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School of Engineering

Physical & chemical treatment processes of water and waste

Lecture 4 Precipitation, coagulation and flocculation

WAT - E2120

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Lecture content

Group discussion on different compounds of interest

Theory on precipitation

Theory on coagulation and flocculation

Group discussion on real life cases

Applications of precipitation and coagulation&flocculation

NOTE!! Guest lecturer Outi Grönfors from Kemira on Jan 23rd

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GROUP DISCUSSION

**What kind of compounds do
we want to separate, remove or
recover?**

Discussion in groups (10 min)

**Outcomes on the black board
(5 min)**

Precipitation, coagulation, flocculation - **THEORY**

Precipitation = dissolved → solid
Coagulation = destabilization of small suspended and colloidal particles
Flocculation = aggregation of destabilized particles

Precipitation

Ion product (Q_{sp}) > Solubility product (K_{sp})

Coagulation

The negative surface charge of colloids is neutralised by adding positively charged coagulant, ie. colloid is destabilized. Time required typically 10 - 30 s.

Flocculation

Aggregation of destabilized particles and (possible) the precipitation products. Time required for slow mixing typically 20-30 mins.
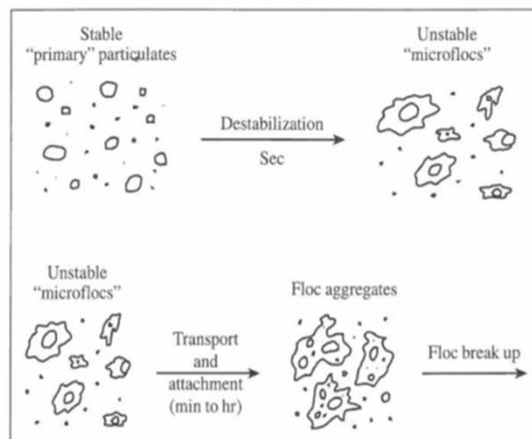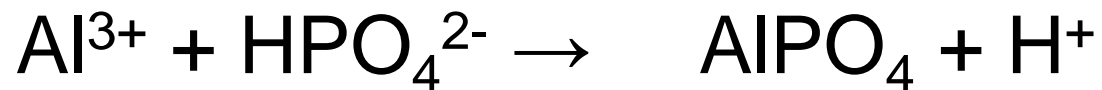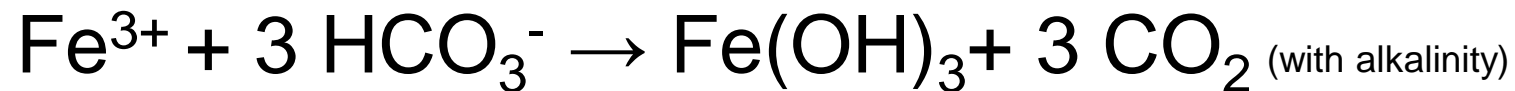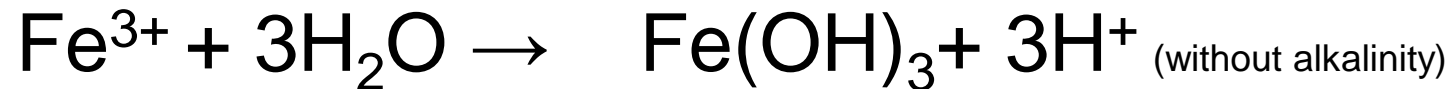

Fig. 4.8 – Floc formation and growth

Precipitation Theories

Precipitation reactions

$$Fe^{3+} + HPO_4^{2-} \rightarrow \quad FePO_4 + H^+$$

$$Fe^{3+} + 3H_2O \rightarrow \quad Fe(OH)_3 + 3H^+ \text{ (without alkalinity)}$$

$$Fe^{3+} + 3\ HCO_3^- \rightarrow Fe(OH)_3 + 3\ CO_2 \text{ (with alkalinity)}$$

$$Al^{3+} + HPO_4^{2-} \rightarrow \quad AlPO_4 + H^+$$

$$Al^{3+} + 3H_2O \rightarrow \quad Al(OH)_3 + 3H^+$$
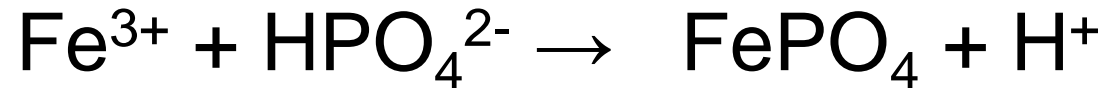
- Insoluble phosphates are formed in wastewater
- Insoluble hydroxide is formed as well.
- All reactions produce hydrogen ions
    - Alkalinity (carbonate) compensates against pH decrease

Precipitation chemicals

Aluminum Chloride [$AlCl_3$]

Aluminum Sulphate [alum, $Al_2(SO_4)_3$ x 14-18 H_2O]

Polyaluminium chloride (e.g. PAX)

Ferrous sulphate [$FeSO_4$ x 7 H_2O] (Note, divalent iron)

Ferric Chloride [$FeCl_3$] – Typically sold in solution form. (e.g. PIX)

Ferric sulphate [$Fe_2(SO_4)_3$]

$Ca(OH)_2$

Formation of particles in precipitation

- **stepwise: complexes→ clusters → nuclei**
- **Primary and secondary nucleation**
- **Factors influencing formation:**
  - Transport to the boundary layer
  - Composition and surface of growth sites
  - Other constituents in particles

- **Amorphous solids = particles that contain more water and are less dense than products of crystallization**
- **Amorphous solids are formed when water is supersaturated and growth proceeds rapidly**
- **$Al(OH)_3$ and $Fe(OH)_3$ are typically amorphous**

