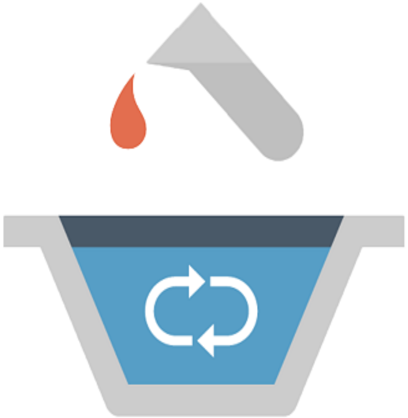
CHAPTER (6)

Chemical and Advanced Chemical Processes in Wastewater Treatment

1. Ammonia Stripping
2. Chemical Coagulation and Flocculation
3. Electrocoagulation
4. Chemical Precipitation
5. Oxidation/ Reduction
6. Chemical Oxidation
7. Electrochemical Oxidation



Ammonia stripping (chemical)

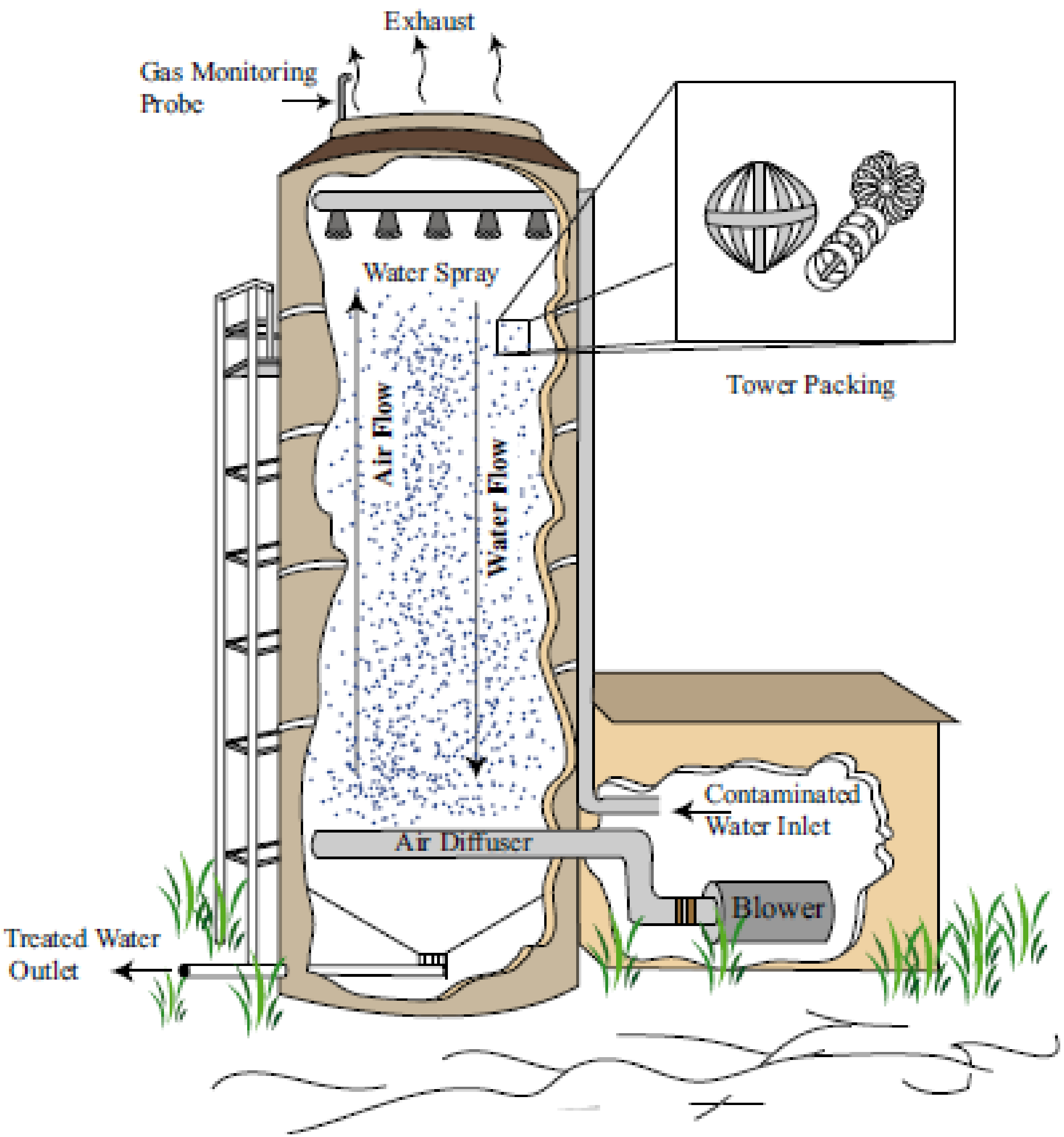
- Nitrogen in the form of ammonia can be removed chemically from water by
  1) raising the pH to convert the ammonium ion into ammonia gas.
  2) NH_3 then be stripped (expelled) from the water by passing large quantities of air through the water.

