Low Cost Nutrient Removal for Wastewater Operators Day 2

DBS&A
a Geo-Logic Company

Review of Day 1

- Regulatory Impacts to Permit Limits
- Nitrification/Denitrification
- Phosphorus Removal

Review of Day 1

- Wastewater treatment = saving the planet
- Metazoa are "higher life forms"
- Autotrophs are prima donnas
- Critical to monitor 3 things: ammonia, nitrate and DO

State WQ Standards and TMDL Allocations

- Under the federal National Pollutant Discharge Elimination System (NPDES) Program, the State establishes TMDL's where needed to maintain or achieve water quality.
- This is effecting NPDES permits for wastewater treatment plants, and could effect more of them going forward.

What are plant nutrients? (cont.)

- Permit limits for nitrogen and phosphorus are designed to protect against eutrophication:
  - excessive algal growth
  - reduced light transparency
  - shifts in pH and dissolved oxygen
  - release of toxic levels of ammonia through decay
- Eutrophication can have detrimental effects on recreational opportunities, stream aesthetics, fisheries, aquatic life, and drinking water supply

www.siosa.org

www.bucknell.edu

Rio Ruidoso (2003)

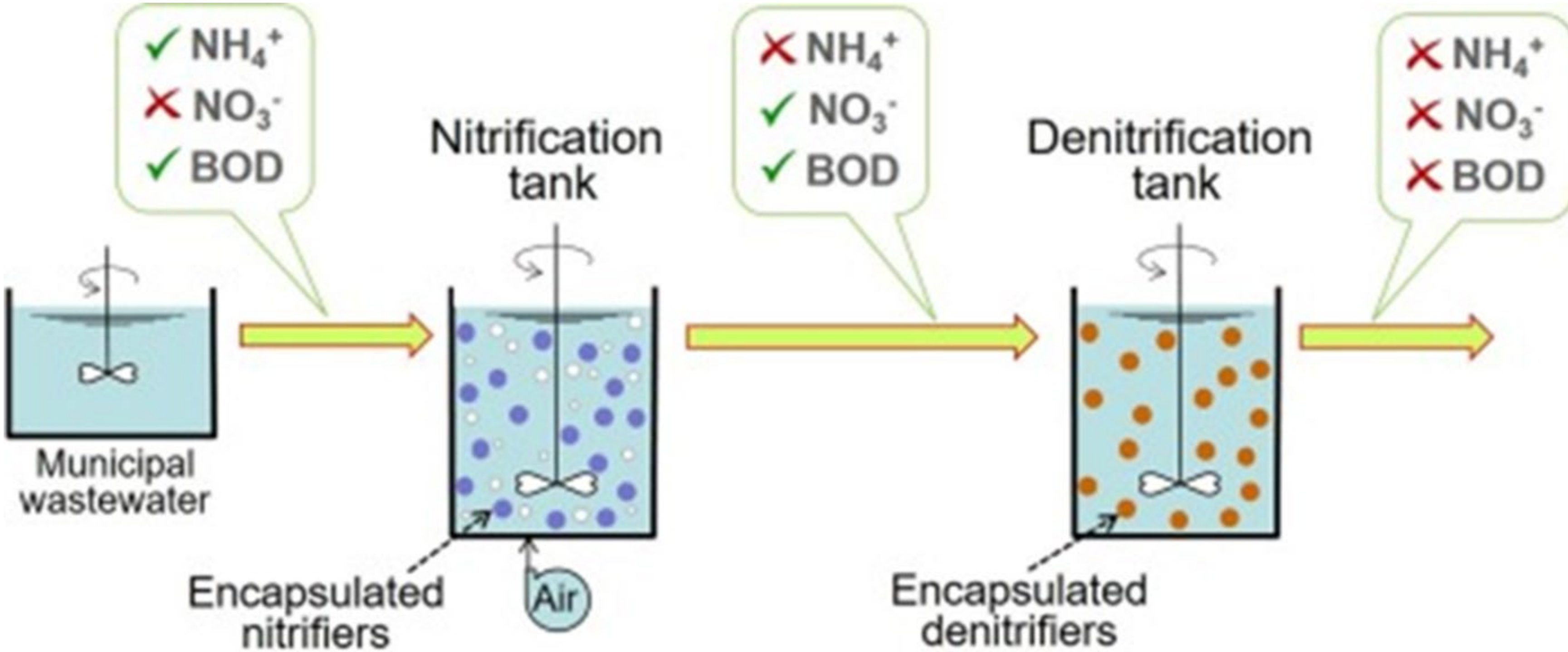
Forms of Nitrogen in Wastewater

1) Ammonia (NH_3-N)
2) Nitrite (NO_2-N)
3) Nitrate (NO_3-N)
4) Nitrogen Gas (N_2)

Nitrification/Denitrification

- https://www.youtube.com/watch?v=koG0mCFaJXA

Biological Nitrification



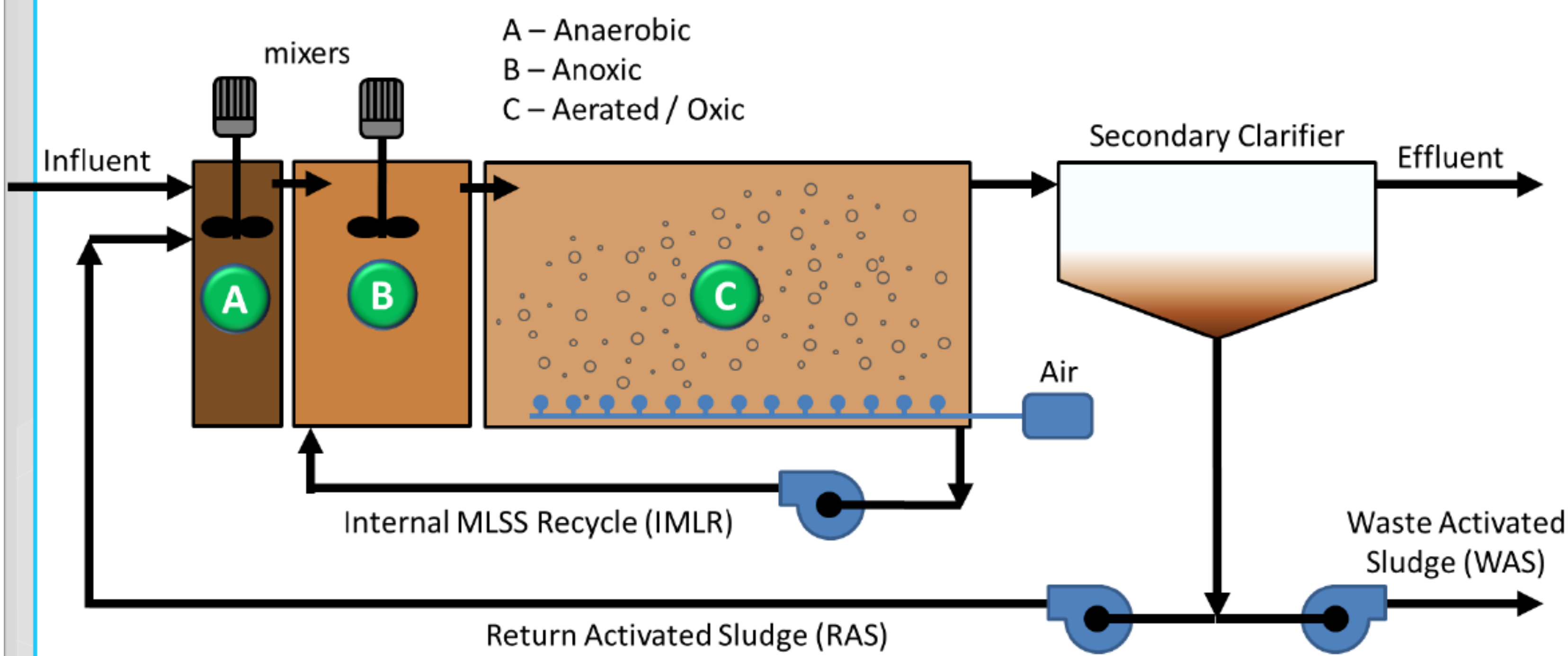
Definitions

Aerobic
- Oxygen (always)
- Nitrite + Nitrate (sometimes)