# 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

Equilibrium constants of solubility = Solubility product

Table 7.5. Equilibrium Constants Related to the Solubility of Phosphates of Fe(III), Al(III), Fe(II), and Ca^{2+}

|	$\log K$ (25°C, $I = 0$)
$FePO_4 \cdot 2H_2O(s)$ (strengite) $= Fe^{+3} + PO_4^{-3} + 2H_2O$	-26
$AlPO_4 \cdot 2H_2O(s)$ (variscite) $= Al^{+3} + PO_4^{-3} + 2H_2O$	-21
$CaHPO_4(s) = Ca^{+2} + HPO_4^{-2}$	-6.6
$Ca_4H(PO_4)_3(s) = 4Ca^{+2} + 3PO_4^{-3} + H^+$	-46.9
$Ca_{10}(PO_4)_6(OH)_2(s) = 10Ca^{+2} + 6PO_4^{-3} + 2OH^-$	-114
$Ca_{10}(PO_4)_6(F)_2(s) = 10Ca^{+2} + 6PO_4^{-3} + 2F^-$	-118
$Ca_{10}(PO_4)_6(OH)_2(s) + 6H_2O = 4[Ca_2(HPO_4)(OH)_2] + 2Ca^{+2} + 2HPO_4^{-2}$	-17
$CaHAl(PO_4)_2(s) = Ca^{+2} + Al^{+3} + H^+ + 2HPO_4^{-3}$	-39
$CaF_2(s) = Ca^{+2} + 2F^-$	-10.4
$MgNH_4PO_4(s) = Mg^{+2} + NH_4^+ + PO_4^{-3}$	-12.6
$FeNH_4PO_4(s) = Fe^{+2} + NH_4^+ + PO_4^{-3}$	~ -13
$Fe_2(PO_4)_2(s) = 3Fe^{+2} + 2PO_4^{-3}$	~ -32

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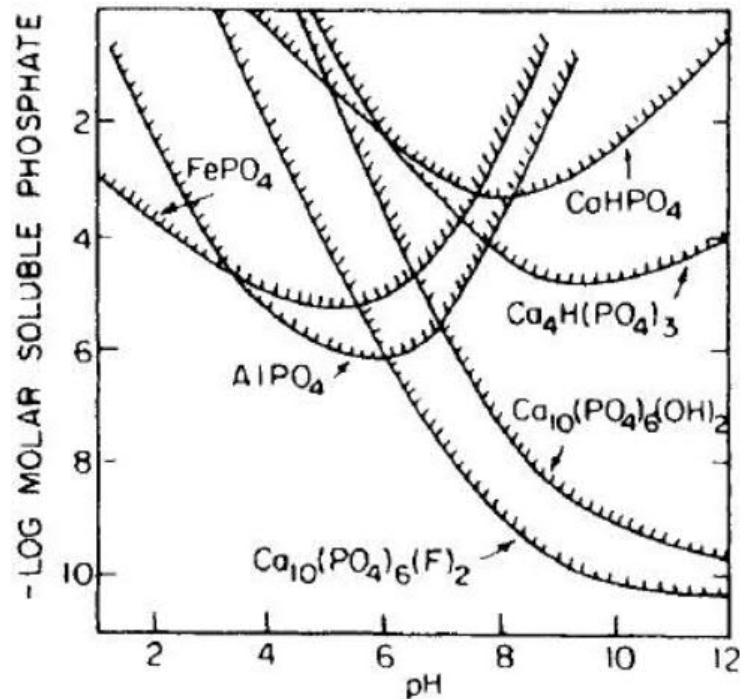
- There is an optimum pH for each phosphorus precipitation reaction
  - When the remaining soluble phosphate is at its lowest
  - Aluminium 6.2
  - Iron 5-5.5
- If needed, extra addition of chemical to move the pH to the right range
  - The Fe and Al chemicals decrease pH

Precipitation in complex mixtures

- Models are used to predict
the reactions taking place.

Mbamba, 2016

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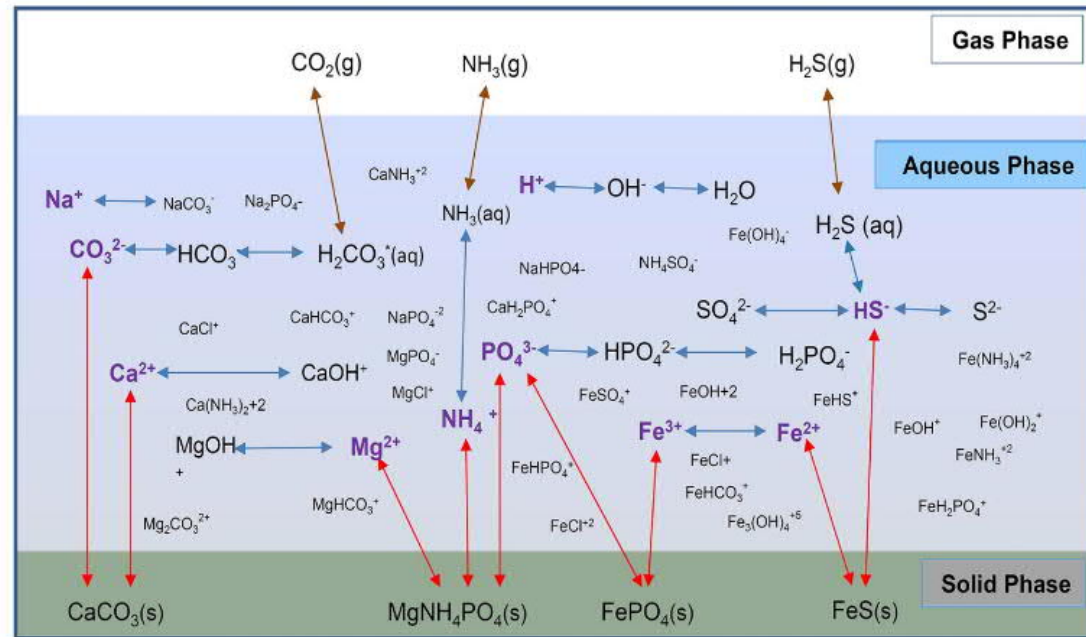
Example: Aluminum sulfate precipitation

Aluminum sulfate was used to coagulate raw drinking water. Determine the amount of aluminum hydroxide and carbon dioxide formed from 1 g of aluminum sulfate [$Al_2(SO_4)_3 x14\ H_2O$.]. Reaction equation:

$$Al_2(SO_4)_3 x\ 9\ H_2O + 6HCO_3^- \rightarrow 2Al(OH)_3 \downarrow + 3SO_4^{2-} + 9\ H_2O + 6\ CO_2$$

