Chemical unit processes

Chemical processes in wastewater treatment

- **Usually applied as a unit process for tertiary treatment or for supplementary processes**
  - To deal with refractory organics, phosphorus, heavy metals, etc.
- **As a major unit of wastewater treatment** (for soluble COD removal), **biological process >> chemical process** (from 1920~30's to present)
  - Chemical process: cost ↑↑ due to chemical consumption & sludge disposal
- **But..**
  - Increased value of treated wastewater
    - Need something more than biological treatment to obtain drinking-water quality
  - Wastewater management in the next generation – decentralized treatment??
    - Chemical processes are more reliable against significant variations in flowrates & loadings that occur at small scales
- **So, the matter of "biological processes vs chemical processes" should be re-assessed**

Chemical unit processes

Processes	Application
Advanced oxidation	Removal of refractory organic compounds
Chemical coagulation	Chemical destabilization of particles in wastewater to bring about their aggregation during flocculation
Chemical disinfection	Disinfection with chlorine, chlorine compounds, bromine, and ozone Control of odors
Chemical neutralization	Control of pH
Chemical oxidation	Removal of BOD, grease, etc. Removal of ammonium Destruction of microorganisms Control of odors in sewers, pump stations, and treatment plants Removal of resistant organic compounds

Chemical unit processes

Processes	**Application**
Chemical precipitation	Enhanced removal of TSS and BOD in primary sedimentation facilities Removal of phosphorous Removal of ammonium Removal of heavy metals Physical-chemical treatment Corrosion control in sewers due to H_2S
Chemical scale control	Control of scaling due to calcium carbonate and related compounds
Chemical stabilization	Stabilization of treated effluents

Considerations in chemical processes

- **External substances are often added**
  - There is often a net increase in certain dissolved wastewater constituents

    ex1) addition of coagulants → increase in wastewater TDS

    ex2) addition of chlorine for disinfection: increase in TDS and generation of disinfection byproducts

- **Generation of chemical precipitation sludge**
  - Handling, treatment, and disposal of the chemical sludge requires additional cautions

- **Cost of chemicals & sustainability**

Chemical unit processes – today's topics

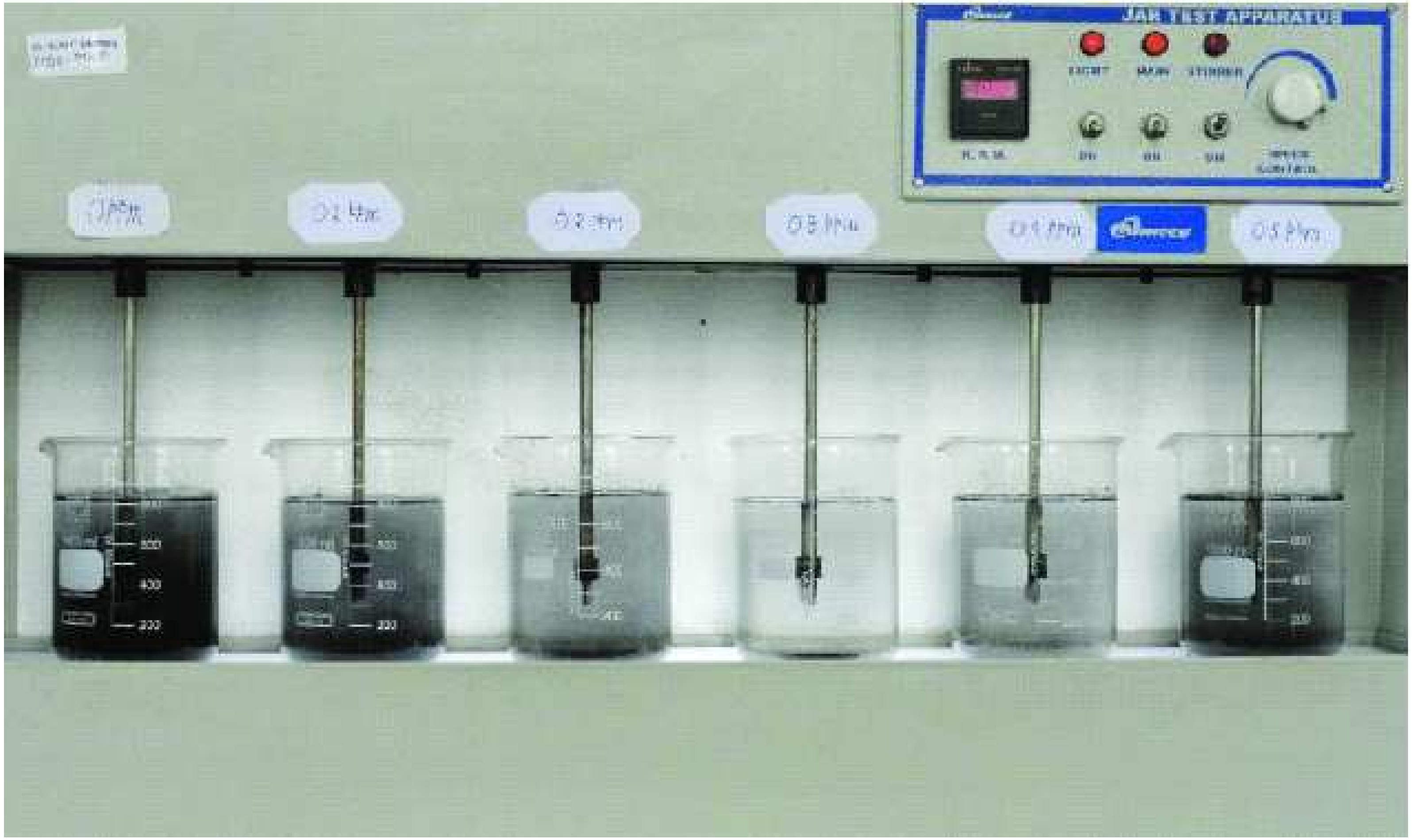
- Chemical coagulation
- Chemical phosphorus removal
- Chemical precipitation for heavy metal removal
- Chemical oxidation
  - Conventional oxidation
  - Advanced oxidation