Anoxic
- NO Oxygen
- Nitrite + Nitrate (always)

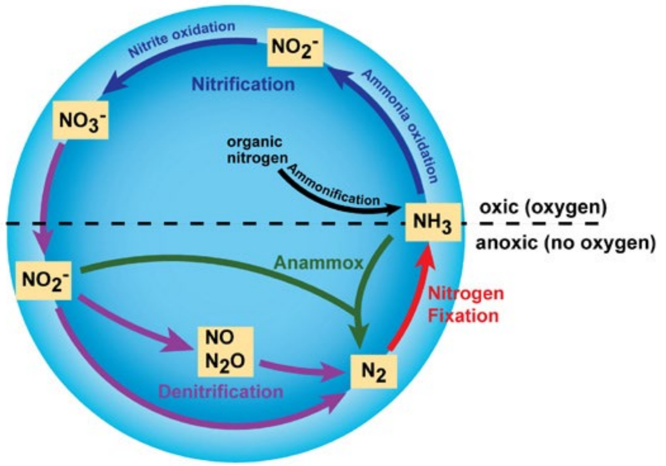
Anaerobic
- NO Oxygen
- NO Nitrite or Nitrate

Anaerobic, Anoxic and Aerated Zones



Chemical Reactions of Nitrification/Denitrification

Process	Reaction
Fixation	N_2 (g) + $8H^+$ + $8e^-$ → $2NH_3$ (g) + H_2 (g)
Ammonification	NH_2-CO-NH_2 + H_2O (l) → $2NH_3$(g) + CO_2 (g)
Nitrification (Two Steps)	(1) NH_4^+ + 1.5O_2 (g) → NO_2^- + $2H^+$ + H_2O (l) (2) NO_2^- + 0.5O_2 (g) → NO_3^-
Denitrification	NO_3^- → NO_2^- → NO → N_2O → N_2



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Biological Nitrogen Removal (BNR)

- Influent ammonia oxidized to nitrite (NO_2) by AOBs
- Nitrite oxidized to nitrate (NO_3) by NOBs
- Nitrification requires both oxygen and alkalinity to buffer against pH drop
- Denitrification is performed by heteroptrophic bacteria in an a anoxic environment: reduces nitrate to N gas

Bacteria

- Heterotrophs get their carbon and energy from BOD
- Nitrifying autotrophs: ammonia + carbonate + oxygen => Nitrate + byproducts
- get their fuel from ammonia, use inorganic carbon, must have DO

Process Variables for Nitrification

- Temperature
- Aerobic solids retention time (SRT)
- organic loading rate (OLR)
- Dissolved Oxygen (DO)
- pH
- Alkalinity
- Nitrogen Loading Patterns
- Presence of Inhibitory compounds

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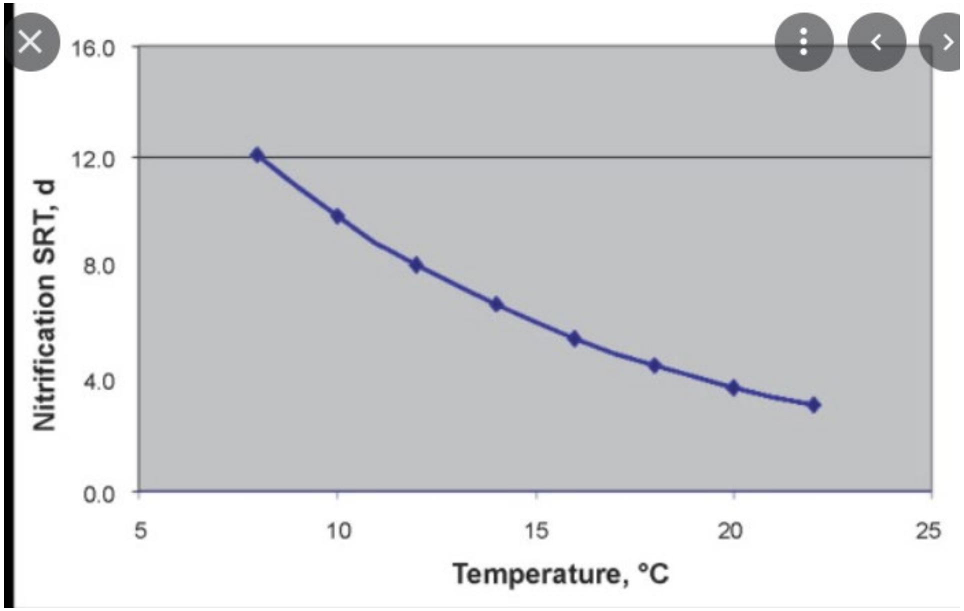
Process Variables for Nitrification

- Temperature: typical between 39 and 113°F; optimum is about 86°F
- Aerobic SRT: most important variable for removing ammonia in activated sludge processes



Process Variables for Nitrification

- Organic Loading Rate (OLR) - high OLRs favor growth of heterotrophic bacteria over nitrifying bacteria. NOB won't become a significant portion of the biofilm until soluble BOD5 is <20 mg/L or the 5 day CBOD is less than 20 mg/L
- For biofilm process, removal and nitrification are generally sequential, so this will be more of a factor.