- The amount of moles of aluminum sulfate was used to coagulate raw drinking water:

$$n_{Al_2(SO_4)_3.14H_2O} = \frac{1\ g}{27\times2+(32+16\times4)\times3+14\times(2+16)\ g/mol} = \frac{1\ g}{594\ g/mol} = 1.68\times10^{-3}\ mol$$

The amount of iron hydroxide and carbon dioxide

$$m_{Al(OH)_3} = n_{Al(OH)_3} \times M_{Al(OH)_3} = 2\times n_{Al_2(SO_4)_3.14H_2O} \times M_{Al(OH)_3} = 2\times1.68\times10^{-3}\times(27+17\times3) = 0.26\ g$$

$$m_{CO_2} = n_{CO_2} \times M_{CO_2} = 6\times n_{Al_2(SO_4)_3.14H_2O} \times M_{CO_2} = 6\times1.68\times10^{-3}\times(12+16\times2) = 0.44\ g$$

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Coagulation and flocculation Theories

Colloids

negative

colloidal
particle

(A)

colloidal
particle

negative

3-
3-
3-
3-
3-
3-

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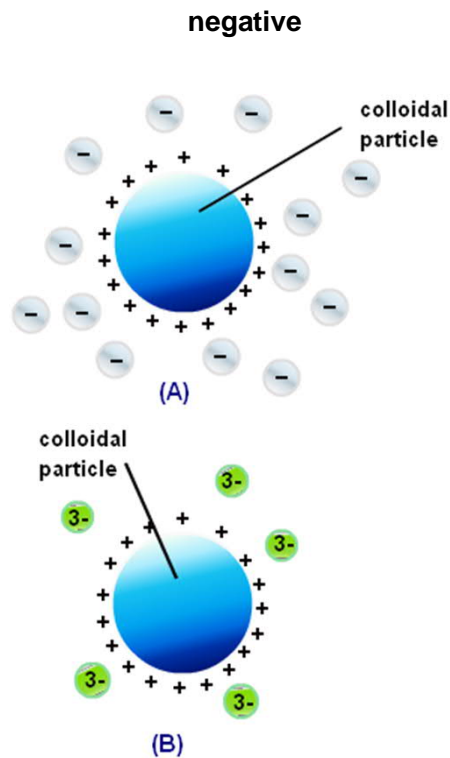
- Colloidal particles size ranging 1 nm-1μm
  - Cause turbididy
  - Color in raw surface water
- It is difficult to separate colloids from water
  - Colloids do not settle by gravity
  - They pass through the pores of most common filter media
- Colloidal particles adsorb water molecules and oppositely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

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Coagulation and flocculation

Removal of colloids

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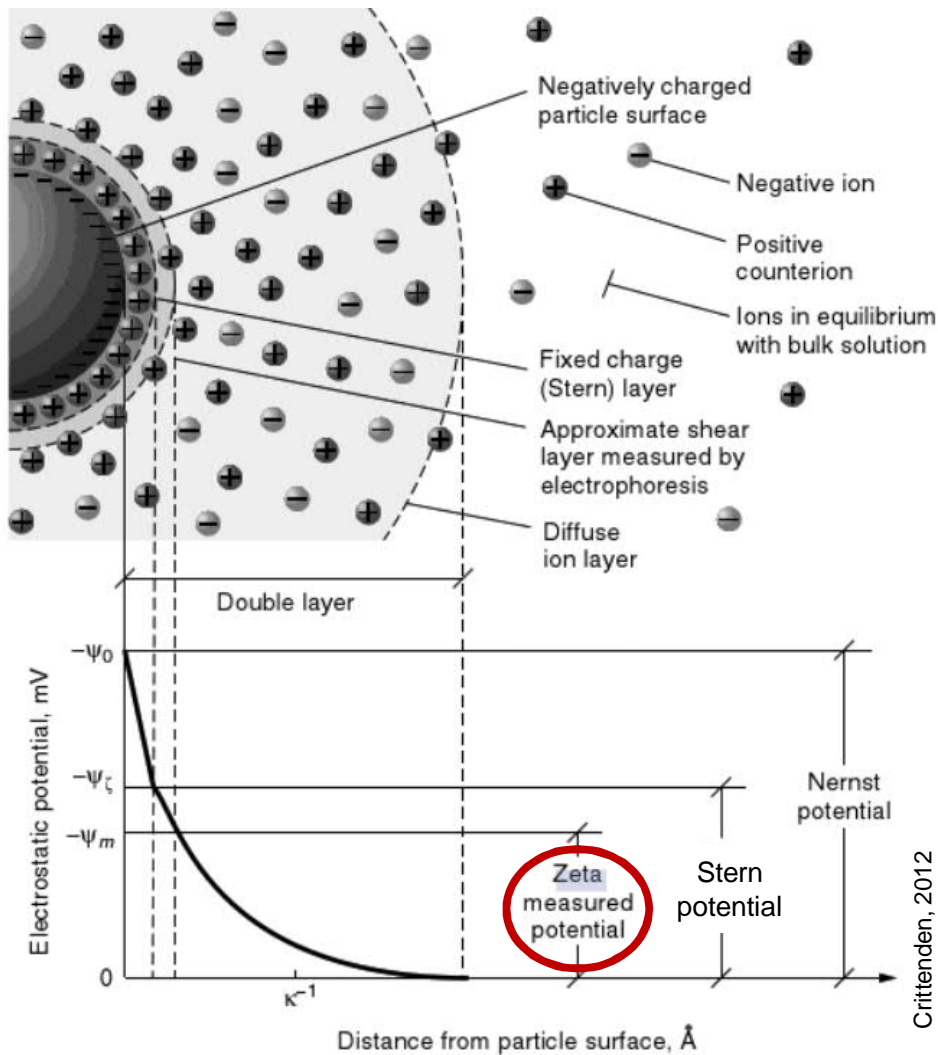- Coag. & flocc. are used to agglemorate colloids prior to separation of solids

