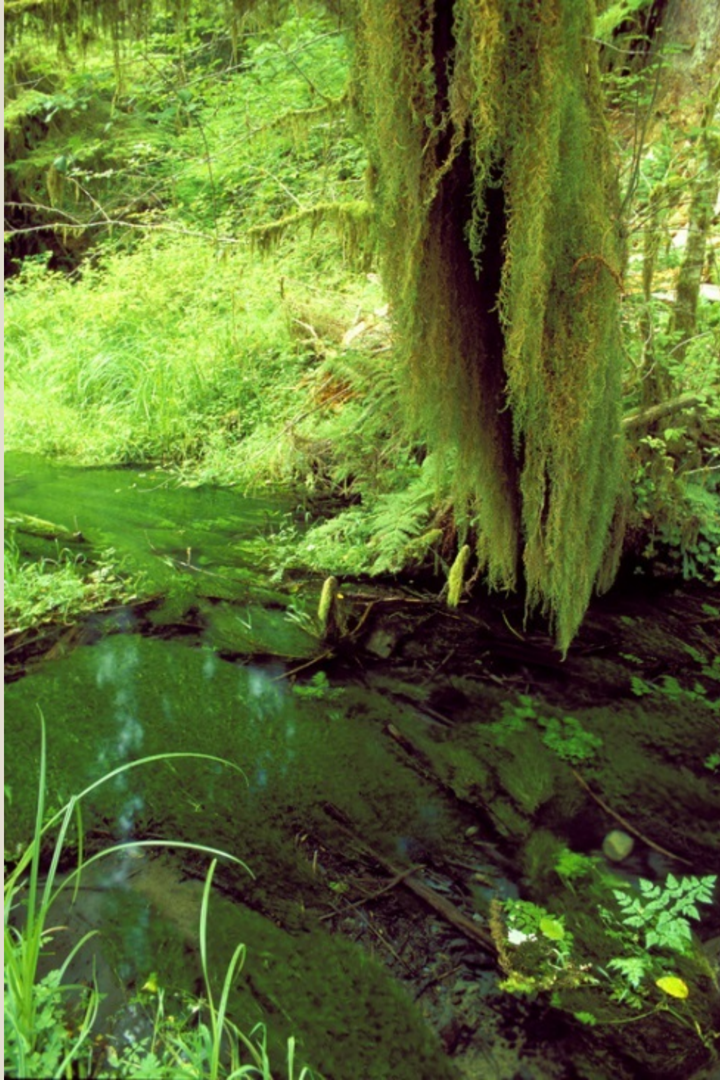
1 Basics

P present in different forms; soluble, colloidal and particulate

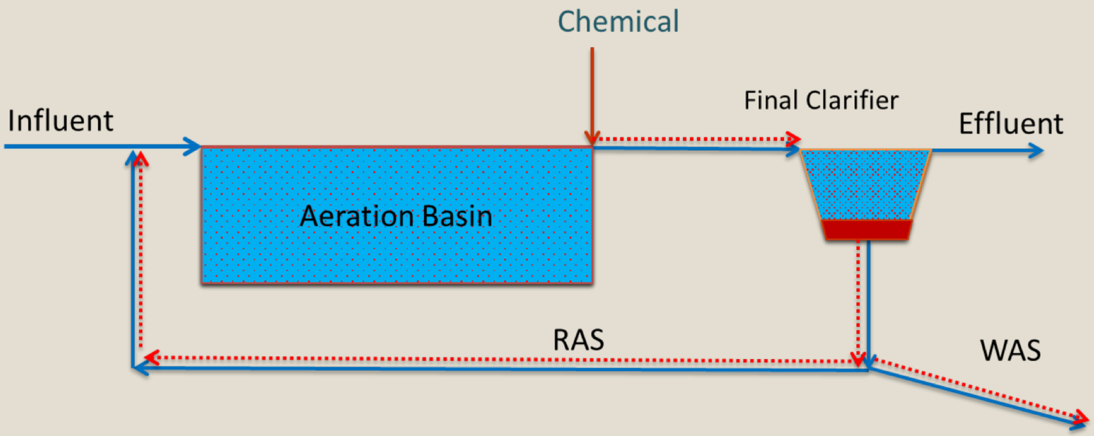
- orthophosphates $(PO_4)^{3-}$ could be precipitated

$$Al^{3+} + (PO_4)^{3-} \rightarrow \underline{AlPO_4} \downarrow$$

- After biological treatment almost all residual P is in orthophosphate form
- Small concentration (<0.05 mg/L) of non-reactive, dissolved organic P may be present