Process Variables for Nitrification

- Dissolved Oxygen (DO) concentration - Nitrification not limited if DO>2.0 mg/L

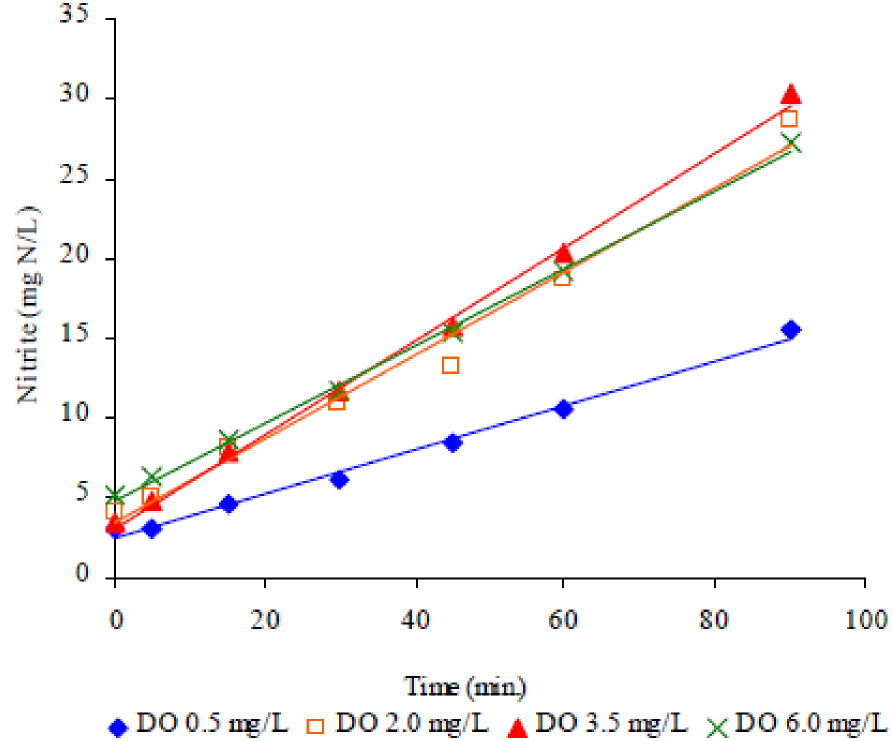


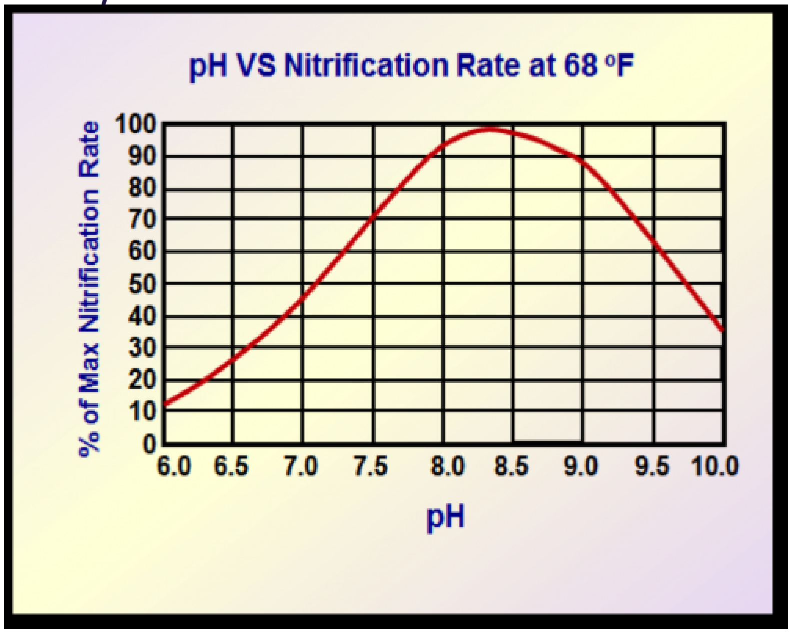
Fig. 3: Nitrite accumulation at different DO concentrations

Solids Retention Time

- SRT = **mass of MLSS in the aeration tank (lb) divided by the mass of solids wasted each day** (lb/d)
- Must be long enough for nitrifying bacteria to reproduce
- Nitrification "all of nothing" = either they have enough time to reproduce and build up a stable population – or NOT
- Theoretical minimum is 2 days at 20°C (68°F) and about 5 days at 10°C(55°F)
- Safety factors between 2 and 3.5 are usually used.

Process Variables for Nitrification

- pH and Alkalinity - nitrification rates decrease rapidly if pH<6.8
- However, nitrification produces acid which consumes alkalinity.
- If enough alkalinity is consumed, the pH will decrease.
- A min effluent alkalinity of at least 50 mg/L and preferably 100 mg/L as $CaCO_3$ should be maintained



Nitrogen Loading Pattern

- If environmental factors are not limiting, the quantity or mass of AOB and NOB will be a function of the ammonia loading
- Nitrifiers can't react quickly to peak loading…number reflect average loading

Other Factors

- Hydraulic detection time: not a big factor in activated sludge processes but can be in step-feed processes
- Inhibitory substances: more than 180 organic compounds and heavy metals (include nickel, chromium, cadmium)

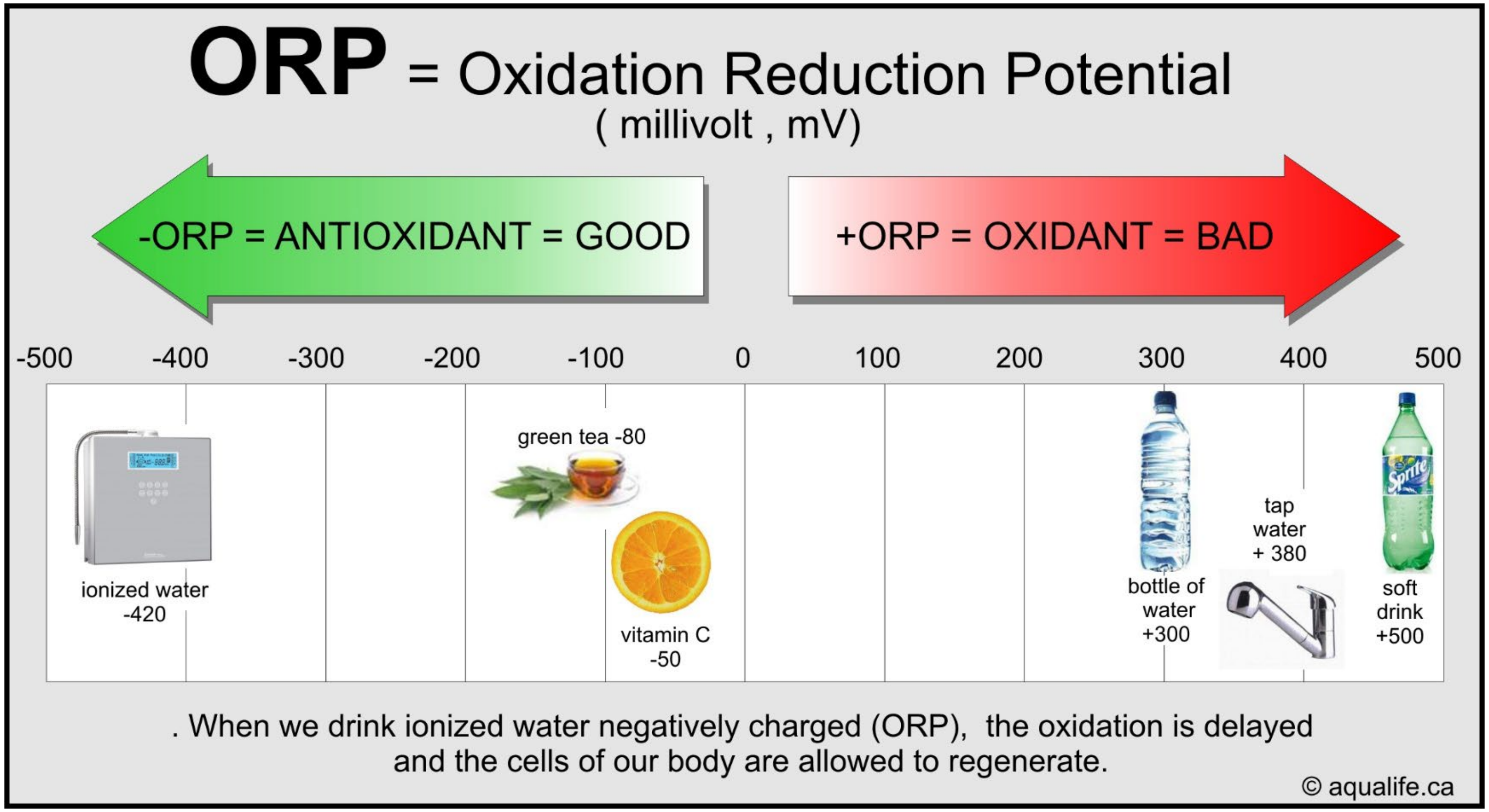
Oxidation/Reduction Potential (ORP)