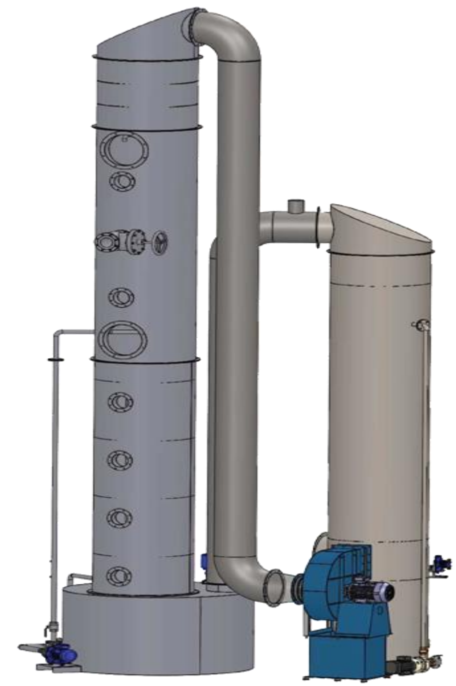
- The ammonia stripping reaction is:

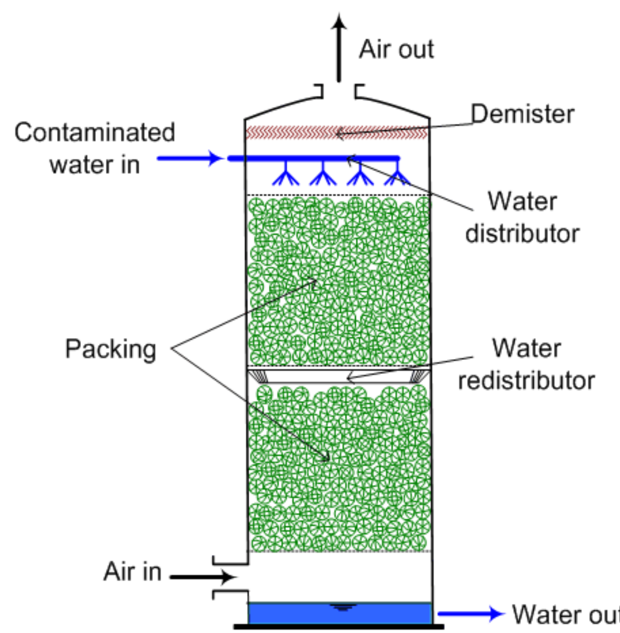
$$NH_4^+ + OH^- = NH_3 + H_2O$$

- The hydroxide is usually supplied by adding lime. Lime also reacts with CO_2 in the air and water to form a calcium carbonate scale, which must be removed periodically.

Ammonia stripping (chemical)







CHEMICAL COAGULATION

Development of Surface Charges in Wastewater

a) Preferential Adsorption

- When oil droplets, gas bubbles or other inert substances (tiny suspended solids) are dispersed in water, they will acquire –ve charge through adsorption of ions (hydroxide ions, OH-).

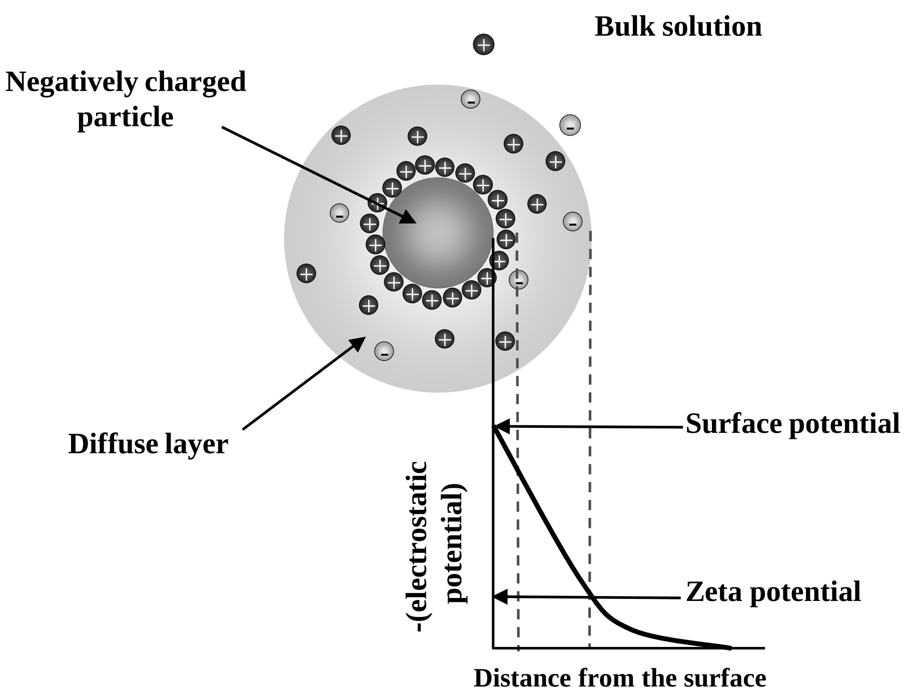
b) Ionization

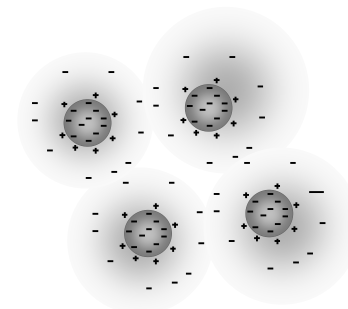
- Ionization of carboxyl and amino groups (at different level of pH)

- **Colloidal particles found in wastewater :**
  1. net negative surface charge and 0.01 to 1 µm in size
  2. attractive body forces between particles **<<** repelling forces
  3. this stable conditions plus Brownian random motion keeps the particles in suspension (colloidal dispersion).
- **Coagulation**

  Process of destabilizing colloidal particles so that particle growth can occur as a result of particle collisions.

