Chemical unit processes II

Chemical precipitation

- The addition of chemicals to alter the physical state of dissolved and suspended solids and facilitate their removal by sedimentation

- **Major application**
  - Improve the performance of primary settling facilities
  - Basic step in the independent physical-chemical treatment of wastewater
  - Removal of phosphorus
  - Removal of heavy metals
  - Softening for reuse of treated water

Common chemical reactions for precipitation

- **Commonly used reactants**
    - Alum ($Al_2(SO_4)_3 \cdot 18H_2O$)
    - Lime ($Ca(OH)_2$)
    - Ferric chloride ($FeCl_3$)
    - Ferrous sulfate ($FeSO_4 \cdot 7H_2O$)
    - Ferric sulfate ($Fe_2(SO_4)_3$)

Alum precipitation

- Reacts with calcium or magnesium bicarbonate alkalinity to form insoluble $Al(OH)_3$

$$3Ca(HCO_3)_2 + Al_2(SO_4)_3 \cdot 18H_2O \rightleftharpoons 2Al(OH)_3 + 3CaSO_4 + 6CO_2 + 18H_2O$$

Calcium bicarbonate (soluble)	Aluminum sulfate (soluble)	Aluminum hydroxide (insoluble)	Calcium sulfate (soluble)

- Alkalinity is required to form precipitants

“Alk as $CaCO_3$” consumed

$$\frac{3 \times 100\ g/mole}{666.5\ g/mole} = 0.45\ mg\ Alk(as\ CaCO_3)\ /\ mg\ alum$$

MW of alum

- Generally addition of alkalinity not needed because of the presence of sufficient alkalinity in wastewater
- The insoluble $Al(OH)_3$ is a gelatinous floc that settles slowly through the wastewater, sweeping out suspended materials

Ferric chloride precipitation

- React with alkalinity to precipitate into $Fe(OH)_3$

$$2FeCl_3 + 3Ca(HCO_3)_2 \rightleftharpoons 2Fe(OH)_3 + 3CaCl_2 + 6CO_2$$

Ferric chloride (soluble)	Calcium bicarbonate (soluble)	Ferric hydroxide (insoluble)	Calcium chloride (soluble)

- Alkalinity requirement:

$$\frac{3 \times 100\ g/mole}{2 \times 162.2\ g/mole} = 0.92\ mg\ Alk(as\ CaCO_3)\ /\ mg\ FeCl_3$$

- If alkalinity supply needed, add lime ($Ca(OH)_2$)
- Forms gelatinous floc similar to alum

Chemically enhanced primary treatment (CEPT)