- Oxidation: add oxygen, lose hydrogen, or lose electrons
- Reduction: remove oxygen, add hydrogen, or gain electronics
- These reactions always occur together with one chemical being oxidized and the other reduced
- The difference in electrical charge is voltage

Oxidation/Reduction Potential

- Used to monitor anoxic zones in AS processes
- <-200mV anaerobic
- >+50 mV to aerobic
- <+50 mV to trigger denitrification

Oxidation/Reduction Potential



ORP

- Wastewater with high NO_3^- , NO_2^- and DO have + ORPs
- Wastewater with higher concentrations of H_2S tend to have – ORPs

ORP Monitoring

Microbial Activity	Approximate ORP (mV)
Carbon oxidation (conversion of BOD to biomass, carbon dioxide and water with oxygen)	+50 to +200
Polyphosphate accumulation	+50 to +250
Nitrification	+150 to +350
Denitrification	-50 to +50
Polyphosphate release	-40 to -175
Volatile fatty acid (VFA) formation	-40 to -200
Sulfide formation	-50 to -250
Methane formation	-200 to -400

PHOSPHORUS REMOVAL

Phosphorus Removal

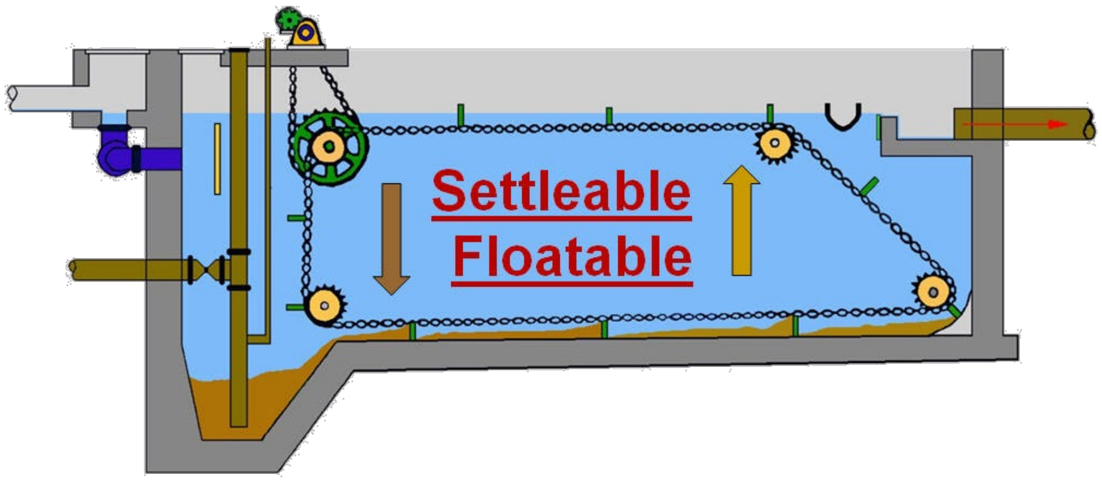
Removal of Ortho-P may Occur Through:

1. Enhanced Biological Update
2. Chemical Precipitation

Settling

- Removal of Settleable Solids can provide some phosphorus removal

Primary Sedimentation 5 - 15 %

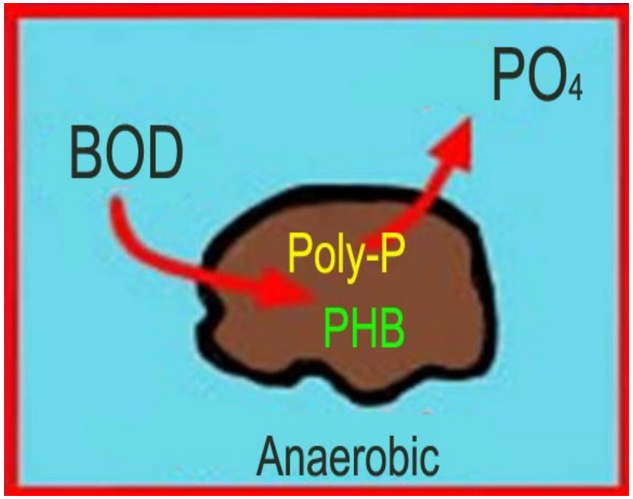


Biological Uptake

- Polyphosphate Accumulating Organisms (PAOs) can be used
- Two stage: 1) anaerobic or “anaerobic selector”, and 2) aerobic

Biological P Removal – Stage 1

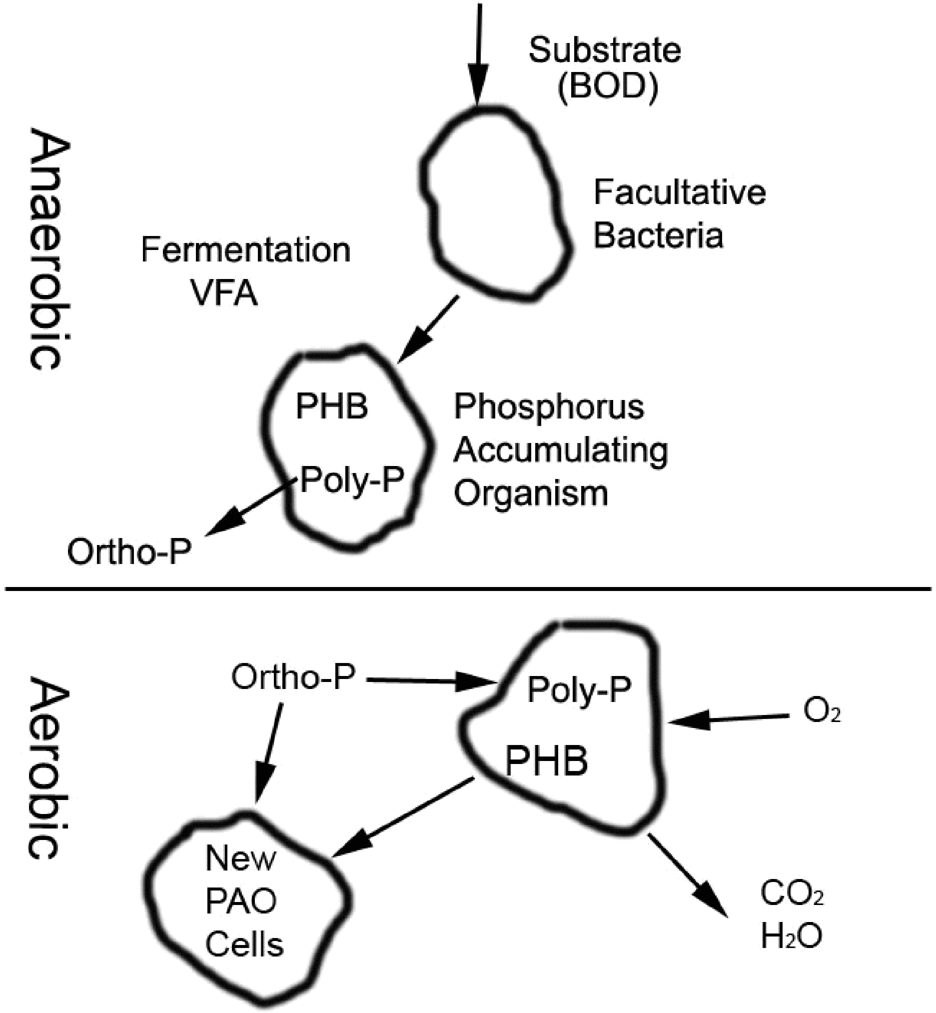
PAO's uptake Volatile Fatty Acids (VFAs) from the organic carbon in the influent (or added as sidestream flow) and store it as polyhydroxyalkanoate (PHA) for later oxidation