Chemical coagulation

- Colloidal particles in wastewater typically have a net negative charge and thus, are at **stabilized** condition
- **Coagulation vs. flocculation**
  - Coagulation
    - A chemical process to destabilize the particles by changing the surface properties so that particles can stick together when they collide
    - But quite often used as a term that includes mechanisms involved both in chemical destabilization of particles and growth in particle size
  - Flocculation
    - A physical process to create conditions (by gentle mixing) that allow particles to grow in size

#1

Coagulation – Jar test



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Nature of particles: electrical double layer

- **The electrical double layer**
  - Charged particles in water are surrounded by ions of opposite charge
  - A compact layer (Stern layer) + a diffuse layer

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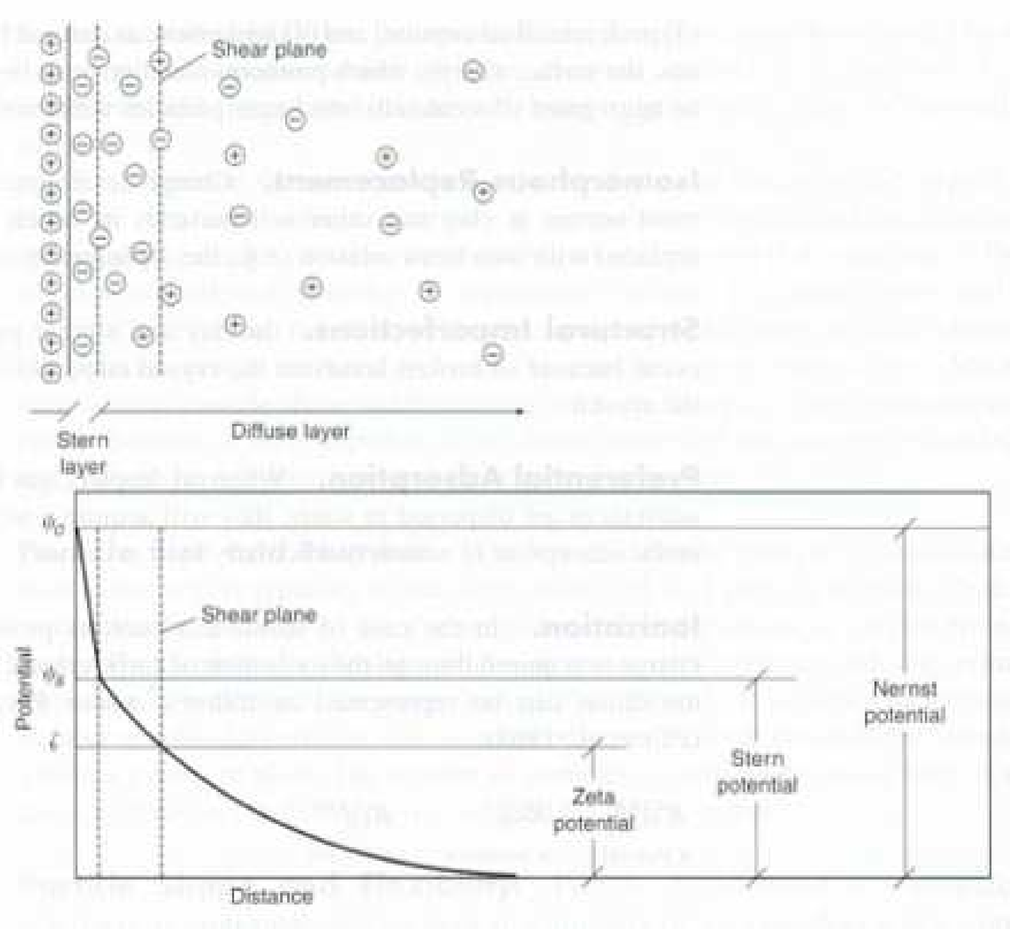