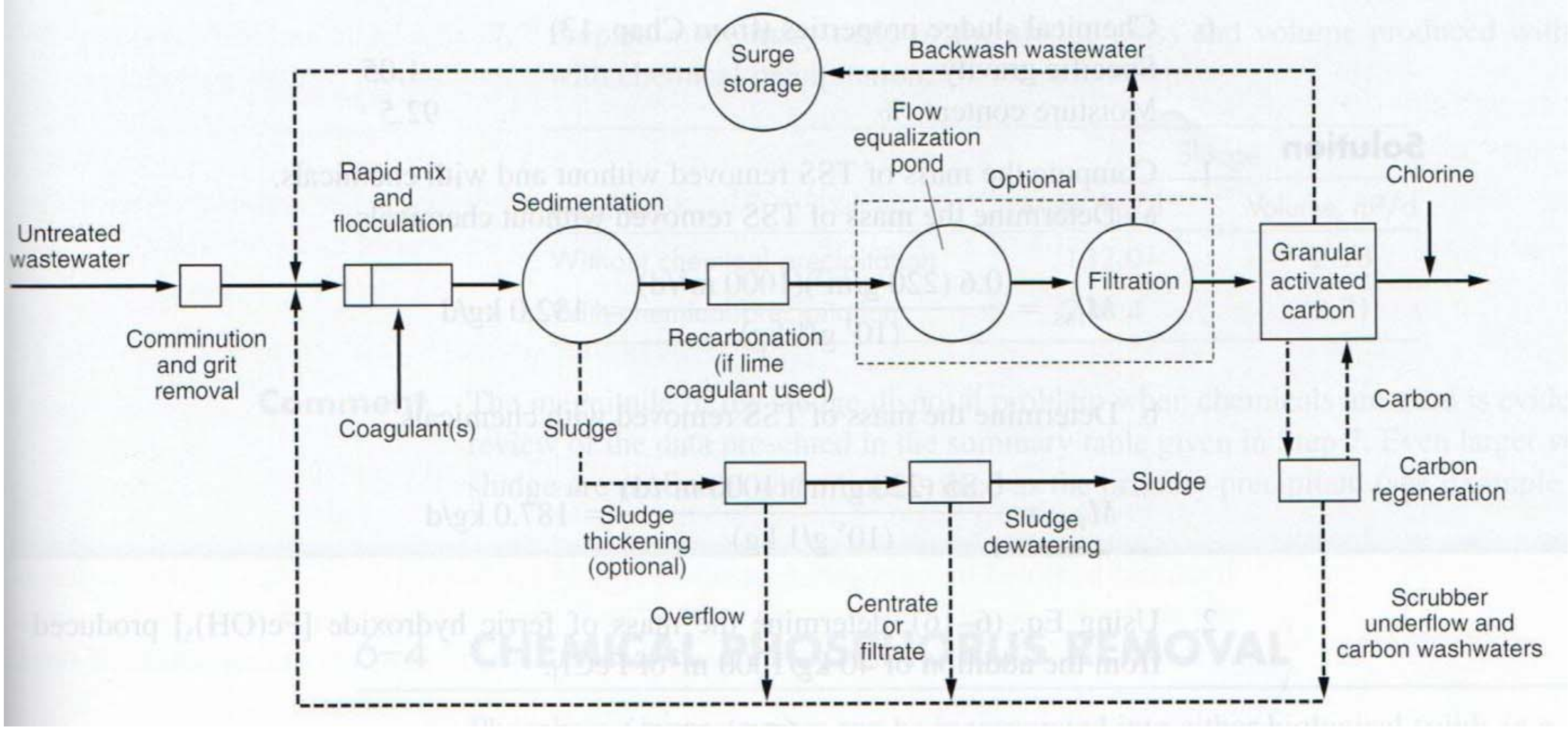
- SS & BOD removal in primary treatment can be substantially improved by using chemical precipitants

- 80-90% TSS removal & 50-80% BOD removal

  cf) 50-70% TSS removal & 25-40% BOD removal for typical primary treatment

- Possible benefits
  - High energy value of primary sludge
  - Reduces oxygen supply demands for secondary treatment