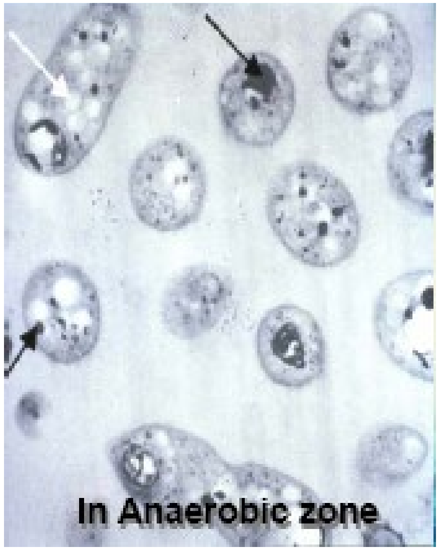


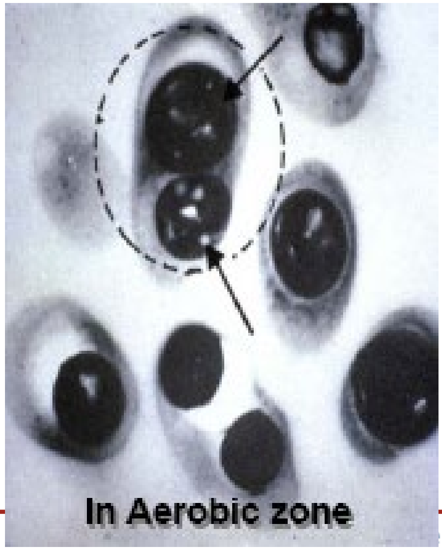
Biological P Removal – Stage 2

- Stored PHA is metabolized, providing energy for cell growth and luxury uptake of soluble orthophosphate, which is stored as polyphosphates. The PAOs uptake and store more phosphorus under aerobic conditions than is released under anaerobic conditions, providing a net uptake an storage of phosphorus.
- Stored phosphorus is removed from the system with waste sludge.

Biological P Removal







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Biological P Removal

The MLSS Cycles From Anaerobic to Aerobic

This Promotes
Phosphate Accumulating Organisms (PAO)

Anaerobic
Fermentation
Acetate Production
P Released to Produce Energy

Aerobic
Stored Food Consumed
Excess P Taken Up
Sludge Wasted

Biological P Removal

Aerobic Conditions

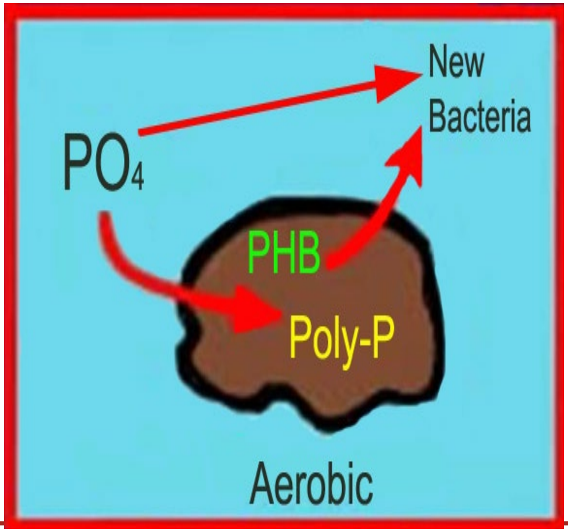
Rapid Aerobic Metabolism of Stored Food (PHB)

Producing New Cells

PO_4 Used in Cell Production

Excess Stored as Polyphosphate

("Luxury Uptake")



Biological P Removal

Aerobic Conditions

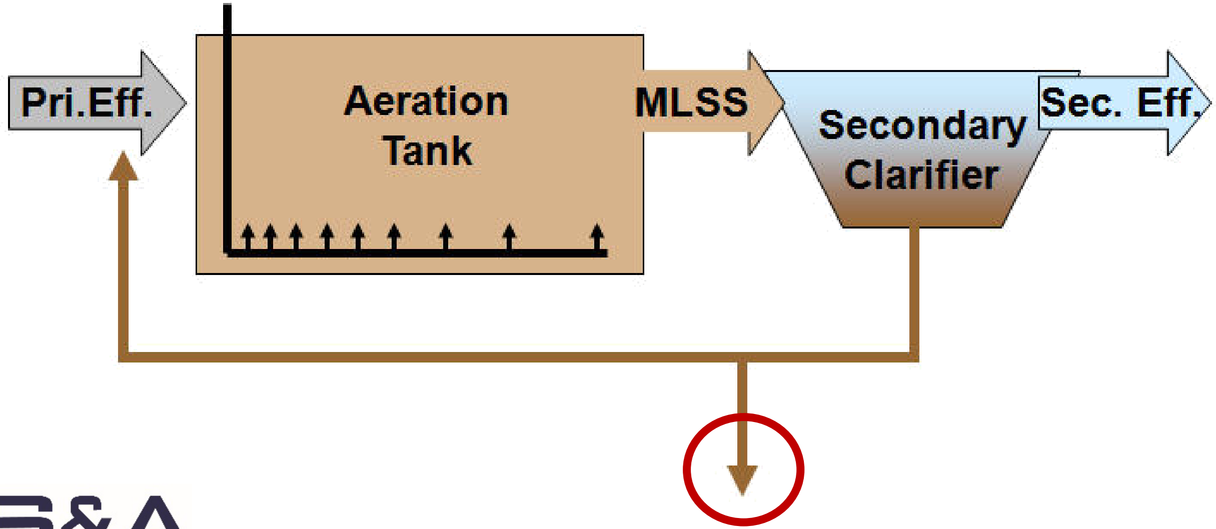
PO_4 Used in Cell Production

Excess Stored as Polyphosphate

Biomass Approximately 5 to 7% P by Weight

(Normal 1.5 to 2 %)

Sludge is Wasted When Loaded With P



Biological P Removal

Anaerobic Conditions

Heterotrophic Bacteria Break Down Organics
Fermentation
Volatile Fatty Acids (VFAs)
Acetate (Acetic Acid)

Also
Selection of PAO - Phosphate Accumulating Organisms
(Able to Out-Compete Other Aerobic Heterotrophic Bacteria for Food When Anaerobic)

Phosphorus Removal

- Biological Wastewater Treatment Systems Will Remove Phosphorus

  100:5:1 (C:N:P)