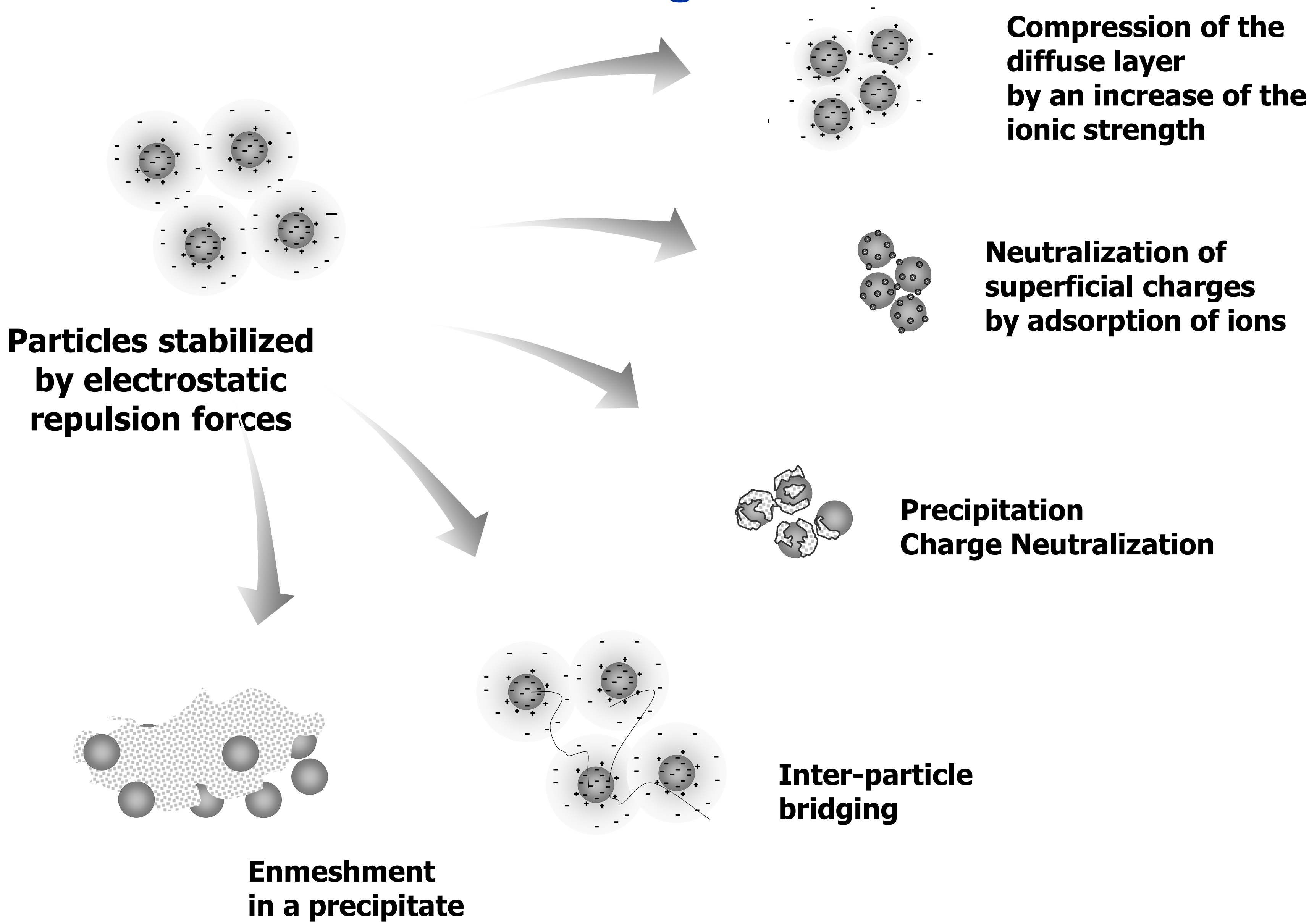
Development of Surface Charges in Wastewater Particles





Particles dispersed in wastewater that are stabilized (difficult to separate) by electrostatic repulsion forces

Mechanism of Coagulation/Flocculation



Coagulants & Coagulant Aids

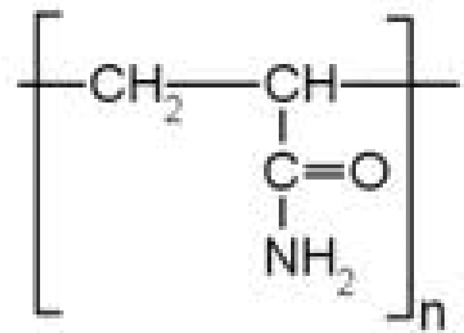
Alum

Magnesium chloride

Ferric Chloride

Chitosan (natural)

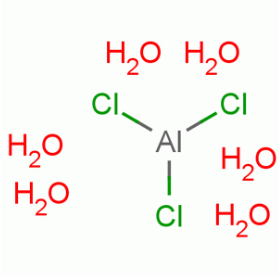
Polyacrylamide



Common Coagulants

Type of coagulant	formula	most common form	reaction with water
aluminum sulfate	$Al_2 (SO_4)_3 .\ 14\text{-}18\ H_2O$	lumps or powder	acidic
Sodium aluminate	$NaAlO_2$ or $Na_2Al_2O_4$	Powder	alkaline
Poly-aluminiumchloride	$Al_n(OH)_mCl_{3n\text{-}m}$**	Solution or powder	acidic
Ferric sulfate	$Fe_2(SO_4)_3.9H_2O$	Small crystals	acidic
Ferris chloride	$FeCl_3 .\ 6H_2O$	Lumps or solution	acidic
Ferrous sulfate	FeSO4. $7H_2O$	Small crystals	acidic

** *a polynuclear complex of polymerized hydro- aluminum ions*



Chemical Coagulation

COAGULANT AIDS

The addition of some chemicals will enhance coagulation by promoting the growth of large settling sludge.

