Precipitation
Coagulation and flocculation

WAT-E2120  Physical and Chemical Treatment of Water and Waste
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What

• Chemical precipitation
• Coagulation
• Flocculation

• Used in water treatment to remove substances that form non-soluble or non-settelable forms with the precipitant.

• Quite often precipitation, coagulation and flocculation are used interchangeably (wrong, though understandable...)

Uses

• Precipitation: Removal of dissolved substances
  • Removal of phosphorus
  • Removal of arsenic
  • Removal of iron
  • Removal of ammonium and phosphate from reject water as magnesiumammoniumphosphate

• Coagulation-flocculation: Removal of colloids
  • Removal or organics
  • Removal of turbidity (e.g. inorganic clay)
  • Removal of pathogenic bacteria

• In most processes both precipitation and coagulation-flocculation happen simultaneously
Applications

- Water treatment
- Wastewater treatment
- Sludge and slurry dewatering
- Water softening
- Treating landfill leachate
- Treating industrial wastewaters, e.g. from dairies and food processing
- Lake restoration
- ...
Precipitation chemicals

- Aluminum Chloride \([\text{AlCl}_3]\)
- Polyaluminium chloride (e.g. PAX)
- Aluminum Sulfate \([\text{alum, Al}_2(\text{SO}_4)_3 \times 14-18 \text{H}_2\text{O}]\)
- Ferrous sulfate \([\text{FeSO}_4 \times 7 \text{H}_2\text{O}]\) (Note, divalent iron)
- Ferric Chloride \([\text{FeCl}_3]\) – Typically sold in solution form. (e.g. PIX)
- Ferric sulphate \([\text{Fe}_2(\text{SO}_4)_3]\)
- \(\text{Ca(OH)}_2\)
Precipitation reactions

\[
\begin{align*}
\text{Fe}^{3+} + \text{HPO}_4^{2-} & \rightarrow \text{FePO}_4 + \text{H}^+ \\
\text{Fe}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \text{(without alkalinity)} \\
\text{Fe}^{3+} + 3 \text{HCO}_3^- & \rightarrow \text{Fe(OH)}_3 + 3 \text{CO}_2 \text{(with alkalinity)} \\
\text{Al}^{3+} + \text{HPO}_4^{2-} & \rightarrow \text{AlPO}_4 + \text{H}^+ \\
\text{Al}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ 
\end{align*}
\]

• Insoluble phosphates form in wastewater
• If phosphate is not present, insoluble hydroxide is formed
• All reactions produce hydrogen ions
  • Alkalinity (carbonate) compensates against pH decrease
Equilibrium constants of solubility = Solubility product

- The lower the solubility product, the more the balance is on the solid product of the solubility reaction.
- Solubility changes by temperature. It may increase by temperature (endothermic reactions) or decrease (exothermic).
- Ionic strength changes solubility. Adding other salts (ions) into the solution increases solubility. (These are with ionic strength $I = 0$)
- General rules:
  - Phosphate and carbonate salts are insoluble
  - Ammonium and nitrate form soluble salts

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**Equilibrium Constants Related to the Solubility of Phosphates of Fe(III), Al(III), Fe(II), and Ca$^{2+}$**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\log K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(25°C, $I = 0$)</td>
<td></td>
</tr>
<tr>
<td>FePO$_4$·2H$_2$O(s) (strengite) = Fe$^{3+}$ + PO$_4^{3-}$ + 2H$_2$O</td>
<td>$-26$</td>
</tr>
<tr>
<td>AlPO$_4$·2H$_2$O(s) (variscite) = Al$^{3+}$ + PO$_4^{3-}$ + 2H$_2$O</td>
<td>$-21$</td>
</tr>
<tr>
<td>CaHPO$_4(s)$ = Ca$^{2+}$ + HPO$_4^{-2}$</td>
<td>$-6.6$</td>
</tr>
<tr>
<td>Ca$_4$H(PO$_4$)$_3(s)$ = 4Ca$^{2+}$ + 3PO$_4^{3-}$ + H$^+$</td>
<td>$-46.9$</td>
</tr>
<tr>
<td>Ca$_{10}$(PO$_4$)$_6$(OH)$_2(s)$ = 10Ca$^{2+}$ + 6PO$_4^{3-}$ + 2OH$^-$</td>
<td>$-114$</td>
</tr>
<tr>
<td>Ca$_{10}$(PO$_4$)$_6$(F)$_2(s)$ = 10Ca$^{2+}$ + 6PO$_4^{3-}$ + 2F$^-$</td>
<td>$-118$</td>
</tr>
<tr>
<td>Ca$_{10}$(PO$_4$)$_6$(OH)$_2(s)$ + 6H$_2$O = 4[Ca$_2$(HPO$_4$)(OH)$_2$] + 2Ca$^{2+}$ + 2HPO$_4^{2-}$</td>
<td>$-17$</td>
</tr>
<tr>
<td>CaHAl(PO$_4$)$_2(s)$ = Ca$^{2+}$ + Al$^{3+}$ + H$^+$ + 2HPO$_4^{3-}$</td>
<td>$-39$</td>
</tr>
<tr>
<td>CaF$_2(s)$ = Ca$^{2+}$ + 2F$^-$</td>
<td>$-10.4$</td>
</tr>
<tr>
<td>MgNH$_4$PO$_4(s)$ = Mg$^{2+}$ + NH$_4^+$ + PO$_4^{3-}$</td>
<td>$-12.6$</td>
</tr>
<tr>
<td>FeNH$_4$PO$_4(s)$ = Fe$^{2+}$ + NH$_4^+$ + PO$_4^{3-}$</td>
<td>$-13$</td>
</tr>
<tr>
<td>Fe$_2$(PO$_4$)$_2(s)$ = 3Fe$^{2+}$ + 2PO$_4^{3-}$</td>
<td>$-32$</td>
</tr>
</tbody>
</table>
Solubility depends on pH