  Primary and TF 20 - 30 %

  Primary and AS 30 - 50 %

  Total Influent P Ranges from 2 to 8 mg/L

Biological Phosphorus Removal

https://www.youtube.com/watch?v=uc3mDP0OVUc

EBPR

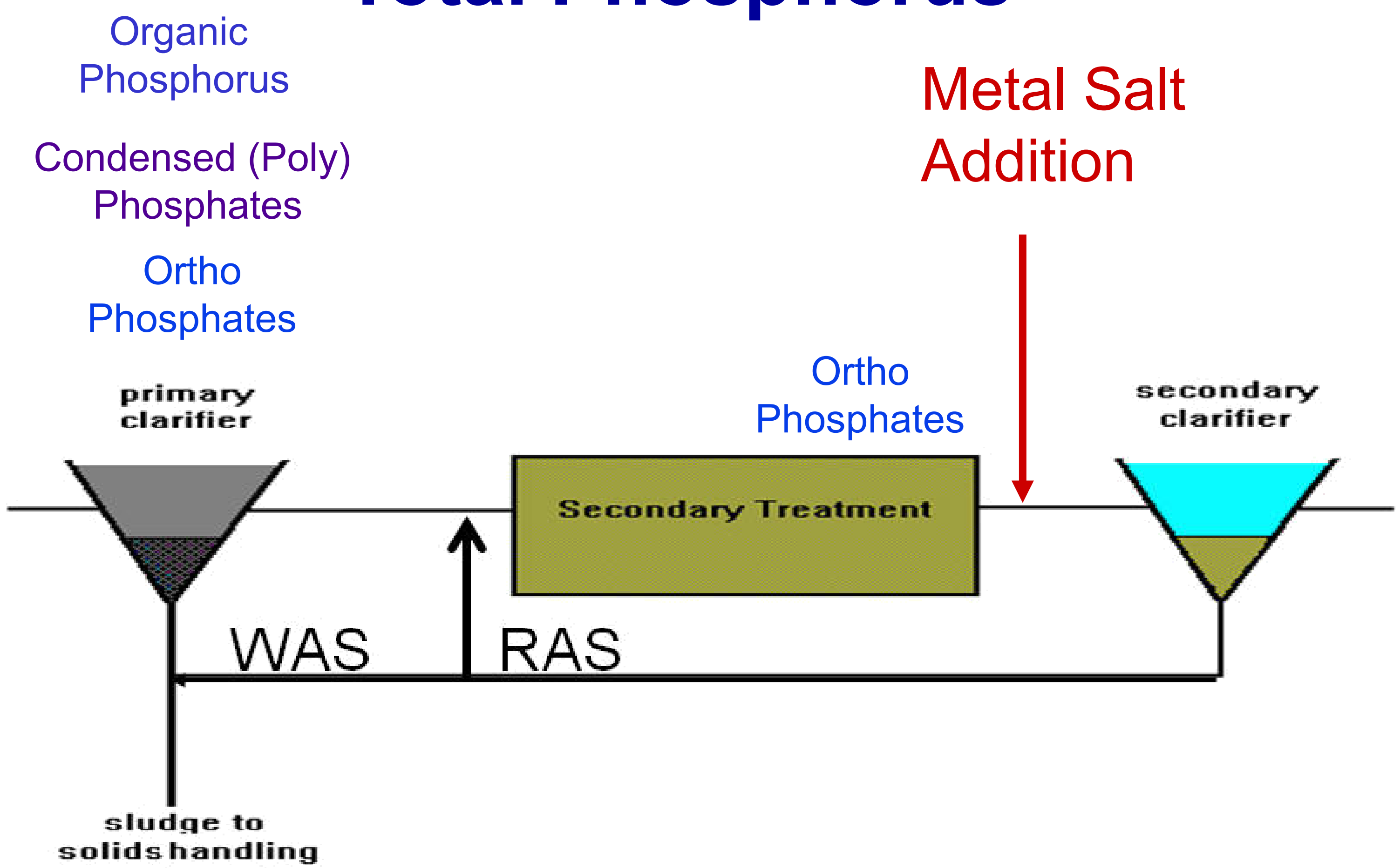
- Up to 4 times as much phosphorus can be removed biologically using EBPR than conventional activated sludge treatment
- EBPR can be added to AS by creating an anaerobic selector zone at the front of the secondary treatment process (must be upstream of the IMLR)
- Soluble VFAs can be provided through primary sludge fermentation

Process Control for EBPR

- Ensuring adequate supply of VFAs
- Protecting the anaerobic zone
- Maintaining a strongly negative ORP in the anaerobic zone
- Maximizing solids capture
- Minimizing recycle loads
- Avoiding secondary release of phosphorus, and minimizing competition from GAOs

Chemical Phosphorus Removal

Total Phosphorus



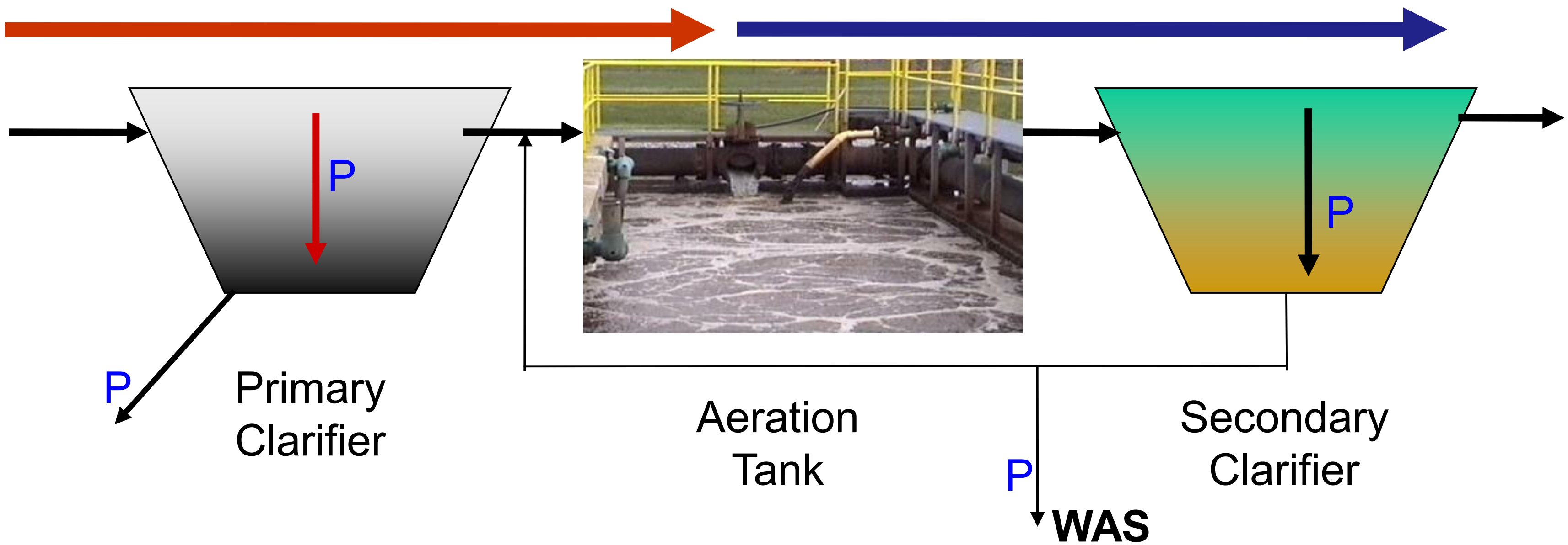
Chemicals Used for Phosphorus Precipitation