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

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

Crittenden, 2012

DLVO theory

established by Derjaguin, Landau, Verwey, and Overbeek in the 1940s
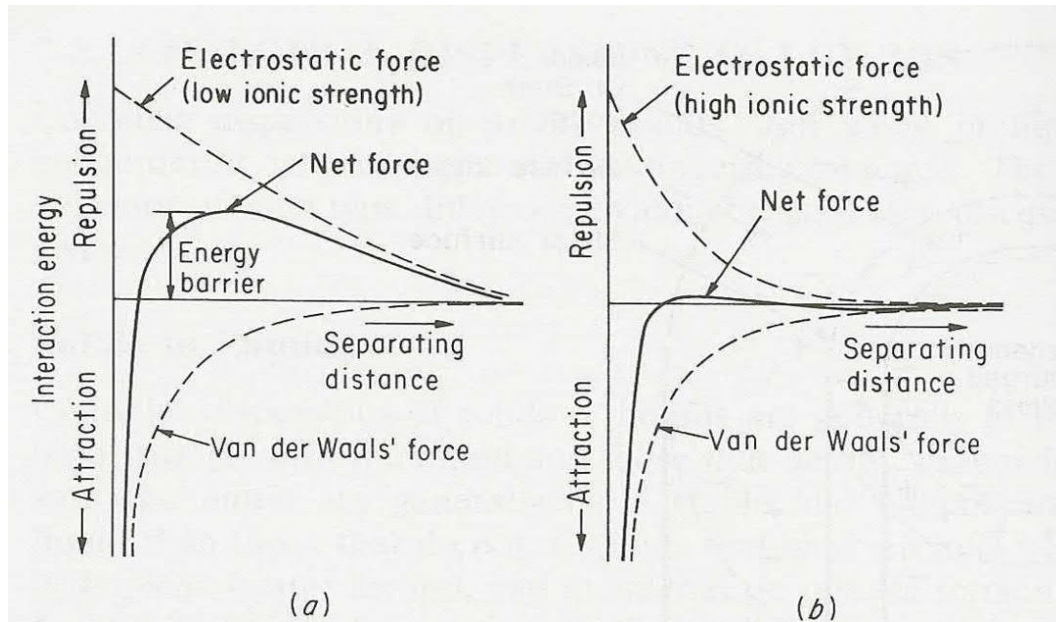
- DLVO theory explains the repulsive and attractive forces between colloidal particles
- Repulsive Forces
  - Result from Electrical Double Layer
- Attractive Forces
  - Result from Van der Waals forces of intermolecular attraction

- Interactions between these forces contribute to the overall stability of colloidal dispersion

# Particle destabilization

1) **Compression of diffuse layer**

2) **Adsorption on the surface and charge neutralization**

3) **Enmeshment in a precipitate (sweep flocs)**

4) **Bridging (=flocculation)**

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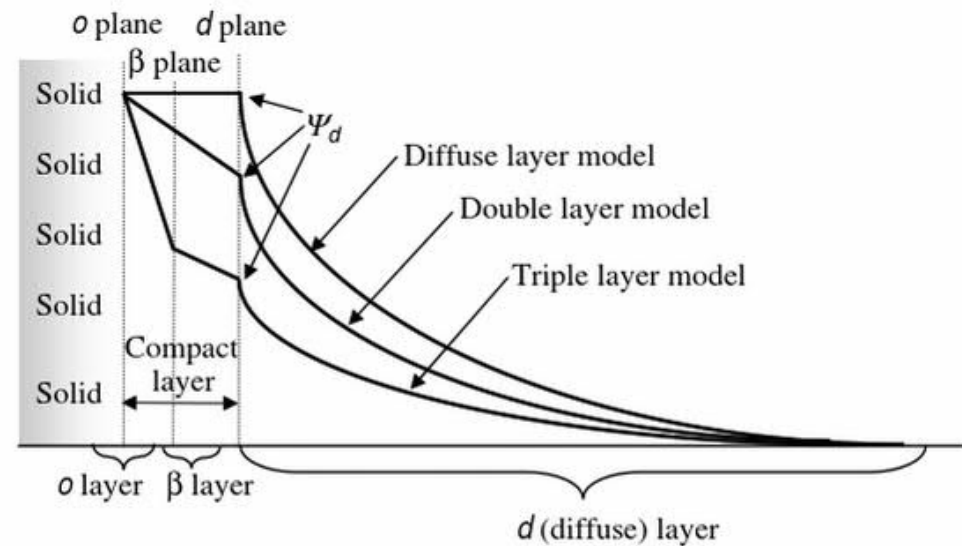
Compression of diffuse layer

- If the ionic strength is increased, the availability of counterions increases and the diffuse layer becomes smaller

Low ionic strength

Higher ionic strength

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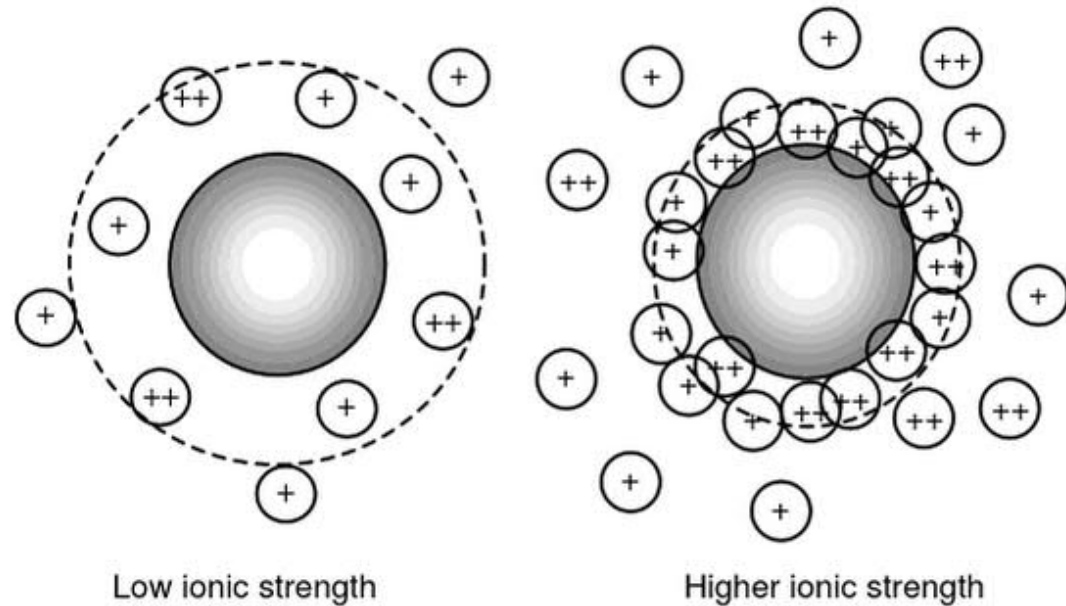
Schulze-Hardy rule