1 Basics – Fate of Added Chemicals



- Chemical reacts with orthophosphate and precipitates as, say, aluminum orthophosphate
- Excess chemical also precipitates (aluminum hydroxide)
- Both forms settle and return with RAS to Aeration Basin

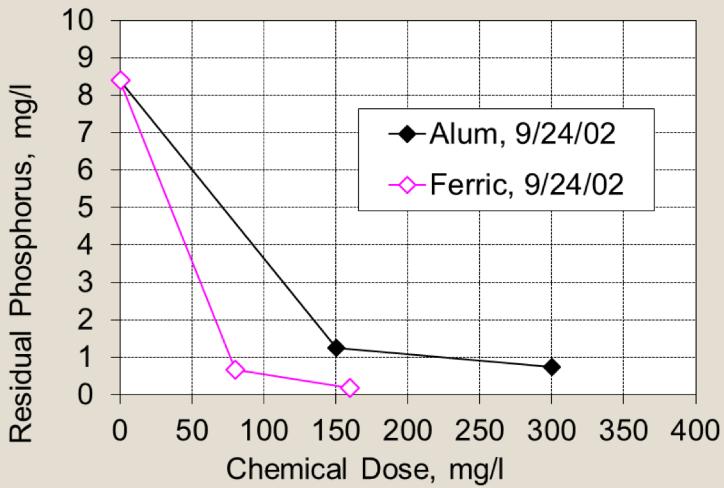
2 Chemicals for P Removal

- Aluminum-based chemicals
  - Alum (aluminum sulfate)
  - Polyaluminum chloride(PACl)
  - Sodium aluminate
- Iron-based compounds
  - Ferric chloride ($FeCl_3$) or sulfate
  - Ferrous salts (acidic spent pickle liquor)
- Other (lime, magnesium hydroxide)
- Water sludges
- Proprietary formulations

2 Chemicals - Selection

- Alternative chemicals are manufactured with, or contain, neutralizing agent (caustic)
- Could help with pH and be easier to handle
- Conduct side by side tests comparing effectiveness of alternative chemicals at various dosages and factor in unit costs

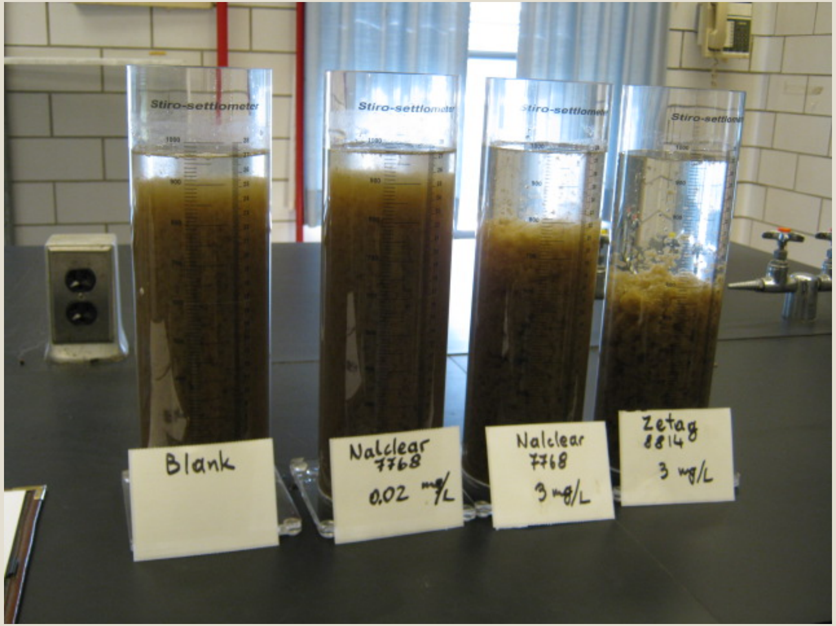
2 Chemical - Selection



- With application costs established, consider intangibles such as ease of handling, need for additional chemicals (caustic), help with odor, impact on UV