Ferric Chloride
Ferrous Chloride
Alum

Conversion to Ortho-P

Ortho
Poly
Organic

Ortho



Chemical Phosphorus Removal

Cations of the following metals can be used for phosphorus precipitation

- Aluminum
- Iron
- Calcium
- Magnesium

Chemical Phosphorus Removal

- Chemical precipitation by adding metals salts (aluminum sulfate, ferric chloride)
- Adds to mass of sludge produced
- Best way to estimate additional sludge production is a jar test

Aluminum Salts

- Aluminum sulfate (alum, most popular)
- Polyaluminum chloride (PACl)
- Sodium aluminate

Chemical Phosphorus Removal

$$M^{+3} + PO_4^{-3} \rightarrow MPO_4 \downarrow$$

(M^{+3} = Metal in Solution)

PRECIPITATION

Metals used are: Aluminum, Al
Iron, Fe

Jar Testing

- Before deciding on a product, perform jar testing
- Strength and composition of these product vary considerably
- Jar test will inform about efficcacy and sludge production

Iron Salts

- Ferric chloride ($FeCl_3$)
- Ferric sulfate [$Fe_2(SO_4)_3$]

$$Fe^{3+} + H_nPO_4^{3-n} \leftrightarrow FePO_4 + nH^+$$

- The amount of chemical needed will be larger than the equation predicts because some is used up in side reactions

Calcium Salts

- Lime $Ca(OH)_2$ reacts with natural alkalinity in the wastewater to produce calcium carbonate, which is primarily responsible for enhancing SS removal.

$$Ca(HCO_3)_2 + Ca(OH)_2 \text{ à } 2CaCO_3 \downarrow + 2H_2O$$

- As pH increases above 10, excess Ca will then react with phosphate to precipitate.

$$10\ Ca^{2+} + 6\ PO_4^{3-} + 2\ OH^- \leftrightarrow Ca_{10}(PO_4)^{*}6(OH)_2 \downarrow$$

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Polymers

- Used with aluminum or iron based compound can help precipitation product flocculate.
- Typical dose when used as a coagulant aid is 0.1 to 0.25 mg/L
- Minimum 10 sec lag time recommended between point of metal addition and polymer injection point

Alkalinity

- Aluminum and iron addition consumes alkalinity
- One mole of Al ion reacts with 3 moles of water and produces 2 moles of hydrogen ions
  - Every 1 mg/L of alum will react to produce 0.26 mg/L of insoluble aluminum hydroxide while consuming 0.5 mg/L of alkalinity
  - Every 1 mg/L of ferric chloride produces approx. 0.4 mg/L of ferric hydroxide and consumes 0.56 mg/L of alkalinity.
- Will amount of alkalinity in the influent of the WWTP be enough to remove N and P?

Dosage Rate

$$Al^{3+} + H_nPO_4^{3-n} \leftrightarrow AlPO_4 + nH^+$$

The most important component of a control strategy for chemical phosphorous removal is the calculation of coagulant dosage. Dosage rates for aluminum salts or for iron salts are based on the molar ratio of available metal ion to phosphorous.

Theoretically to remove 1 mg/L of PO4-P you need

- 9.6 mg/L of Alum
- 5.2 mg/L of Ferric Chloride

Real life requires 0.5 to 15 times as much

Biological Phosphorus Removal

- Phosphorus is removed by Polyphosphate accumulating organisms" (PAOs)
- 2 stages required 1) anerobic in which PAO's uptake VFAs, 2) aerobic where stored PHA is metabolized
- First stage sometimes called "anaerobic selector"

Biological P Removal

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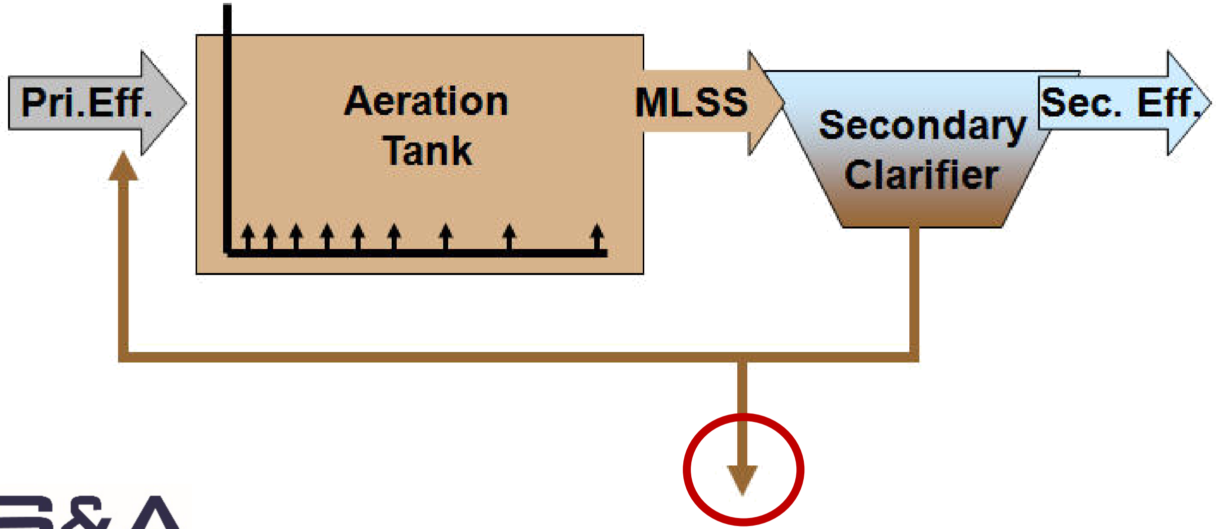