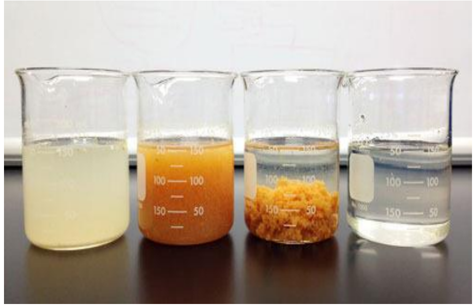
Activated silica

- A short-chain polymer that serves to bind together particles of fine aluminum hydrate.
- At high dosage, silica will inhibit floc formation because of its electronegative properties.
- The usual dosage is 5-10mg/L.

Acid or base

- For pH adjustment at optimum value for coagulation.

Chemical Coagulation



COAGULANT AIDS (Cont'd)

Polyelectrolyte

- High molecular weight polymers which contain adsorbable groups and form ridges between particles or charged flocs.
- Large flocs (0.3-1.0mm) are created when small dosages of polyelectrolyte (1-5 mg/L) are added in conjunction with alum or $FeCl_3$

There are 3 types of polyelectrolyte;

CATIONIC

- Which adsorbs on a negative colloid or floc particles

ANIONIC

- Which replaces the anionic group on a colloidal particle and permit hydrogen bonding between the colloid and polymer

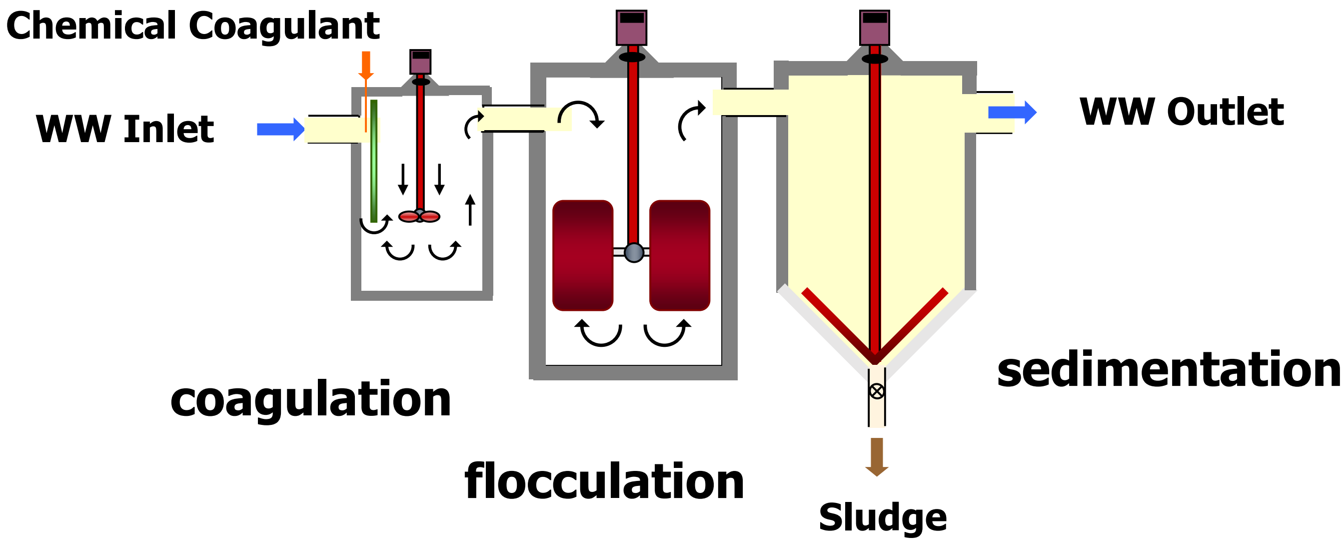
NON-IONIC

- Which adsorbs and flocculates

Chemical Coagulation: EQUIPMENT

- <u>Chemical Coagulation:</u>

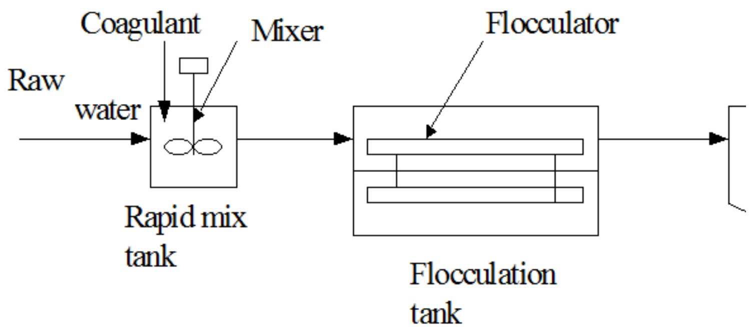
  Direct dosing of coagulant solution to the wastewater flow.



- Flocculation is a physical process in which the collision of coagulated colloids (micro-flocs) is promoted by slow mixing to make possible the formation of larger particles (macro-flocs).