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

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

Charge neutralization and adsorption

- Adding the right amount of ions of opposite charge will result in charge neutralization

- Destabilization = charge neutralization to allow adsorption

- Particle is destabilized in an area around charge 0.

- Energy barrier is lowered or surface is uneven.

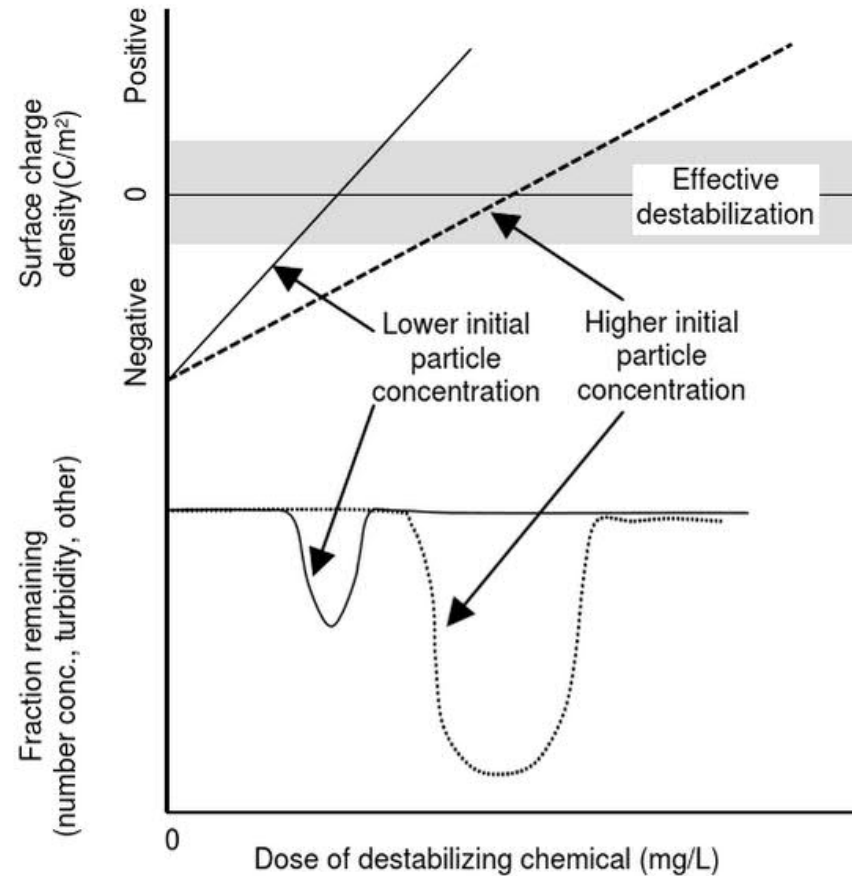- Restabilization occurs when dosing is too high.

FIGURE 11-16. Particle destabilization by charge neutralization.

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Enmeshment or sweep

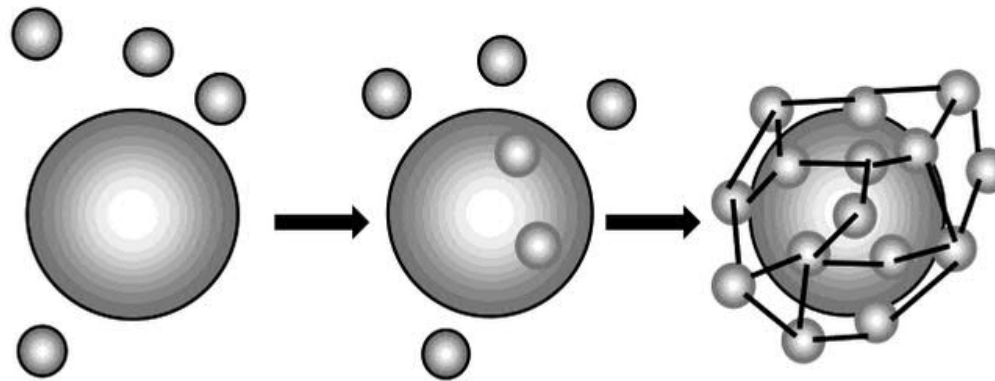- **Hydroxides are formed and they are forming "nets" that caugth particles.**

FIGURE 11-17. Schematic of the adsorption of metal ions (small circles) onto a particle (large circle) leading to the formation of a precipitate. The lines in the right part of the figure indicate the formation of the precipitate.