Stern model of electrical double layer

Nature of particles: Interaction forces

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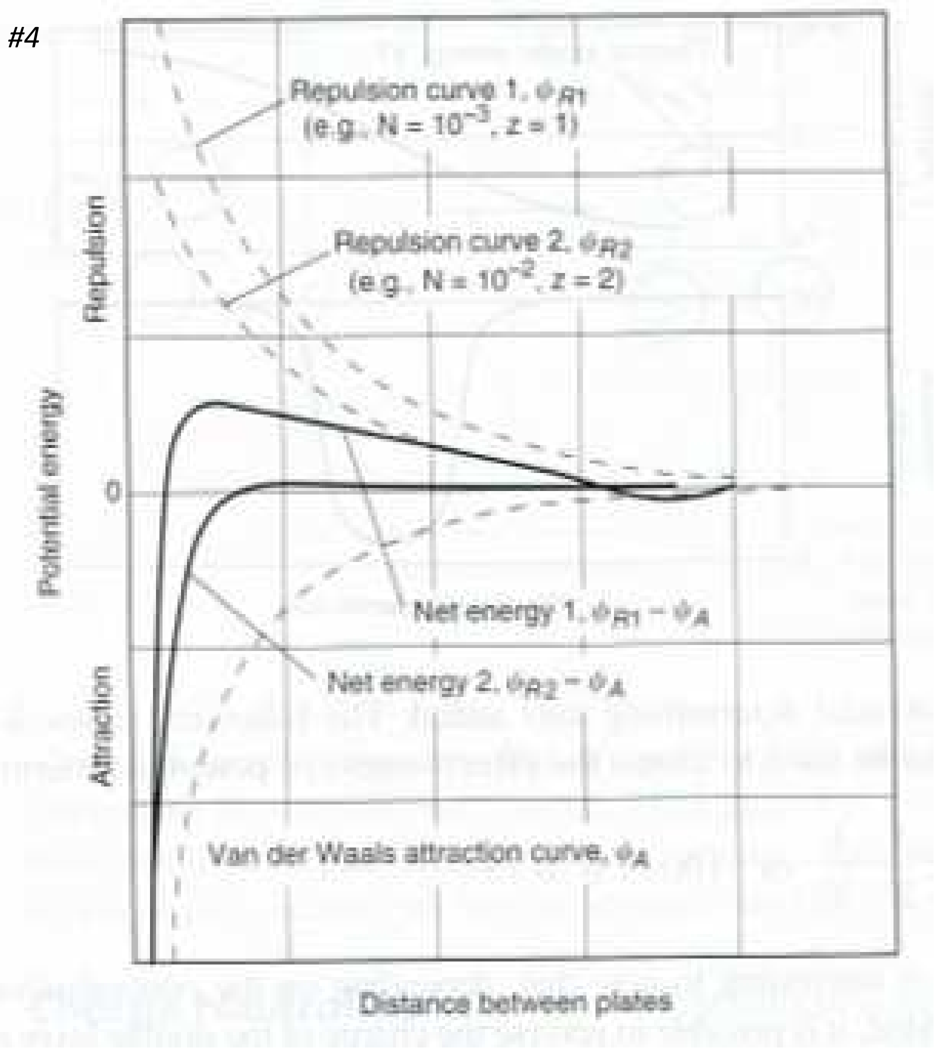
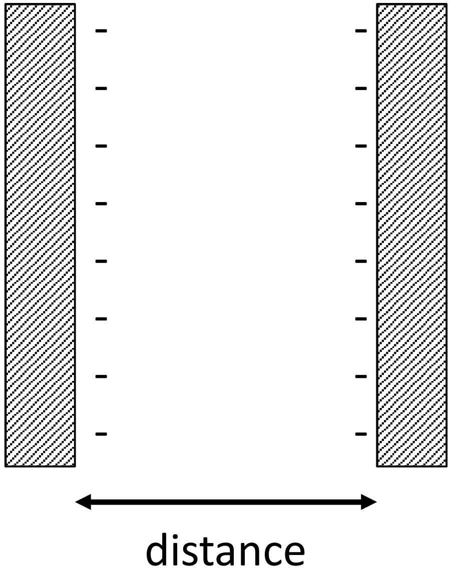




Definition sketch for particle-particle interactions based on the repulsion due to particle surface charge and van der Waals forces of attraction. N = concentration; z = charge.

Nature of particles: Implications

- **Forces between particles**
  - Electrical force (repulsion; when the particles are of the same charge)
  - van der Waals force (attraction)
  - Net energy = electrical force + van der Waals force
  - The energy barrier (maximum repulsive force of the net energy) has to be overcome for particles to be attached to each other

- **How to reduce the energy barrier?**
  - Reduce the particle surface charge by attachment of ions of opposite charge
    - Charge neutralization
  - Add electrolytes to reduce the electrical double layer thickness
    - Ionic strength ↑ → Compression of electrical double layer

Coagulation – mechanisms and coagulants

- **Mechanisms of particle removal by coagulation**
  - Charge neutralization
  - Compression of electrical double layer
  - Inter-particle bridging
  - Enmeshment in sweep floc