Independent physical-chemical treatment



Independent physical-chemical treatment

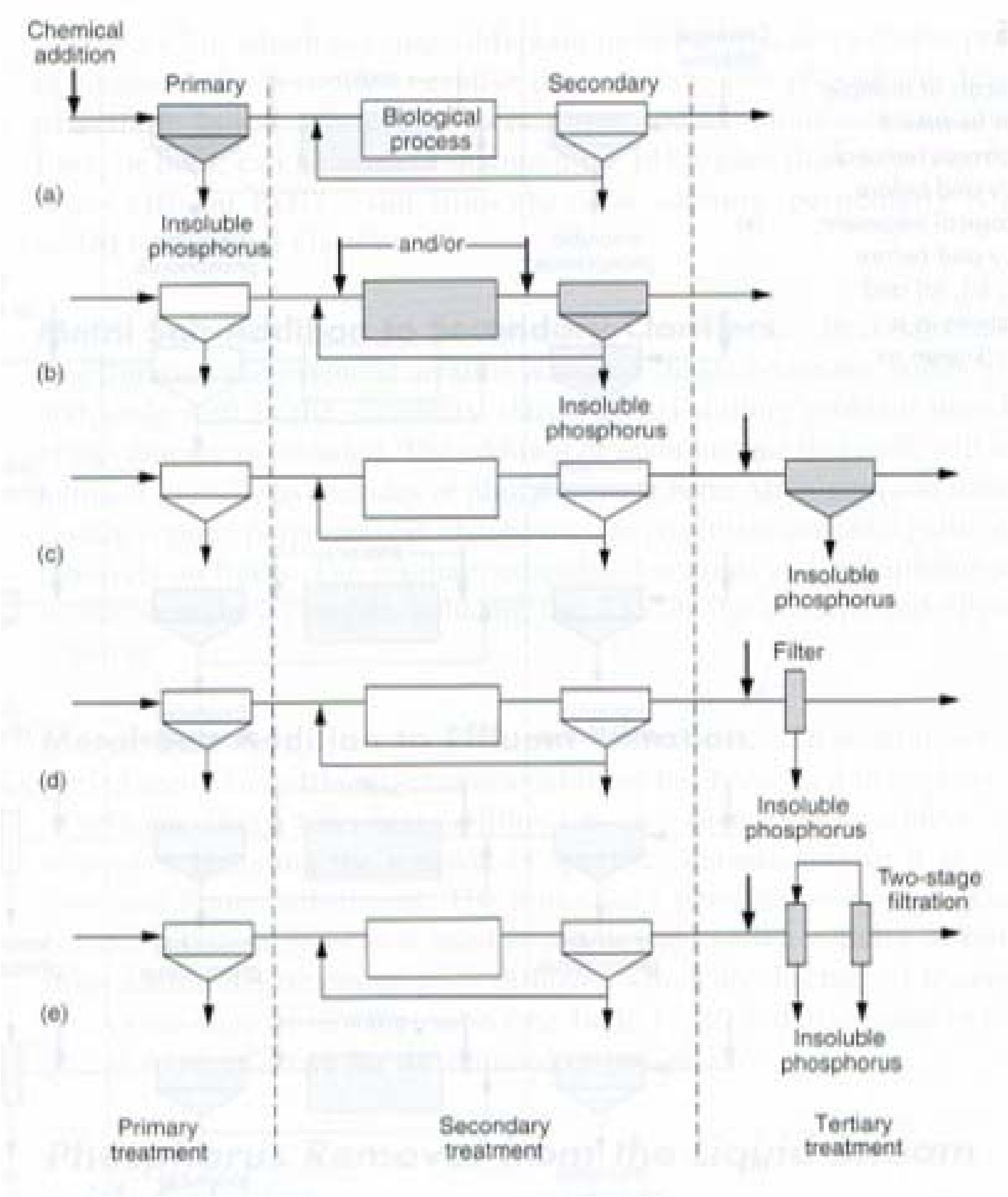
- Applied when biological treatment is not applicable (industrial wastewater with toxic compounds)
- Disadvantages
  - Inconsistency in meeting discharge requirements
  - High chemical cost
  - Handling and disposal of large volume of sludge

→ Generally not successful for municipal wastewater treatment

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+}



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:

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

  - 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)
  - Combine removal of NH_4^+ & P is possible

http://umanitoba.ca

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_s*** as:

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

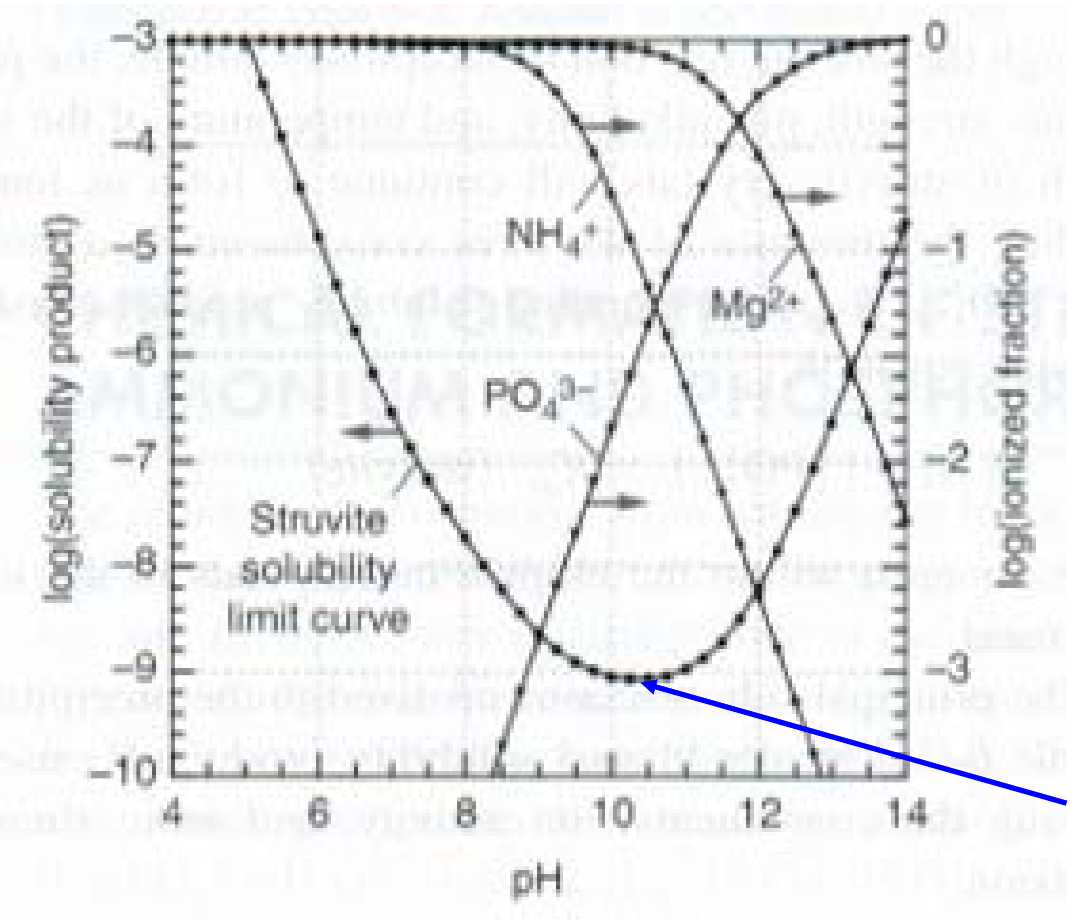
$\alpha_{Mg^{2+}}, \alpha_{NH_4{}^+}, \alpha_{PO_4{}^{3-}}$ = *ionization fraction of individual constituents*

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



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 Ps at higher ionic strength → unfavorable for precipitation
  - **Temperature**: reaction constants are function of temp. – generally, Ps increase with temp. to some point (20-35^{o}C) 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