2 Chemical – Role of Polymer

- Not a P- precipitating agent on its own
- Could greatly improve settling
- Should be added downstream of precipitating chemicals
- 0.5 to 1 mg/L typical dose for dry polymer, higher for emulsion



3 Summary Dose Formula - **Alum**

Formula for calculating approximate alum dose for P removal is as follows (from MOP 37):

US Units

$$A = 11.8*(Xi - Xe)*(Q/(1-0.95*(\exp(-1.9*Xe))$$

- A = 49% alum solution application rate (gpd)
- Xi = soluble phosphorus concentration at the application point (mg/L)
- Xe = target effluent soluble phosphorus concentration (mg/L)
- Q = facility flow (mgd)

3 Summary Dose Formula - **Ferric**

US Units

$$A = 15.5*(Xi - Xe)*(Q/(1-1.07*(exp(-2.25*Xe))$$

- A = 37% ferric chloride application rate (gpd)
- Xi = soluble phosphorus concentration at the application point (mg/L)
- Xe = target effluent soluble phosphorus concentration (mg/L)
- Q = facility flow (mgd)

3 Formulas – Example (Ferric)

US Units

A = 15.5*(Xi –Xe)*(Q/(1-1.07*(exp(-2.25*Xe))

- Xi = 3 mg/L
- Xe = 0.4 mg/L
- Q = 10 mgd

- A = 15.5*(3-0.4)*(10/(1-1.07*exp(-2.25*0.4))
- A = 713 gpd of 37% ferric chloride

As 1 gallon of 37% ferric has 4.2 lb of $FeCl_3$, the applied dose will be:

713*4.2/10/8.34 = 36 mg/L (as $FeCl_3$)

3

Formulas – Notes on Alum

Alum dose is customarily expressed as dry aluminum sulfate or “filter alum” with composition of:

$$Al_2(SO_4)_3.14H_2O$$

49% Alum solution has dry alum (($Al_2(SO_4)_3$*14H_2O) content of 0.647 kg/L (**5.4 lb/gal**), and aluminum metal content of 0.059 kg/L (0.492 lb/gal)

Dry alum, includes crystallization water!

3

Formulas – Notes

- 37% Ferric chloride solution has specific density of 1.36 kg/L (11.4 lb/gal), dry $FeCl_3$ content of 0.504 kg/L (**4.2 lb/gal**) and iron metal content of 0.173 kg/L (1.44 lb/gal)
- Many factors (wastewater chemistry, pH, application point, mixing) will impact the actual dose
- Formulas are valid in a limited concentration range (for alum - 0.1 to 0.8 mg/L residual P)
- Multi-point addition of coagulant (e.g. some to primary clarifier, some to secondary clarifier) will result in reducing the overall chemical use