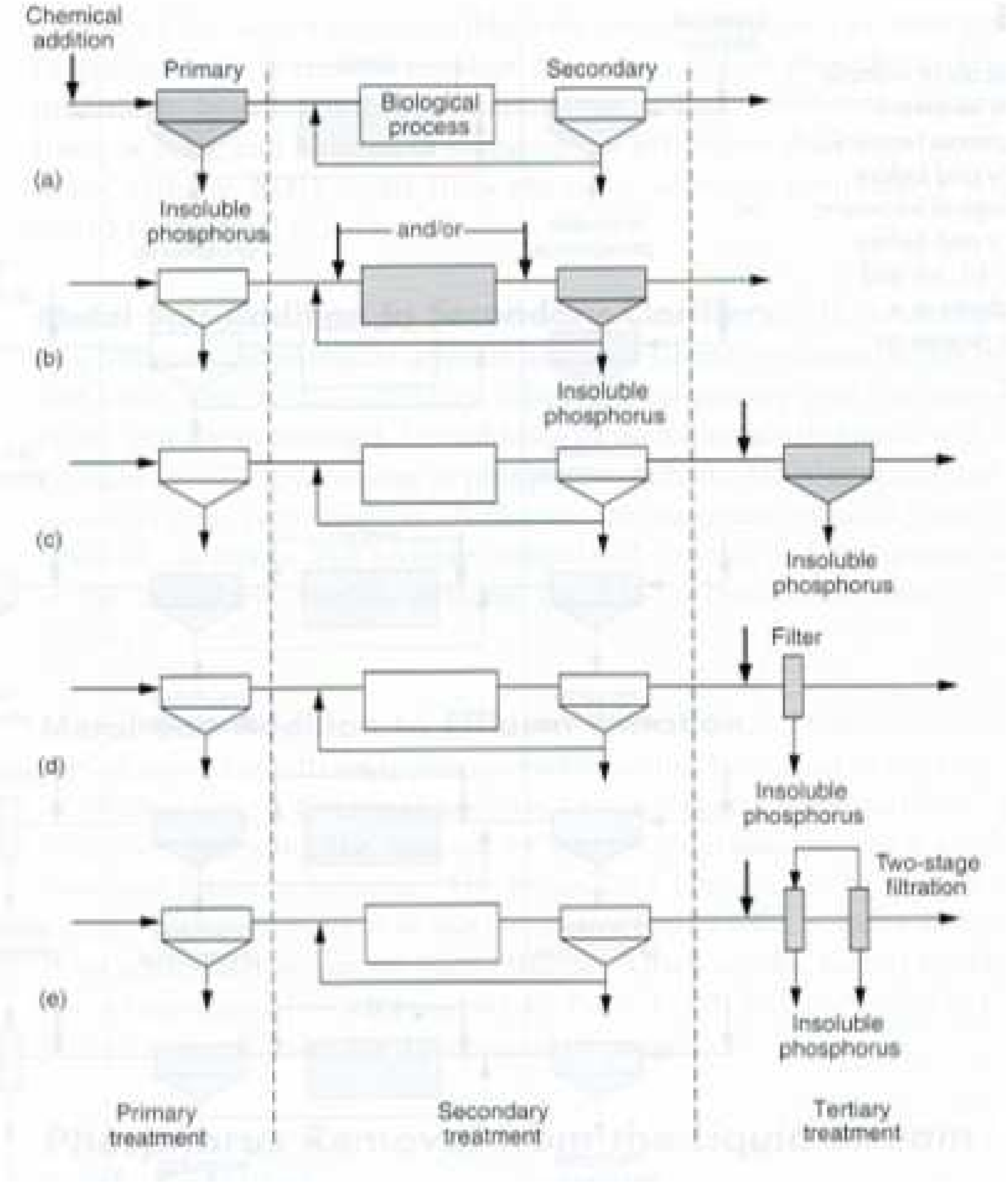
- **Use of polyelectrolytes**
  - Ions of multiple charge are good at charge neutralization & electrical double layer compression (+1 << +2 << +3)
  - Commonly used coagulants: Al^{3+} or Fe^{3+} salts

  (Alum, $Al_2(SO_4)_3 \cdot 14H_2O$: most common)

Chemical phosphorus removal

- **Two general approaches for P removal**
  - Chemical treatment
    - Chemical can be added at various points of the treatment train
  - Biological treatment
    - Modification of secondary treatment (to be discussed later)

- **Chemicals used for P removal by precipitation**
  - Al^{3+}, Fe^{3+}, Fe^{2+}, Ca^{2+}



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Addition of chemicals at a single dosing point at various locations for P removal: (a) before primary sedimentation; (b) before and/or after biological treatment; (c) after secondary treatment; (d) chemical addition prior to single-stage filtration; and (e) chemical addition prior to dual-stage filtration

Phosphate precipitation using Al and Fe

- **Al or Fe phosphates are insoluble**

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

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

  - But this is a very simple representation

- **The precipitation mechanism is complicated – generally thought to occur by:**
  - Phosphate adsorption onto hydrous ferric or aluminum oxide precipitates
  - Incorporation of phosphate into the hydrous oxide structure
  - Formation of mixed cation phosphates (Ca, Mg, Fe, or Al phosphates)
  - Formation of ferric or aluminum phosphate