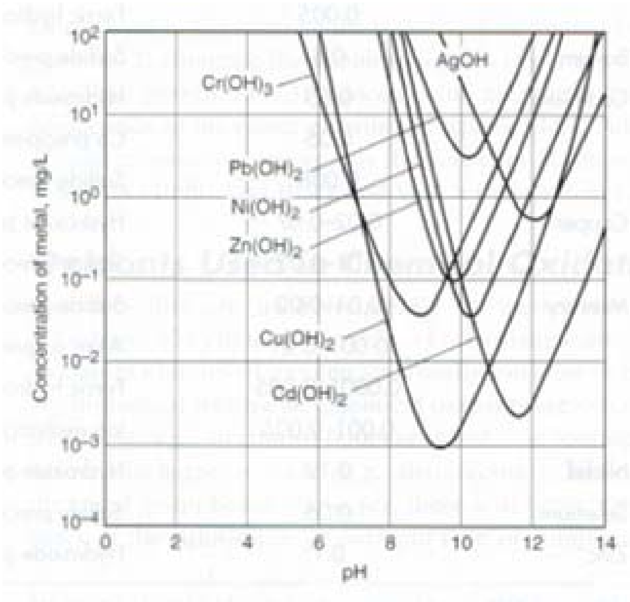
Chemical precipitation for HM removal

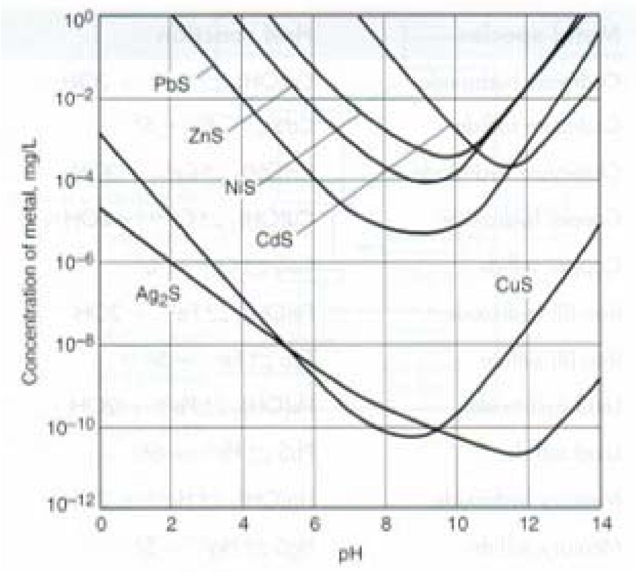
- **Common precipitants**
  - Hydroxide (OH^-), sulfide (S^{2-}): most metal salts with these anions are insoluble
  - Carbonate (CO_3^{2-}) is sometimes used

- **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





Conventional vs. advanced chemical oxidation

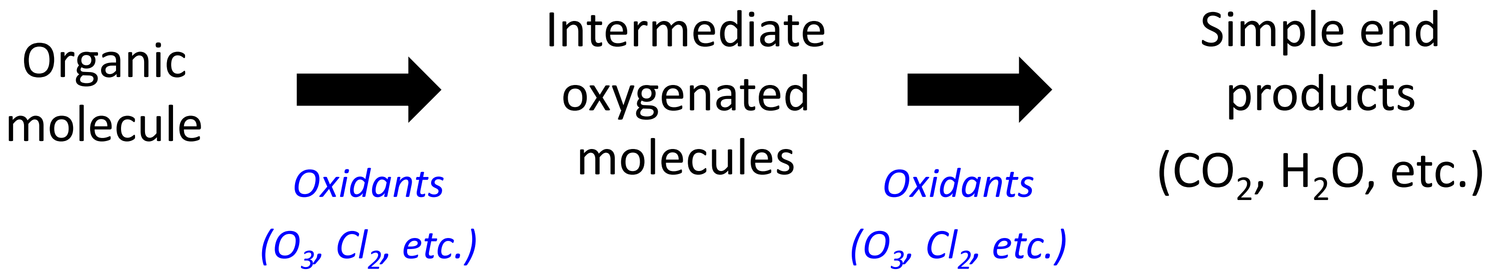
- **Conventional oxidation processes**
  - The use of oxidizing agents such as ozone (O_3), hydrogen peroxide (H_2O_2), permanganate (MnO_4), chlorine dioxide (ClO_2), chlorine (Cl_2 or HOCl), and oxygen (O_2) to bring about the change in the chemical composition of a compound

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

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

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 (HO·): 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 HO· & compound to be oxidized)
  - 2nd order rate constant for HO· 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

     $$R + HO \cdot \rightarrow ROH \cdot$$

  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.

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

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.

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

4. By radical combination:

Two radicals can combine to form a stable product.

$$HO\cdot + HO\cdot \rightarrow H_2O_2$$

Advanced oxidation processes

- **Processes for advanced oxidation**

  = processes for the production of HO·

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

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

    - 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

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

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

$$H_2O_2 + UV(\lambda \approx 200{\sim}280\ nm) \rightarrow 2HO\cdot$$

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 HO· 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 HO· → reduced AOP effectiveness