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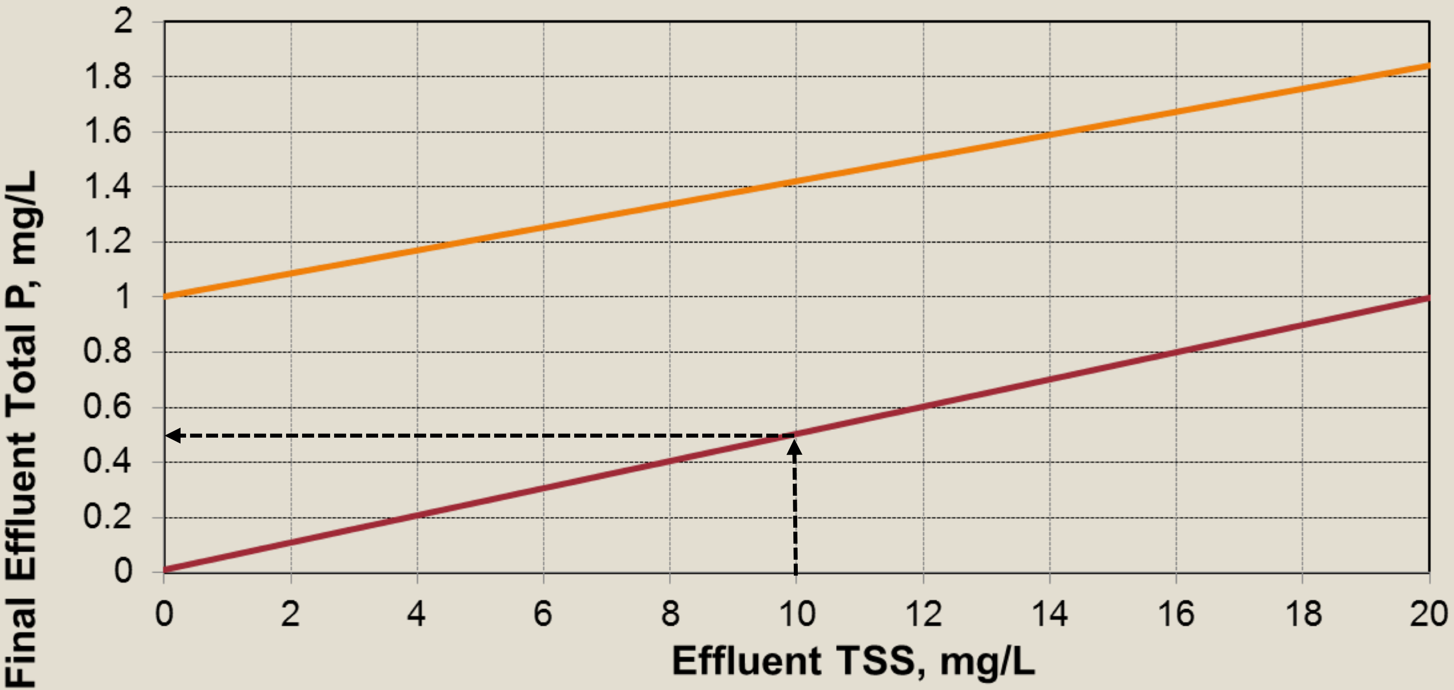
Role of Solids Separation

- P limits are commonly expressed as total P, so precipitating soluble P is only part of the job
- This is particularly important for low P limits
- MLSS (and effluent TSS) has approximately 2% of P; this could increase to 4-5% or even higher for plant removing P to a low level

4 Role of Solids Separation – Impact of Effluent TSS on Effluent TP



Moderate P limit (effl. ortho-P = 1 mg/l), 0.042 mg P/mg TSS

Low P limit (effl. ortho-P < 0.02 mg/l), 0.049 mg P/mg TSS

Primary effluent composition: tP = 5.25 mg/L, TSS = 84 mg/L, BOD5 = 142.5 mg/L. Alum added to activated sludge. Results obtained with BioWin modeling at SRT of 8 days

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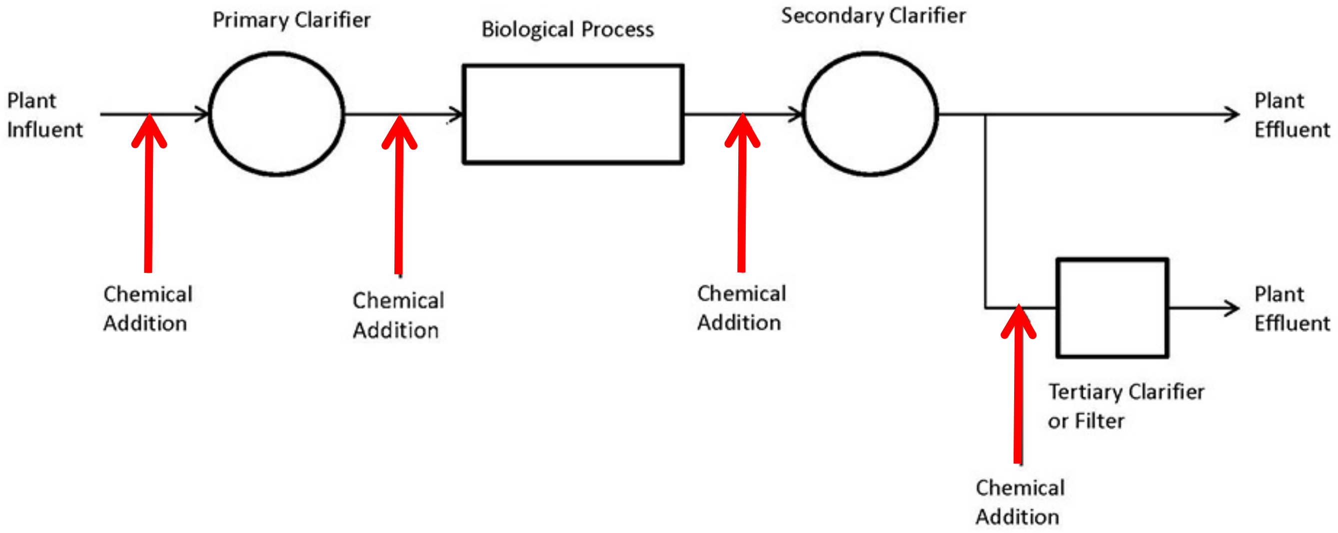
Point of Addition Locations