Bridging

Typically high molecular weight synthetic polymers attaching to several particles and forming "bridges"
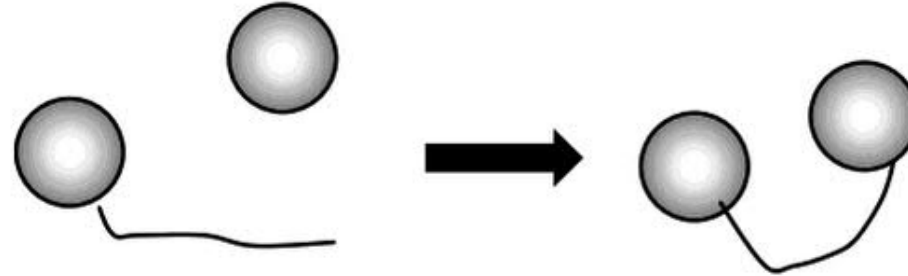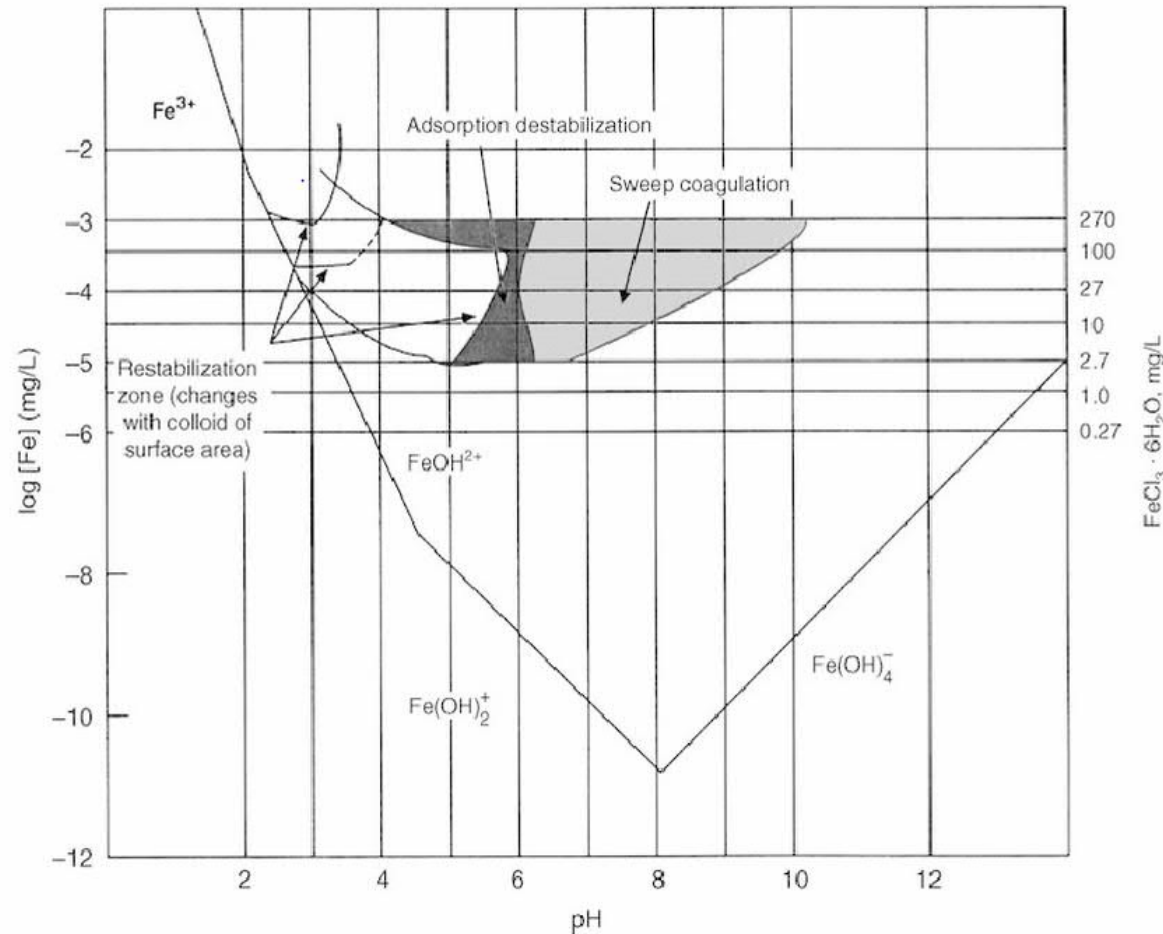
Strong flocs

FIGURE 11-22. Schematic of interparticle bridging by a high-molecular weight polymer.
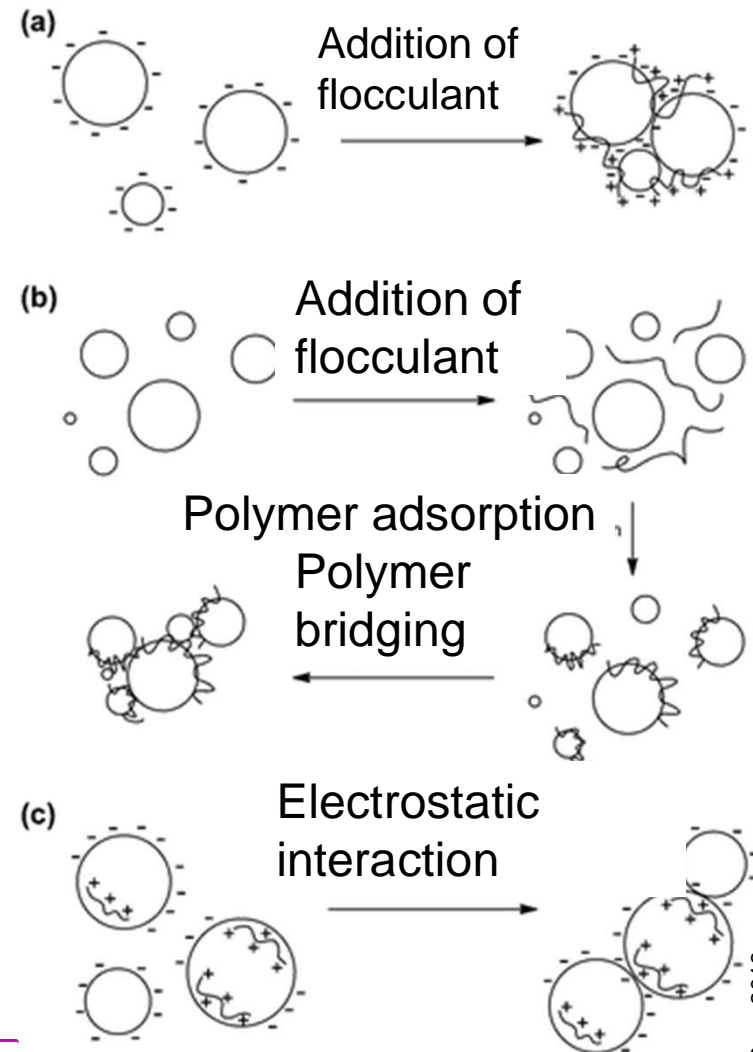
Solubility diagram of coagulation-flocculation with iron