- The result of both processes is a wastewater in which the size of the particles is enough to be separated by a settling (or a flotation) unit.

Coagulation /Flocculation Calculations



Measuring the degree of mixing

Velocity gradient: $$G = \sqrt{P/(\mu V)}$$

P = power input (W)
V = volume of basin(cu. m)
μ = fluid viscosity (Pa.s)

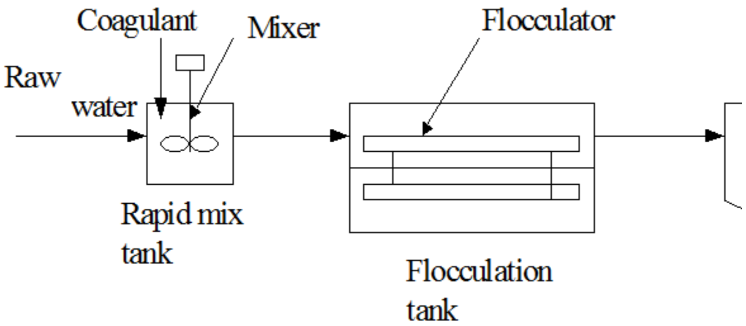
G values for rapid mixing

Detention time, t_0 (s)	G (s^{-1})
0.5	3500
10 – 20	1000
20 – 30	900
30 – 40	800
Longer	700

Gt_0 values for flocculation

Type	G (s^{-1})	Gt_0
Low turbidity, color removal coagulation	20 – 70	60,000 – 200,000
High turbidity, solids removal coagulation	50 - 150	90,000 – 180,000
Softening, 10% solids	130 - 200	200,000 – 250,000
Softening, 39% solids	150 - 300	390,000 – 400,000

Coagulation /Flocculation Calculations



Designing a flocculator

Power input:

$$P = \frac{K_T (n)^3 (D_i)^5 \rho}{g}$$

K_T = impeller constant
n = rotational speed (rpm)
Di = impeller dia (m)

Values of impeller constant K_T

Type of impeller	K_T
Propeller, pitch of 1, 3 blades	0.32
Propeller, pitch of 2, 3 blades	1.00
Turbine, 6 flat blades, vaned disc	6.30
Turbine, 6 curved blades	4.80
Fan turbine, 6 blades at 45°	1.65
Shrouded turbine, 6 curved blades	1.08
Shrouded turbine, with stator, no baffles	1.12

Power and rotational speed of some standard mixers

Model	n (rpm)	P (kW)
JTQ50	30, 45	0.37
JTQ75	45, 70	0.56
JTQ100	45, 110	0.75
JTQ150	45, 110	1.12
JTQ200	70, 110	1.50
JTQ300	110, 175	2.24
JTQ500	175	3.74