5 Point of Addition Considerations

- Point of addition should be upstream of the solids separation step (clarifier or filter)
- Vigorous mixing at the point of coagulant addition improves removal effectiveness
- If addition to filter or tertiary clarifier is possible, recycling sludge to primary clarifier will lower chemical use

6 Response Time and Start-Up

- Can be initiated on demand, with quick initial response
- When adding to activated sludge (final clarifier), full effects may take several days
  - Coagulation of biomass inventory
  - Unused chemical returned with RAS
  - HRT in any downstream processes

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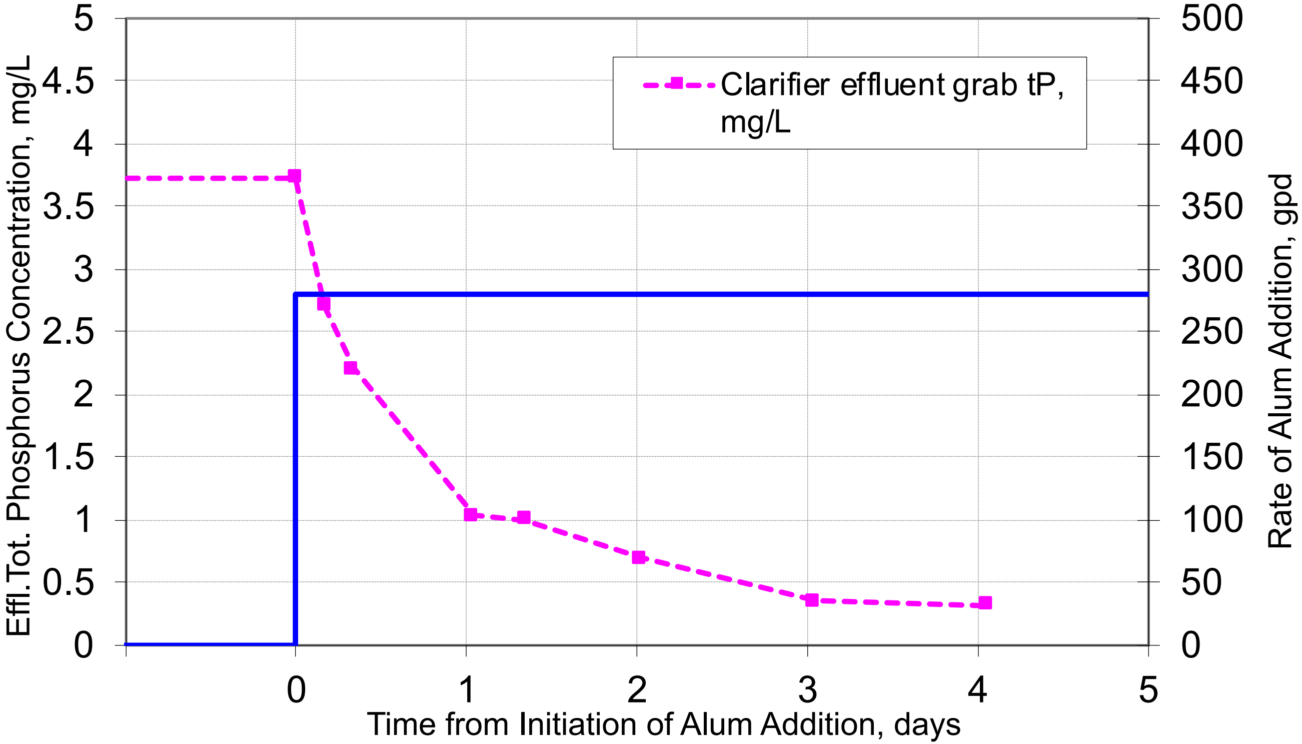
Start-Up of Chemical Addition