- **pH- concentration diagram of iron in water**
- **pH > 6 mainly sweep**
- **pH < 6 mainly adsorption and charge stabilization**

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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)

(a)
Addition of flocculant

(b)
Addition of flocculant

Polymer adsorption
Polymer bridging

(c)
Electrostatic interaction

(d)

$Al_2(SO_4)_3$

$Al_2(SO_4)_3$ +

Al^{3+} ... + $Al(OH)_3$ (FLOC)

$Al(OH)_3$

Dao, 2016

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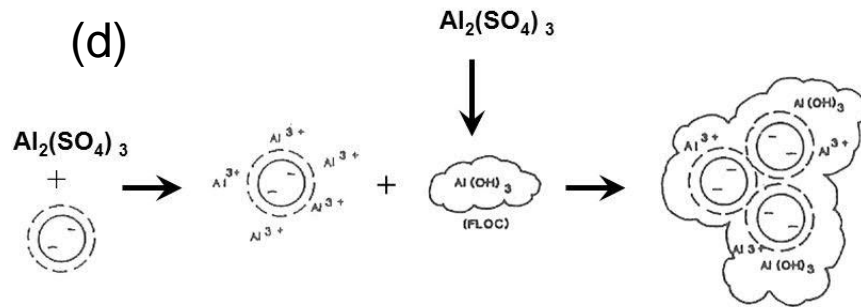
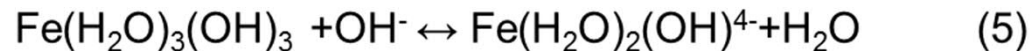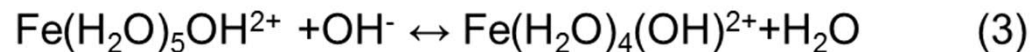# Flocculation chemicals

Mineral flocculants

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

Hydrolyzed forms of Fe(III) salt:

$FeCl_3 \leftrightarrow Fe^{3+} + 3Cl^-$ (1)

$Fe(H_2O)_6^{3+} + OH^- \leftrightarrow Fe(H_2O)_5OH^{2+} + H_2O$ (2)

$Fe(H_2O)_5OH^{2+} + OH^- \leftrightarrow Fe(H_2O)_4(OH)^{2+} + H_2O$ (3)

$Fe(H_2O)_4(OH)^{2+} + OH^- \leftrightarrow Fe(H_2O)_3(OH)_3 + H_2O$ (4)

$Fe(H_2O)_3(OH)_3 + OH^- \leftrightarrow Fe(H_2O)_2(OH)^{4-} + H_2O$ (5)

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
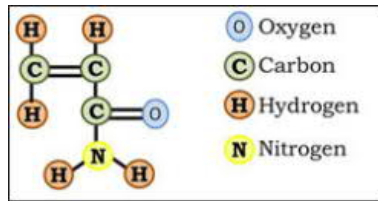
Other polymers display specific properties and are used under specific conditions

- Polyethylene-imines
- Polyamides-amines
- Polyamines
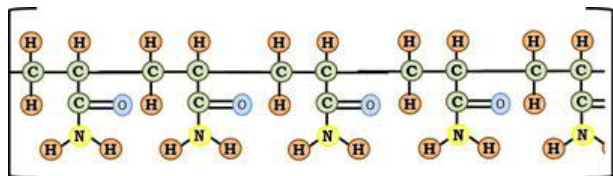- Polyethylene-oxide
- Sulfonated compounds

Polyacryl amides

Acryl amide monomer and polymer

Buttice, 2011

- O Oxygen
- C Carbon
- H Hydrogen
- N Nitrogen

Buttice, 2011

Anionic character by copolymerizing acrylamide with acrylic acid.

Cationic character by copolymerizing acrylamide with a cationic monomer.
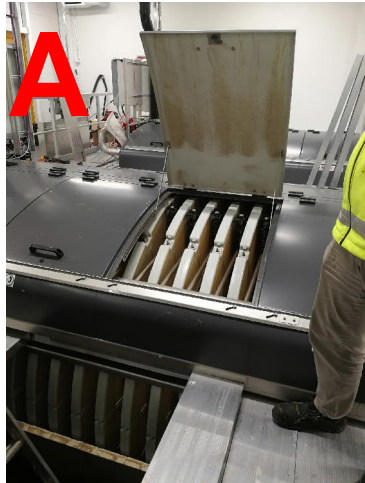
For each suspension, a certain degree of anionic, cationic or nonionic character is beneficial.

Flocculating power increases with the molecular weight.
Polyacrylamides molecular weight in the range of 10-20 millions (Huge!)

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Group discussion

What kind of mechanisms are involved in the following cases?

A

Phosphates and suspended solids are removed in disc filters using polyalunimium-chloride (PAX) and polymer.

B
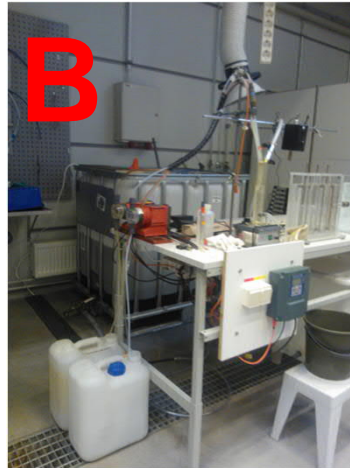
Natural organic matter is removed in our lab reactor using ferric chloride (PIX).