Phosphate precipitation with calcium

- Precipitate into an insoluble hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$]
- Ca^{2+} is usually provided in the form of lime ($Ca(OH)_2$)
- Note that the lime added to water first reacts with bicarbonate alkalinity to precipitate $CaCO_3$:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightleftharpoons 2CaCO_3 \downarrow + 2H_2O$$

(reaction for lime softening)

- As more $Ca(OH)_2$ is added, excess Ca^{2+} will react with the phosphate to precipitate into hydroxyapatite:

$$\boldsymbol{10Ca^{2+} + 6PO_4{}^{3-} + 2OH^- \rightleftharpoons Ca_{10}(PO_4)_6(OH)_2\downarrow}$$

  - The quantity of lime required will depend primarily on the alkalinity of the wastewater

Struvite formation for NH_4^+ & P removal

- **Struvite**
  - Magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$
  - Serious problem in the processing of primary sludge and waste activated sludge
  - Formation of accumulation of struvite crystals cause problems in pipelines, pumps, etc.

- **Controlled struvite precipitation is of recent interest because:**
  - Of its value as a fertilizer (nutrients in wastewater into valuable product)
  - Combined removal of NH_4^+ & P is possible

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Struvite formation for NH_4^+ & P removal

- **Formation of struvite**

$$Mg^{2+} + NH_4{}^{+} + PO_4{}^{3-} + 6H_2O \rightleftharpoons MgNH_4PO_4 \cdot 6H_2O$$

  - Molar ratio of 1 : 1 : 1 for precipitation
  - Solubility product, K_s:

$$K_s = \{Mg^{2+}\}\{NH_4{}^{+}\}\{PO_4{}^{3-}\} \approx [Mg^{2+}][NH_4{}^{+}][PO_4{}^{3-}]$$

$pK_s = 13.0$ for struvite

  - Struvite dissolution/precipitation is a function of Mg^{2+}, NH_4^+, PO_4^{3-} concentrations
  - Various reactions are involved in Mg^{2+}, NH_4^+, PO_4^{3-}

Reactions involved in struvite chemistry

Reaction	pK
$NH_4{}^+ \rightleftarrows NH_3\,(aq) + H^+$	9.25
$H_3PO_4 \rightleftarrows H_2PO_4{}^- + H^+$	2.1
$H_2PO_4{}^- \rightleftarrows HPO_4{}^{2-} + H^+$	7.2
$HPO_4{}^{2-} \rightleftarrows PO_4{}^{3-} + H^+$	12.3
$MgOH^+ \rightleftarrows Mg^{2+} + OH^+$	2.56
$MgH_2PO_4{}^+ \rightleftarrows Mg^{2+} + H_2PO_4{}^-$	0.45
$MgHPO_4 \rightleftarrows Mg^{2+} + HPO_4{}^{2-}$	2.91
$MgPO_4{}^- \rightleftarrows Mg^{2+} + PO_4{}^{3-}$	4.8
$MgNH_4PO_4 \cdot 6H_2O \rightleftarrows Mg^{2+} + NH_4{}^+ + PO_4{}^{3-} + 6H_2O$	13.0

$$C_{T,Mg} = [Mg^{2+}] + [MgOH^+] + \left[MgH_2PO_4{}^+\right] + [MgHPO_4] + [MgPO_4{}^-]$$

$$C_{T,NH_3} = [NH_4^+] + [NH_3]$$

$$C_{T,PO_4} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] + \left[MgH_2PO_4{}^+\right] + [MgHPO_4] + [MgPO_4{}^-]$$

Struvite solubility change with pH

Define the **"conditional solubility product"**, ***P***

$$P_s = C_{T,Mg} \cdot C_{T,NH_3} \cdot C_{T,PO_4} = \frac{K_s}{\alpha_{Mg^{2+}} \cdot \alpha_{NH_4{}^+} \cdot \alpha_{PO_4{}^{3-}} \cdot \gamma_{Mg^{2+}} \cdot \gamma_{NH_4{}^+} \cdot \gamma_{PO_4{}^{3-}}}$$

$\alpha_{Mg^{2+}}, \alpha_{NH_4{}^+}, \alpha_{PO_4{}^{3-}}$ = *ionization fraction of individual constituents*

ex) $\alpha_{Mg^{2+}} = [Mg^{2+}]/C_{T,Mg}$

$\gamma_{Mg^{2+}}, \gamma_{NH_4{}^+}, \gamma_{PO_4{}^{3-}}$ = *activity coefficients of individual constituents*

- From the reactions in the previous slide, we see that the α values are a function of pH