7 Sludge Generation

- Chemical addition generates additional, inert sludge
- Chemical sludge is enmeshed with biomass and WAS (if added to activated sludge)
- Coagulants will increase capture of colloidal solids
- Approximate extra sludge generation can be calculated from conversion factors

7 Sludge Generation (&TDS) Conversion Factors

Chemical/Process	TSS increase factor (F), kg per kg (or mg/L per mg/L) of chemical added	TDS increase factor, kg per kg (or mg/L per mg/L) of chemical added
Typical alum application for chemical P removal (at 3:1 alum to phosphorus stoichiometric rate), w/o neutralization	0.312	0.378
Typical alum application for chemical P removal (at 3:1 alum to phosphorus stoichiometric rate), with full neutralization with caustic	0.312	0.533
Typical ferric application for chemical P removal (at 3:1 ferric to phosphorus stoichiometric rate), w/o neutralization	0.748	0.460
Typical ferric application for chemical P removal (at 3:1 ferric to phosphorus stoichiometric rate), with full neutralization with caustic	0.748	0.745
pH adjustment with caustic	0	0.575
pH adjustment with sulfuric acid	0	0.980

7 Waste Sludge Generation - Example

- In our previous example, the 37% ferric application rate at a 10 mgd plant was 713 gpd or 36 mg/L
- From the Table, TSS conversion factor for Ferric (with 3:1 excess) was 0.748
- Thus extra sludge generated will be:

US Units

0.748 * 36 mg/L = 27 mg/L extra TSS

or,

713 gpd * 4.2 lb $FeCl_3$/gal = 2,995 lb $FeCl_3$/day

0.748 * 2,995 lb $FeCl_3$/day = 2,240 lb/d sludge

7 Insert Sludge Accumulation in MLSS

- Inert, precipitated chemicals accumulate in aeration tankage, increasing non-volatile MLSS concentration
- Higher MLSS concentration required to maintain the same MLVSS (or sludge age)
- If the same MLSS is maintained, MLVSS concentration (and sludge age) will be lower (nitrification!)

7 Insert Sludge Accumulation in MLSS

$$MLSSci = D * F * SRT/HRT$$

- MLSSci = chemical inerts concentration, mg/L
- D = chemical dose applied, mg/L
- F = TSS conversion factor for chemical used (from table)
- SRT = sludge age, days
- HRT = hydraulic retention time, days

7 Insert Sludge Accumulation - Example

- Flow = 10 mgd (37,850 m3/d)
- Tankage volume = 5 mg (18,925 m3)
- HRT = 0.5 day
- SRT = 12 days
- Ferric (37%) dose = 36 mg/L
- F = 0.748

MLSSci = 36 mg/L * 0.748 * 12 d/0.5 d = 646 mg/L

8 Summary – Pros and Cons

- Advantages:
  - Reliable
  - On demand
  - No issues with return streams P loading
  - Addition to primaries could help with lowering organic and N loadings to AS
  - Could help with odors (ferric)

8 Summary – Pros and Cons

- Disadvantages:
  - Operational costs of chemicals
  - Extra sludge disposal costs
  - Inert sludge impact on nitrification
  - Alkalinity consumption
  - TDS increase
  - Potential negative impact on UV (ferric)
  - Potential negative impact on WAS thickening (alum)
  - Overdosing could lead to P deficiency in downstream processes (denitrifying filter)

Questions?

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