C

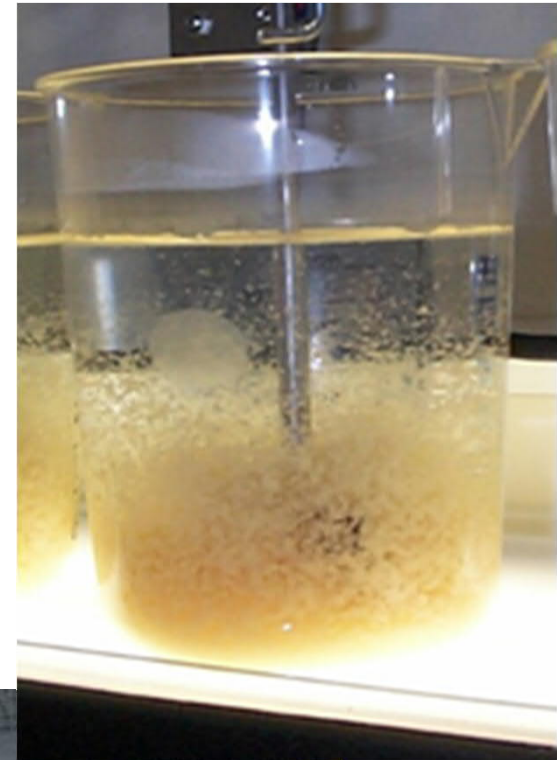Heavy metal removal from mining wastewater using hydrogen sulfide.

Applications

Applications

Water treatment

Wastewater treatment

Sludge and slurry dewatering

Water softening

Treating landfill leachate

Treating industrial wastewaters, e.g. from dairies and food processing, mining wastewaters

Lake restoration

...

Filterpressed sludge cake

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How are precipitation and coagulation&flocculation used?

- Chemical precipitation: Removal of dissolved substances
  - Removal of phosphorus
  - Removal of arsenic
  - Removal of iron
  - Removal of heavy metals
  - Removal of ammonium and phosphate from reject water as magnesiumammoniumphosphate (struvite)
- 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

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Molar ratio in precipitating phosphorus from wastewater

Defined as moles of precipitating cation to moles of phosphorus

Usually equal or higher than stoichiometric ratio

- Stoiciometric ratio = 1 for Fe(III):P and Al:P
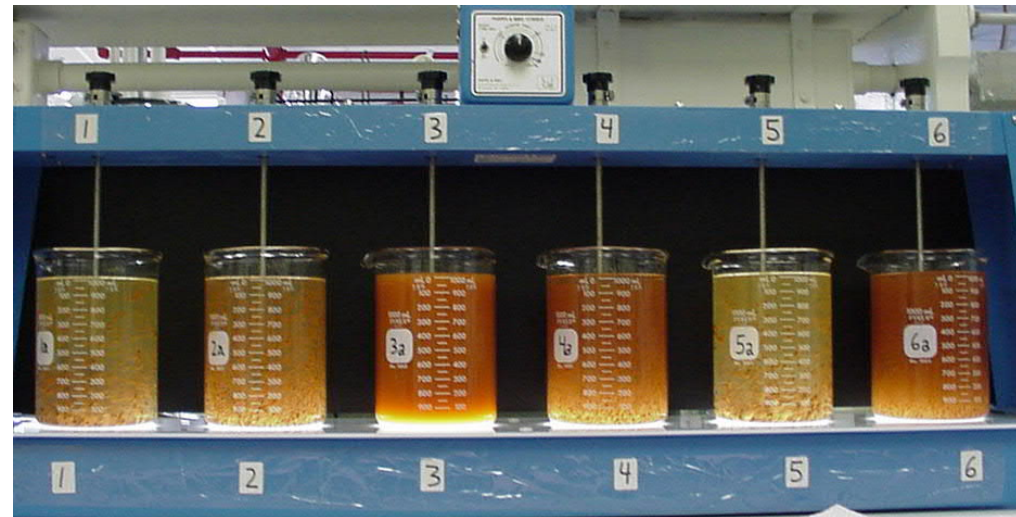
Pre- and postprecipitation

In wastewater treatment precipitation can be before or after the biological reactor

Pre-precipitation:

- Reveices 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)

http://www.phlush.org

Typical brown sludge formed in simultaneous precipitation

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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

Example of precipitation

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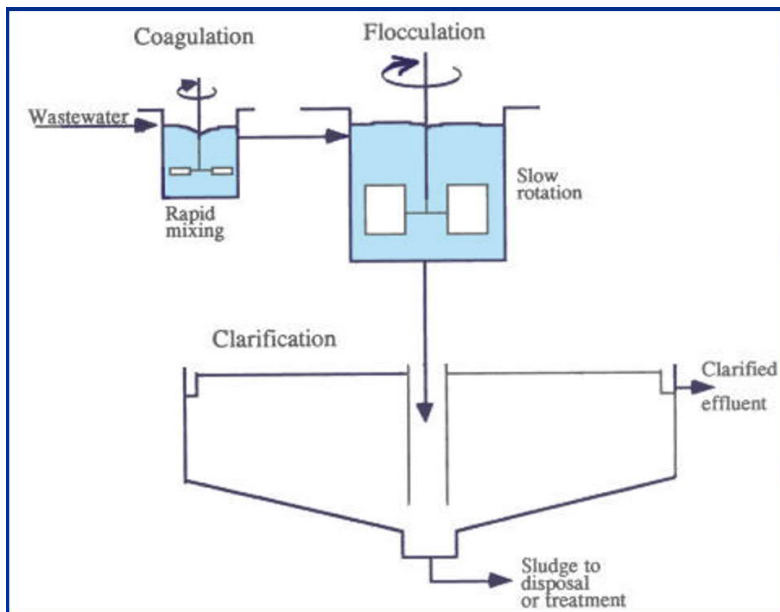
- Wastewater and chemical are combined in rapid mixing
  - Precipitation (and/or coagulation)
  - Microflocs are formed
  - HRT 30-60 s
- Flocculation
  - Slow mixing
  - Microflocs are combined into larger flocs
  - Large flocs are settleable
  - HRT minimum 20 min
- Dosing system:
  - Basin for solution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

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

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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

Dewatering by centrifuge

From thickener / digester

CM442

Promag 50H

Cerabar M PMC51

Promag L 400

CUS51D + CUA451

Flocculant

Alternative:

Promass 80I

Promag L 400

Back to inlet

Skip

Endress + Hauser

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