Struvite solubility change with pH

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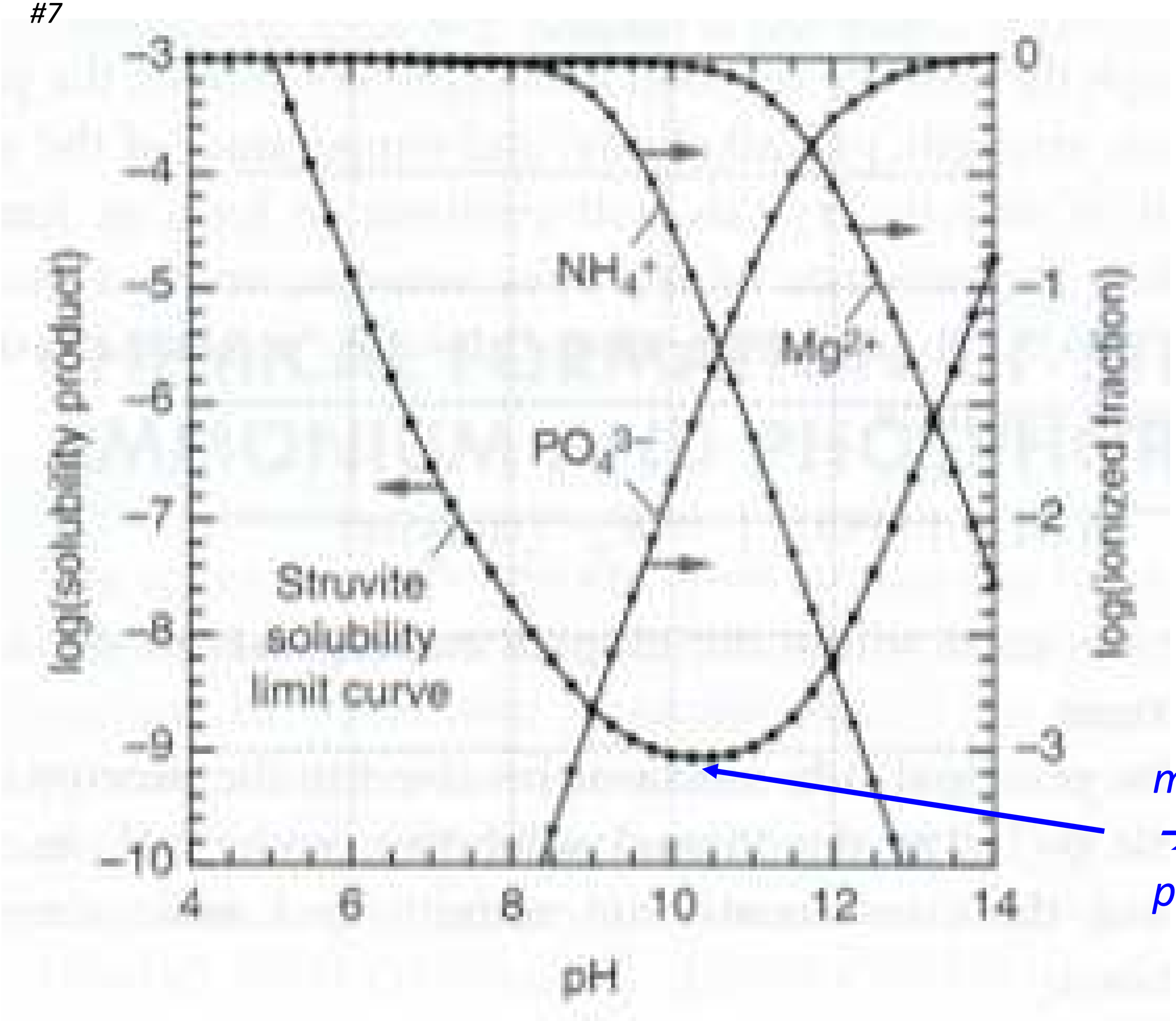

minimum solubility at pH ≈ 10.3
→ most favorable for precipitation

Enhancing struvite formation

- So, the struvite formation is a function of
  - **pH**
  - **Ionic strength**: higher P_s at higher ionic strength → unfavorable for precipitation
  - **Temperature**: reaction constants are functions of temp. – generally, P_s increase with temp. to some point (20-35^oC) and then decrease

- **Enhanced struvite formation for nutrient removal**
  - Form struvite in controlled settings (reactors)
  - Add an excess amount of Mg^{2+} into high pH liquid waste

Chemical precipitation for HM removal

- **Common precipitants**
  - Hydroxide (OH^-), sulfide (S^{2-}): most metal salts with these anions are insoluble
  - Carbonate (CO_3^{2-}) is sometimes used

- **Co-precipitation with phosphorus**
  - During chemical precipitation of P (using alum, iron, or calcium), heavy metals may co-precipitate with the major precipitant

Chemical precipitation for HM removal

- **pH dependence**
  - Solubility of metal hydroxides and sulfides is a function of pH
  - The point of minimum solubility (optimum pH) varies for different metals