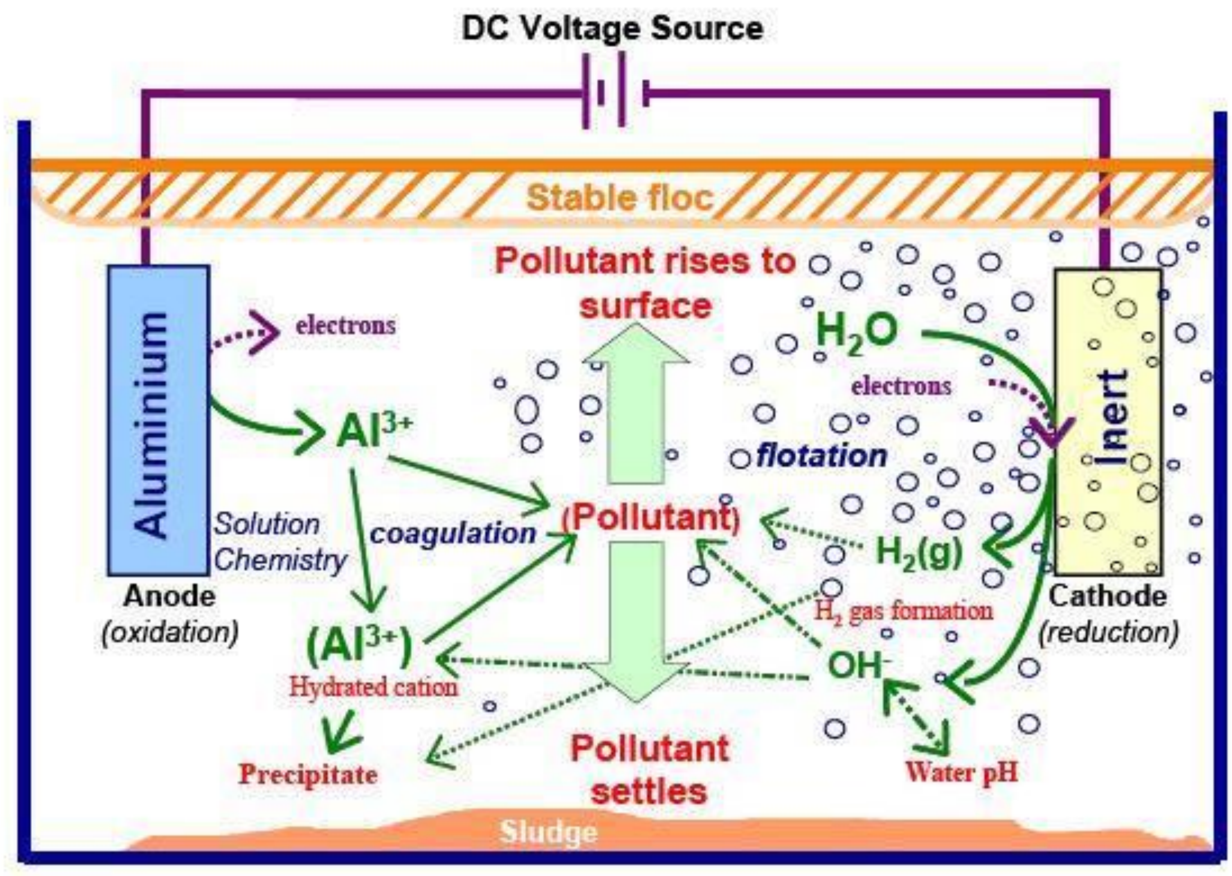
JWI, Inc. of Holland

Electrocoagulation

- A type of electrochemical technology, where electrolytic cell is used to produce coagulants instead of chemical addition.
- Many industries are using Electrochemical Coagulation (EC) process to *remove colloidal Color and COD by over 80-90%.*
- Contaminated liquids pass over electrically charged plates creating a reaction which causes the contaminants to be precipitated as solid sludge.
- Current is passed through a metal electrode (typically iron or aluminum) oxidizing the metal to its cation. Simultaneously, water is reduced to hydrogen gas and hydroxide ions (OH-).
- The process introduces the metal cations directly into the water electrochemically using sacrificial anodes.
- A strong floc is produced creating a concentrated sludge which will settle or float that is easily removed with various proven technologies.

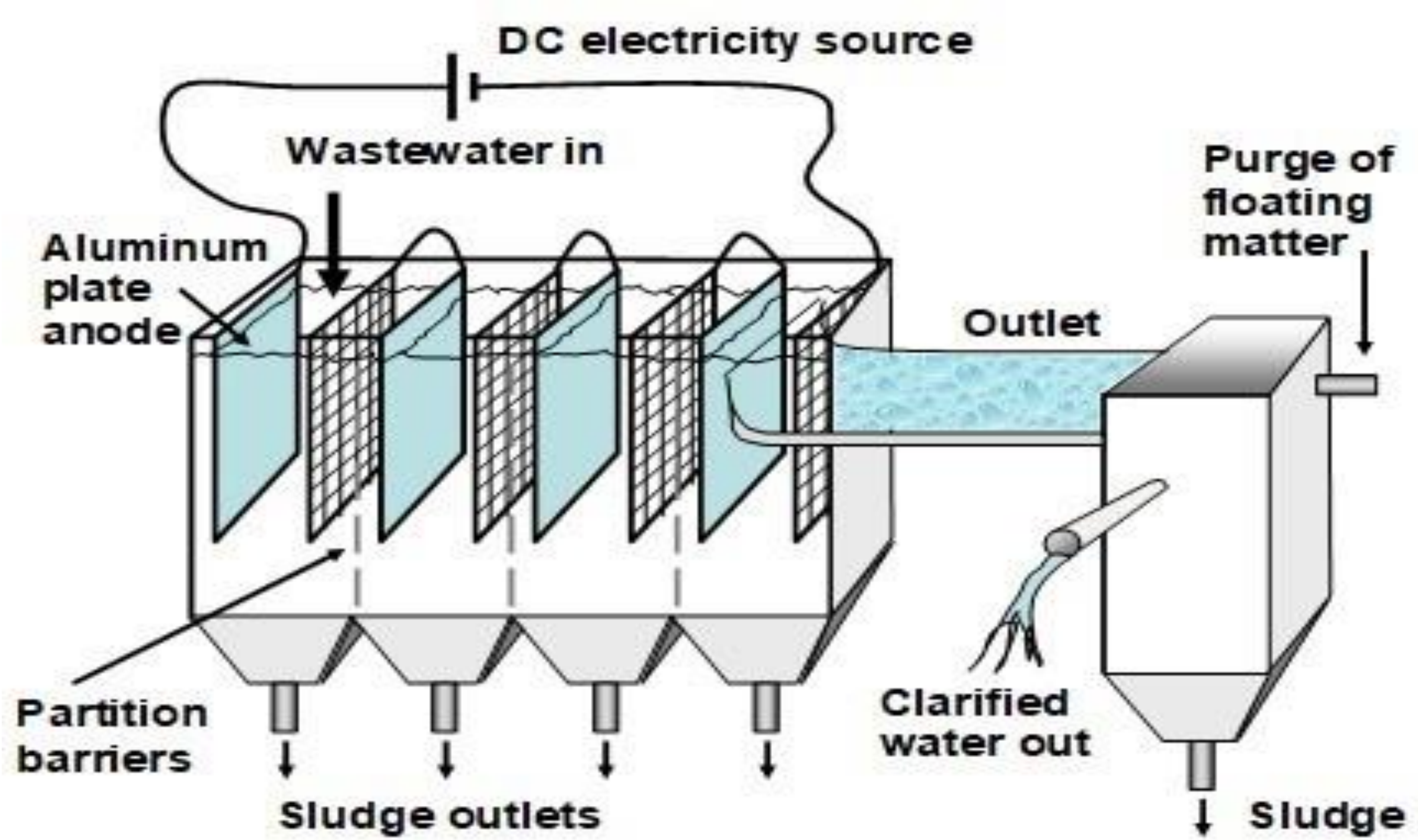
Electrocoagulation

- Sacrificed anodes dissolve to form active coagulants which are used to remove pollutants by precipitation as well as flotation (See Figure below). The electrochemical process of Electrocoagulation is highly dependent on the chemistry of the wastewater, especially its conducti