Sludge Production

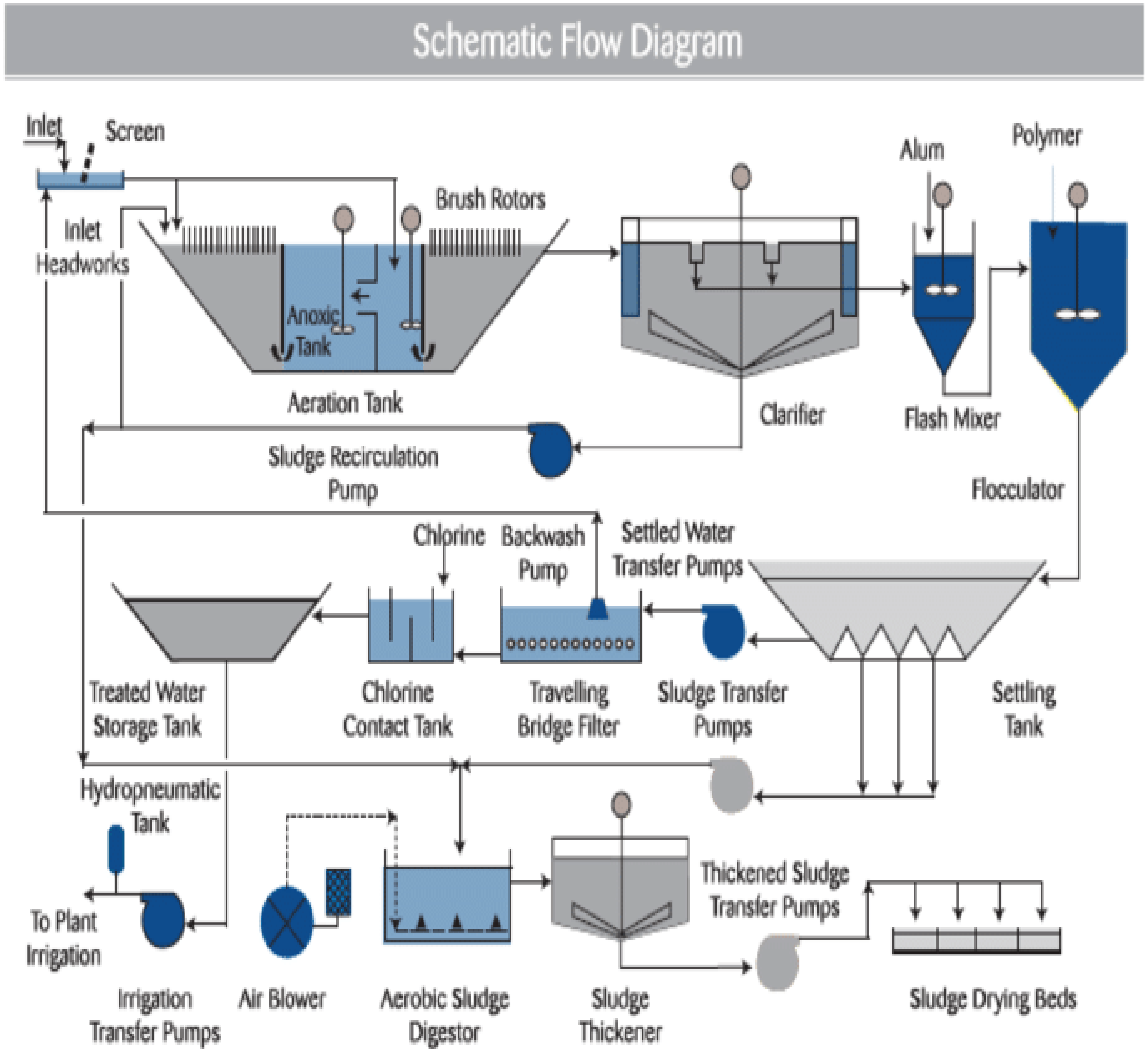
- General rule – about 10 g of chemical sludge will be produced per gram of P removed by chemical addition
- But a jar test will tell you more definitively

pH Range

- Phosphorus removal is highly dependent on pH
- If the PH is too low, Al and Fe phosphates become more soluble and dissolve back into solution
- Optimal pH depends on chemical used
  - Alum – 5.5 to 6.5 (up to 7)
  - Ferric chloride – 3.5 and 5 (up to 6.5)

Chemical Addition Points

- Collection system
- Upstream of primary clarifiers
- Upstream of secondary treatment
- Upstream of secondary clarifier
- Between secondary clarifier and tertiary filter
- Depends!



Schematic Flow Diagram
Inlet
Screen
Inlet
Headworks
Brush Rotors
Anoxic
Tank
Aeration Tank
Clarifier
Alum
Polymer
Flash Mixer
Flocculator
Sludge Recirculation
Pump
Chlorine
Backwash
Pump
Settled Water
Transfer Pumps
Treated Water
Storage Tank
Chlorine
Contact Tank
Travelling
Bridge Filter
Sludge Transfer
Pumps
Settling
Tank
Hydropneumatic
Tank
To Plant
Irrigation
Irrigation
Transfer Pumps
Air Blower
Aerobic Sludge
Digestor
Sludge
Thickener
Thickened Sludge
Transfer Pumps
Sludge Drying Beds

Chemical Addition Points

- $FeCl_3$ typically added to collection system, headworks, and solids handling processes primarily to precipitate sulfides for odor and corrosion control
- Primary clarifiers: Al or Fe help with flocculation.. This increases BOD and TSS removed and reduces load to secondary treatment

Chemical Addition Points

- Primary Clarifiers: limited in 2 ways: 1) only 50% of P entering is Ortho that can be precipitate and 2) only settleable P removed.
- If too much BOD is removed, denitrification will be limited
- If not enough P remains in primary effluent, downstream biological processes can be limited
- Removes alkalinity before nitirification

Chemical Addition Points

- Before or after AS: 1) total phosphate concentrations in the final effluent may be reduced below 1 mg/L, 2) sludge settling characteristics are often improved, 3) effluent turbidity may be reduced, 4) tertiary filters are typically not required, 5) simple operation

Chemical Addition Points

- Upstream of AS:
  - consumes alkalinity that could be used to support nitrification
  - Increases the mass of MLSS in the process and decreases the MLVSS b/c only a portion of the chemical sludge is removed each day
  - increases solids loading rate to secondary clarifiers

Chemical Addition Points

- After AS: facilities that must meet discharge limits of 0.5 mg/L as P or less typically do this
- Organic and condensed phosphates have been converted to orthophosphate so nearly all of the remaining phosphorus can be precipitated

Chemical Addition Points

- For Fixed Film processes is typically done upstream of the primary clarifier or upstream of the secondary clarifier, or a combination
- Adding to FF process does not cause operational problems but short HDT and lack of mixing limits removal

Phosphorus Removal Case Study

https://www.tpomag.com/video/profile/getting-phosphorus-discharges-under-control-without-the-expensive-upgrade

Acronym Test

- AOB
- NOB
- SRT
- PAO
- EBPR

REVIEW A FEW ITEMS

Definitions

Aerobic	• Oxygen (always) • Nitrite + Nitrate (sometimes)
Anoxic	• NO Oxygen • Nitrite + Nitrate (always)
Anaerobic	• NO Oxygen • NO Nitrite or Nitrate

Forms of Nitrogen in Wastewater

1) Ammonia (NH_3-N)
2) Nitrite (NO_2-N)
3) Nitrate (NO_3-N)
4) Nitrogen Gas (N_2)

Nitrifying Bacteria

- Nitrifying bacteria use ammonia or nitrite as their fuel
- DO as their oxygen source
- Outputs from nitrifying bacteria – nitrite, nitrate, carbon dioxide, and water
- They are formed when carbon dioxide is dissolved in water
- For every 1 mg/L of ammonia that is converted to nitrite 7.14 mg/L of alkalinity will consumed

3 Conditions for Denitrification

1. Carbon source (measured as BOD_5 or COD).
2. Low DO
3. Sufficient HDT

Quiz

1. What is the conversion from cubic feet to gallons?
2. What is the chemical formula for nitrate?
3. What is the full chemical name for alum?
4. What 2 zones are required for EBPR?
5. What 2 zones are required for nitrification/denitrification?

Biological Nutrient Removal

Nitrogen Removal Basics

https://www.youtube.com/watch?v=M3VDmhYQRrU

Microbiology of Wastewater

https://www.youtube.com/watch?v=epAh6hHOq3c

Day 2 – Wrapup

- Pdf of Day 2 presentation to be posted
- Certificates will be emailed
- Training credits will be entered if we have your operation ID#
- Email with any additional questions

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