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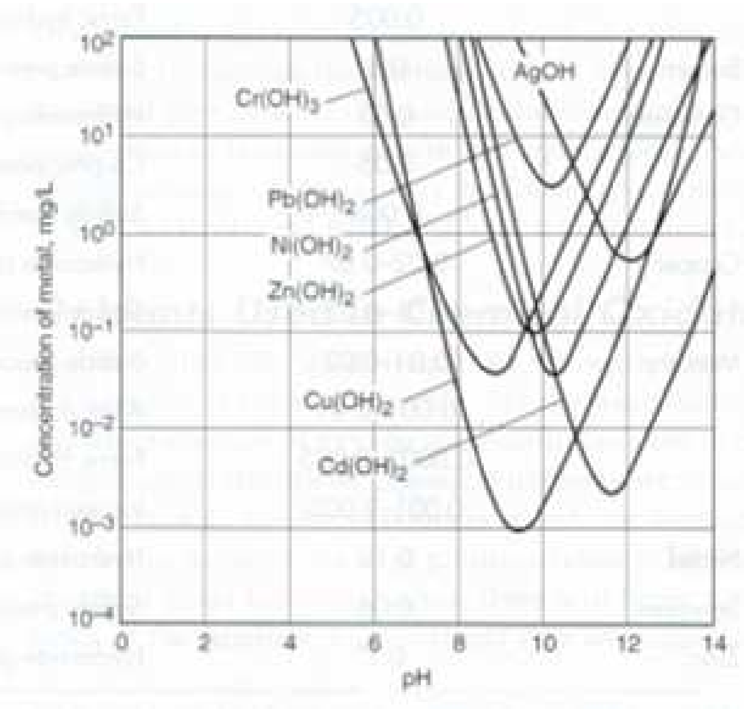
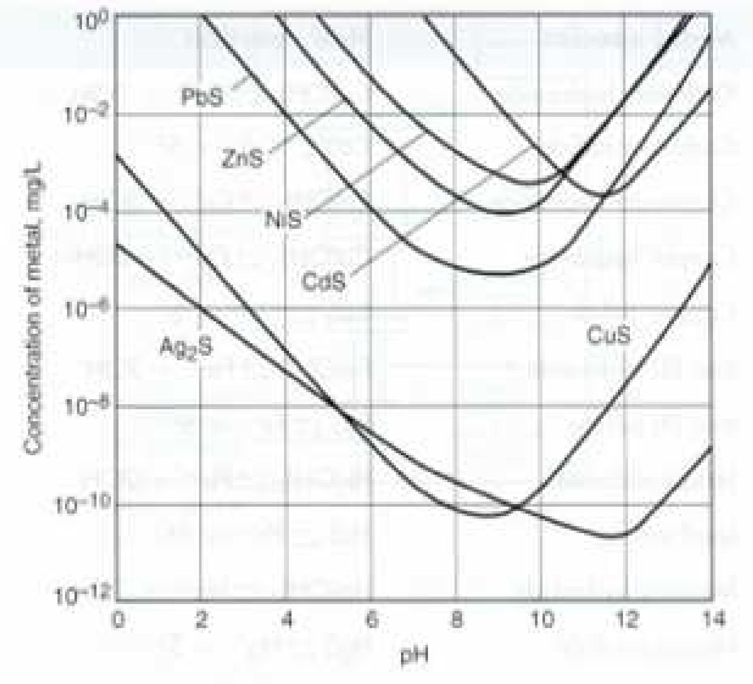




Conventional vs. advanced chemical oxidation

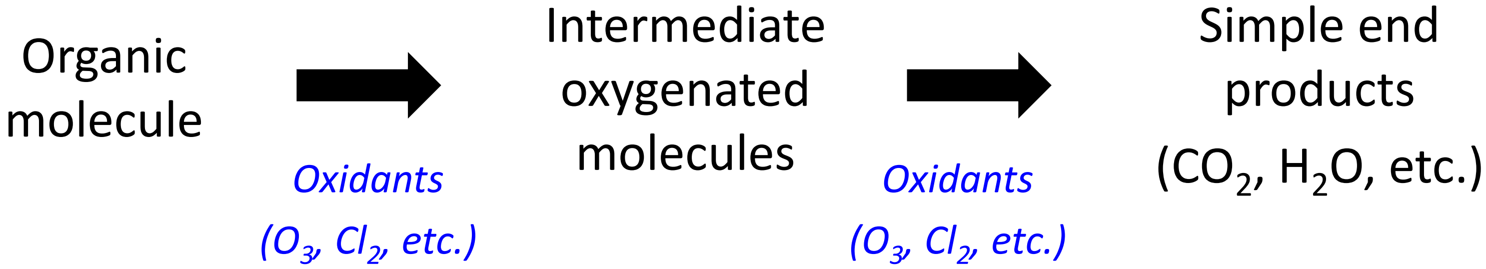
- **Conventional oxidation processes**
  - The use of oxidizing agents such as ozone (O_3), hydrogen peroxide (H_2O_2), permanganate (MnO_4), chlorine dioxide (ClO_2), chlorine (Cl_2 or HOCl), and oxygen (O_2) to bring about the change in the chemical composition of a compound

- **Advanced oxidation processes (AOPs)**
  - The **free hydroxyl radical (·OH)** is used as a strong oxidant to destroy specific organic compounds that cannot be oxidized easily by conventional oxidants

- **Typical strength of oxidants**
  - $\cdot OH > O_3 > H_2O_2 > HOCl > ClO_2 > MnO_4^- > O_2 > OCl^-$

Conventional chemical oxidation

- **Chemical oxidation of organic constituents**
  - Oxidation of residual COD



Organic molecule

Oxidants *(O_3, Cl_2, etc.)*

Intermediate oxygenated molecules

Oxidants *(O_3, Cl_2, etc.)*

Simple end products (CO_2, H_2O, etc.)