Electrocoagulation concept and mechanism

Electrocoagulation



Electrocoagulation with aluminum anodes

https://bioresources.cnr.ncsu.edu/wp-content/uploads/2016/08/BioRes_11_3_7953_Hubbe_REVIEW_MHBYHLKKE_Wastewater_Treat_Reclam_Pulp_Paper_Review_9906.pdf

Electrocoagulation (EC)

- Mixing can be accomplished either by mechanical stirrers or by the evolved gases. The process combines both:
  Coagulation/flocculation, and Sedimentation/flotation
- Mass transport is not controlling the overall rate of the process.
- The activity of the anode can decrease with time due to the formation of insoluble hydroxides or sludge layer.
- These can be avoid by using motion electrodes or by using turbulence promoters.
- Hydrogen evolution can disturb the sedimentation process.
- For this reason, if possible, it is better to separate the cathodic process from the sedimentation.

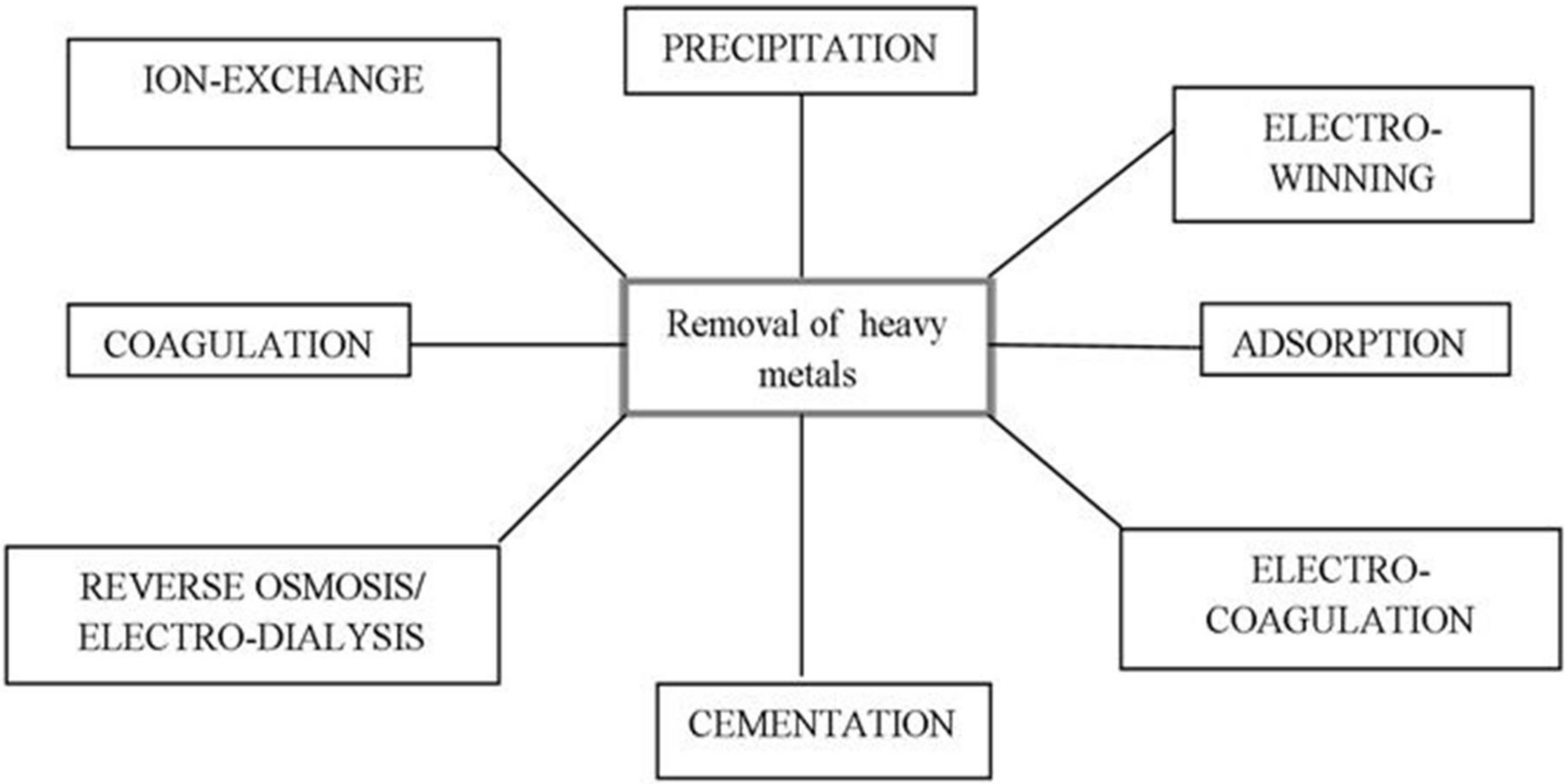
Advantages: EC can handle most polluted wastewater, no need for chemicals, systems are simple, easy to operate and maintain, sludge formed is readily settable and easy to dewater, the gas bubbles produced during electrolysis can carry the pollutant to the top of the solution (Electroflotation), where it can be easily concentrated, collected and removed.