- There is an optimum pH for each phosphorus precipitation reaction
  - When the remaining soluble phosphate is at its lowest
  - Aluminium 6.2
  - Iron 5-5.5
- If needed, extra addition of chemical to move the pH to the right range
  - The Fe and Al chemicals decrease pH
Molar ratio in precipitating phosphorus from wastewater

- Defined as moles of precipitating cation to moles of phosphorus
- Usually equal or higher than stoichiometric ratio
  - Stoichiometric ratio = 1 for Fe(III):P and Al:P
Pre- and postprecipitation

• In wastewater treatment precipitation can be before or after the biological reactor
• Pre-precipitation:
  • Receives untreated water with high phosphorus concentration
  • Removes phosphorus and organic matter ⇒ smaller biological reactor
  • Molar ratio (cation:phosphorus) 1-1.5
• Postprecipitation:
  • Receives lower phosphorus concentrations and traces of solid biomass from the biological process and separation
  • Polishes the phosphorus and solids removal of the treatment plant
  • Molar ration (cation:phosphorus) 2 (sometimes higher)
Simultaneous precipitation

- Phosphorus removal from wastewater
- Usually done with divalent iron
  - Ferrous sulphate (inexpensive chemical)
  - Trivalent iron is also used
- Dosed into two points in wastewater treatment:
  - Before pre-sedimentation
  - Into activated sludge reactor
- Iron(II) is oxidized into trivalent iron in the aerated activated sludge reactor
- Molar ratio $Fe:P \ 1-2 \ (1.5)$

Typical brown sludge formed in simultaneous precipitation

http://www.phlush.org
Practical notions

• If nothing else is known, ~100-200 g/m³ of precipitant is a good starting point in simultaneous precipitation
  • Or ~20 g/m³ of cation

• Overdosing ruins the precipitation – wrong pH range, too low alkalinity
  • This happens in real life at WWTPs when operators try to compensate poor phosphorus result by adding more of the precipitation chemical
  • E.g. if the precipitant dose is 350 g/m³ and the phosphorus result is still poor and the operator wants to raise the dose, it’s your task to blow the whistle – and lower the dose, or organize jar tests

WWTP = wastewater treatment plant
Practical notions, 2

• Pre-precipitation with trivalent cations can lead to too low phosphorus concentrations, if a biological process follows
  • =>The microbes lack phosphorus for growth
  • =>Biological process treatment result as BOD (organic matter) is not sufficient
Example of precipitation

- Wastewater and chemical are combined in rapid mixing
  - Precipitation (and/or coagulation)
  - Microflocs are formed
  - HRT 30-60 s
- Flocculation
  - Slow mixing
  - Microflocs are combined into larger flocs
  - Large flocs are settleable
  - HRT minimum 20 min
- Dosing system:
  - Basin for solution storage or dissolution basin, including mixing apparatus
  - Pump for dosing into wastewater stream
  - Solutions are highly corrosive => materials have to be corrosion proof

Note: exercise 2
Coagulation theory
Colloids

- Colloidal particles size ranging 1 nm-1μm
  - Cause turbididy
  - Color in raw surface water
- It is difficult to separate colloids from water
  - Colloids do not settle by gravity
  - They pass through the pores of most common filter media
- Colloidal particles adsorb water molecules and oppositely charged ions from bulk water on their surface gaining repulsion from each other and stability in solution
Zeta potential

- Stern model (1924)
- Negatively charged surface
- First layer of positively charged ions of finite size, tightly adsorbed onto the surface = Fixed (Stern) layer
- Subsequent layers as point charges
- Slipping (shear) plane: at the boundary of the diffuse layer
- Potential difference of bulk water and the shear plane: zeta or electrokinetic potential
- Zeta potential is used because the surface potential cannot be measured
DLVO theory