Conventional chemical oxidation

- **Chemical oxidation of ammonium**
  - "Breakpoint chlorination": addition of chlorine (Cl_2 or HOCl) to the point that all ammonium in water can be just converted into N_2 gas
  - Overall reaction:

$$3HOCl + 2NH_4^{\ +} \rightleftharpoons N_2 + 3HCl + 2H^+ + 3H_2O$$

  - Limitations
    - Chemical cost
    - Buildup of acid which consumes alkalinity
    - Build up of TDS
    - Chlorine-containing byproducts

  - Usually applied for wastewater that has undergone nitrification
    - Treatment of residual ammonium
    - Disinfection prior to discharge

Advanced oxidation processes

- **Destroy trace constituents that cannot be oxidized completely by conventional oxidants**
- **Especially useful when potable reuse is considered**
- **Hydroxyl radical (·OH): very strong oxidant**
  - Capable of the complete oxidation of most organic compounds into simple forms (CO_2, H_2O, HCl, etc.)
  - Presence of unpaired electron → react rapidly with nearly all electron-rich organic compounds
  - Generally 2nd order reaction (function of concentrations of both ·OH & compound to be oxidized)
  - 2nd order rate constant for ·OH generally in the order of 10^8~10^9 L/mole·s (3~4 orders of magnitude greater than the rate constants for other oxidants)

Advanced oxidation processes

- **Characterization of the degree of degradation**
  - *Primary degradation*: a structural change in the parent compound
  - *Acceptable degradation*: a structural change in the parent compound to the extent that toxicity is reduced
  - *Ultimate degradation*: conversion of organic carbon to inorganic CO_2
  - *Unacceptable degradation*: a structural change in the parent compound resulting in increased toxicity

Advanced oxidation processes

- **Reactions by hydroxyl radicals**
  1. By radical addition (common):

     The addition of the hydroxyl radical to an unsaturated organic compound results in the production of a radical organic compound that can be further oxidized into stable products

     $$R + \cdot OH \rightarrow ROH \cdot$$

  2. By hydrogen abstraction (common):

     The hydroxyl radical is used to removal a hydrogen atom from organic compounds, forming a radical organic compound. The radical organic compounds react with oxygen to produce a peroxyl radical, which can react with other organic compounds.

     $$R - H + \cdot OH \rightarrow R \cdot + H_2O$$

Advanced oxidation processes

3. By electron transfer:

Results in the formation of ions of a higher valence. Oxidation of a monovalent negative ion (-1) will result in the formation of an atom or a free radical.

$$R^n + \cdot OH \rightarrow R^{n+1} + OH^-$$

4. By radical combination:

Two radicals can combine to form a stable product.

$$\cdot OH + \cdot OH \rightarrow H_2O_2$$

Advanced oxidation processes

- **Processes for advanced oxidation**

  = processes for the production of ·OH

  - **Ozone/UV**
    - Photodegradation of O_3 in wet air with UV light

      $$O_3 + H_2O + UV(\lambda < 310\ nm) \rightarrow\ O_2 + 2 \cdot OH$$

    - Compounds are degraded by direct ozonation, photolysis, or reaction with the hydroxyl radical

Advanced oxidation processes

- **Ozone/H_2O_2**
  - Effective for compounds that do not absorb UV or photolysis is not effective because of water quality

$$H_2O_2 + 2O_3 \rightarrow 2 \cdot OH + 3O_2$$

- **H_2O_2/UV**
  - Requires relatively high H_2O_2 concentration for ·OH formation → high H_2O_2 concentration in the effluent
  - Not good for drinking water treatment, but OK for water reclamation

$$H_2O_2 + UV(\lambda \approx 200\sim280\ nm) \rightarrow 2 \cdot OH$$

Advanced oxidation processes

- **Limitations**
  - **Byproduct formation**
    - Oxidation of Br^- in water to form bromate (BrO_3^-; carcinogen)
    - Formation of carboxylic acids, or sometimes halogenated acetic acids (HAAs) as organic byproducts
  - **Impact of carbonate species**
    - High concentrations of CO_3^{2-} and HCO_3^- in wastewater react with ·OH to reduce the efficiency
  - **Impact of pH**
    - pH determines the concentrations of carbonate species
    - H_2O_2/UV process is more effective at very high pH
  - **Impact of metal ions**
    - Metal ions such as Fe^{2+} and Mn^{2+} can consume a significant quantity of chemical oxidants and scavenge ·OH → reduced AOP effectiveness

References

#1) https://dir.indiamart.com/vadodara/wastewater-treatment-chemical.html

#2) https://www.researchgate.net/figure/Schematic-representation-of-standard-jar-test-protocol_fig2_334100925

#3, #4, #5) Metcalf & Eddy, Aecom (2014) Wastewater Engineering: Treatment and Resource Recovery, 5th ed. McGraw-Hill, p. 464, 465, 487.

#6) https://ostara.com/nutrient-management-solutions/

#7, #8) Metcalf & Eddy, Aecom (2014) Wastewater Engineering: Treatment and Resource Recovery, 5th ed. McGraw-Hill, p. 494, 499.