- DLVO theory explains the repulsive and attractive forces between colloidal particles
- Repulsive Forces
  - Result from Electrical Double Layer
- Attractive Forces
  - Result from Van der Waals forces of intermolecular attraction
- Interactions between these forces contribute to the overall stability of colloidal dispersion
Coagulation and flocculation

- Removal of colloids
  - The individual colloids must aggregate and grow in size
  - Coag. & flocc. are used to agglemorate colloids prior to separation of solids

- Coagulation: the addition and rapid mixing of coagulant
  - for destabilization of particles
  - for initial aggregation of the destabilized particles

- Flocculation: the slow stirring or gentle agitation
  - to aggregate destabilized particles
  - to form rapidly settling flocs
Flocculation mechanisms

Schematic representation of colloidal suspension flocculation by:
(a) Charge neutralization
(b) Polymer adsorption and bridging
(c) Electrostatic patch
(d) Enmeshment (trapping) in the precipitate or sweep flocculation (with metal cations)

\[ \text{Al}_2(\text{SO}_4)_3 \rightarrow \text{Al}^{3+} + \text{Al}^{3+} + \text{Al}^{3+} + \rightarrow \text{Polymer bridging} \]

Dao, 2016
Flocculation chemicals

• Mineral flocculants
  • Metallic hydroxides with a polymeric structure (alum, ferric hydroxide)
  • Colloidal clays (such as bentonite)

• Natural flocculants
  • Water soluble anionic, cationic or nonionic polymers
  • Alginates: anionic, used in potable water treatment
  • Starch derivatives
  • Polysaccharides
Flocculation chemicals

- Synthetic flocculants:
  - Most common polymers based on polyacrylamide, which is a nonionic polymer
  - The effect is due to bridging between particles by polymer chains
- Other polymers display specific properties and are used under specific conditions
  - Polyethylene-imines
  - Polyamides-amines
  - Polyamines
  - Polyethylene-oxide
  - Sulfonated compounds
Solubility diagram of coagulation-flocculation with aluminium

- pH- concentration diagram of aluminium in water
- Removal of NOM from raw water in drinking water treatment
- Aluminium hydroxide precipitation operating region pH is 7.0-8.0 and dose 20 -60 g/m³
  - Optimal sweep area in the diagram
- Note the difference to precipitation!

Amirtharajah and Mills 1982
Schulze-Hardy rule

• The Schultz-Hardy Rule indicates the relative effectiveness for mono- vs. di- vs. trivalent ions is in the ratio of ca. 1:100:1000

• E.g. for drinking water applications the relative effectiveness of the monovalent (Na+) vs. divalent (Ca^{2+}) vs. trivalent (Al^{3+}) ions is 1:60:700

• =Trivalent cations are most effective
Polyacrylamides

Acrylamide monomer and polymer

Anionic character by copolymerizing acrylamide with acrylic acid.
Cationic character by copolymerizing acrylamide with a cationic monomer.
For each suspension, a certain degree of anionic, cationic or nonionic character is beneficial.
Flocculating power increases with the molecular weight.
Polyacrylamides molecular weight in the range of 10-20 millions (Huge!)
Flocculant polymer uses

• Industrial waste treatment
  • Blast-furnace gas washing
  • Surface treatment industry
  • Petroleum refinery effluent

• Sewage and municipal waste
  • In the case of physico-chemical treatment
  • Prior sludge dewatering
Dosing systems for flocculants

• Industrial scale dissolution of flocculants requires a procedure which has to be adapted to the flocculant specifications
  • solutions are very viscous
  • high shear should be avoided during mixing
  • flocculant particles if not properly dispersed tend to agglomerate lumps of flocculant do not dissolve easily

• A dissolution plant has the following components
  • a disperser system to ensure a proper wetting of the powder without agglomeration
  • a dissolving tank
  • a transfer pump
  • a stock tank
  • a metering pump and dilution system
Separation after precipitation and coagulation-flocculation

**Typical separation processes**

- Sedimentation
- Flotation
- Filtration

**Typical processes**

1. **Organic Coagulant**
   - RAW WATER
   - Coagulation tank (flash mixing)

2. **Mineral Coagulant (Al³⁺, Fe³⁺)**
   - ORGANIC COAGULANT
   - MINERAL COAGULANT

3. **Flocculant**
   - Flocculation tank (slow mixing)

4. **TREATED WATER**
Flocculant addition to dewatering of sludge

- Flocculant added as aid for dewatering
- Note the feeding point: no rapid mixing separately
  - Mixing happens in the centrifuge
Further reading


Coagulation slides at Cornell (more deeply in the subject than this presentation): ceeserver.cee.cornell.edu/jjb2/cee6560/7-Coagulation.ppt