Electrocoagulation

Contaminant	Before (mg/l)	After (mg/l)	Removal (%)
Ammonia	49.00	19.40	60.41
Benzene	90.10	0.36	99.60
BOD	1050.0	14.0	98.67
Cadmium	0.13	0.004	96.81
Nitate	21.00	12.00	42.86
Iron	68.34	0.194	99.72
Lindane (Pesticide)	0.143	0.001	99.30
Magnesium	13.15	0.0444	99.66
Mercury	0.72	0.0031	98.45
Turbidty (NTU)	35.38	0.32	99.1
Hydrocarbon	72.50	0.20	99.72
Lead	0.59	0.0032	99.46
Chromium	139.00	0.10	99.92

http://www.dynameau.co.uk/electrocoagulation.html

Heavy Metal Removal



Cementation: adding powder of more active metal

HEAVY METAL REMOVAL

INDUSTRIES IMPACTED:

- Metal Finishing
- Foundry and Casting
- Mining
- Microchip / Semiconductor Production
- Automotive
- Printing

HEAVY METALS IN QUESTION

- Zinc
- Chromium
- Tin
- Iron
- Silver
- Cadmium
- Nickel
- Copper
- Mercury
- Cobalt
- Aluminum
- Arsenic

CHEMICAL PRECIPITATION:

Heavy Metal Removal

- A heavy metal ion is generally precipitated as HYDROXIDE (or other insoluble compounds) through the addition of LIME {Ca(OH)2} or CAUSTIC {NaOH} to a pH of minimum solubility (several of these compounds are AMPHOTERIC).

- The solubility for Cr^{3+} and Zn^{2+} are minimum at pH 7.5 and 10.2, respectively, and show significant increase in concentration above these pH value.

- For many metals such as As and Cd, co-precipitation with iron or aluminum is highly effective for removal to low residual levels.

CHEMICAL PRECIPITATION

Heavy metals removal
(from Industrial wastewater)

- ❑ Hydroxide precipitation (OH^-)
- ❑ Sulphide precipitation (S^{2-})
- ❑ Carbonate precipitation (CO_3^{2-})

Common Precipitating Agents

1. Calcium Hydroxide - $Ca(OH)_2$
2. Magnesium Hydroxide - $Mg(OH)_2$
3. Sodium Hydroxide - Na(OH)
4. Soda Ash - Na_2CO_3
5. Sodium Sulfide - Na_2S

Precipitation Reactions: Examples

$Zn^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} = Zn(CO_3)_{(ppt)}$

$Zn^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} = Zn(OH)_{2\,(ppt)}$

$Pb^{2+}{}_{(aq)} + 2S^{2-}{}_{(aq)} = PbS_{(ppt)}$

TABLE A-6
Typical solubility product constants

Equilibrium equation	K_{sp} at 25°C
$AgCl \rightleftharpoons Ag^+ + Cl^-$	1.76×10^{-10}
$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$	1.26×10^{-33}
$AlPO_4 \rightleftharpoons Al^{3+} + PO_4^{3-}$	9.84×10^{-21}
$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$	1.05×10^{-10}
$Cd(OH)_2 \rightleftharpoons Cd^{2+} + 2OH^-$	5.33×10^{-15}
$CdS \rightleftharpoons Cd^{2+} + S^{2-}$	1.40×10^{-29}
$CdCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	6.20×10^{-12}
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	4.95×10^{-9}
$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$	3.45×10^{-11}
$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$	7.88×10^{-6}
$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$	2.02×10^{-33}
$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$	4.93×10^{-5}
$Cr(OH)_3 \rightleftharpoons Cr^{3+} + 3OH^-$	6.0×10^{-31}
$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-$	2.0×10^{-19}
$CuS \rightleftharpoons Cu^{2+} + S^{2-}$	1.0×10^{-36}
$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$	2.67×10^{-39}
$FePO_4 \rightleftharpoons Fe^{3+} + PO_4^{3-}$	1.3×10^{-22}
$FeCO_3 \rightleftharpoons Fe^{2+} + CO_3^{2-}$	3.13×10^{-11}
$Fe(OH) \rightleftharpoons Fe^{2+} + 2OH^-$	4.79×10^{-17}
$FeS \rightleftharpoons Fe^{2+} + S^{2-}$	1.57×10^{-19}
$PbCO_3 \rightleftharpoons Pb^{2+} + CO_3^{2-}$	1.48×10^{-13}
$Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$	1.40×10^{-20}
$PbS \rightleftharpoons Pb^{2+} + S^{2-}$	8.81×10^{-29}
$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$	5.66×10^{-12}
$MgCO_3 \rightleftharpoons Mg^{2+} + CO_3^{2-}$	1.15×10^{-5}
$MnCO_3 \rightleftharpoons Mn^{2+} + CO_3^{2-}$	2.23×10^{-11}
$Mn(OH)_2 \rightleftharpoons Mn^{2+} + 2OH^-$	2.04×10^{-13}
$NiCO_3 \rightleftharpoons Ni^{2+} + CO_3^{2-}$	1.45×10^{-7}
$Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$	5.54×10^{-16}
$NiS \rightleftharpoons Ni^{2+} + S^{2-}$	1.08×10^{-21}
$SrCO_3 \rightleftharpoons Sr^{2+} + CO_3^{2-}$	5.60×10^{-10}
$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^-$	7.68×10^{-17}
$ZnS \rightleftharpoons Zn^{2+} + S^{2-}$	2.91×10^{-25}

(Sources: Linde, 2000; Sawyer, McCarty, and Parkin, 2003; Weast, 1983.)

HEAVY METAL REMOVAL

Solubility of Metals

- Major anions in controlling precipitation (e.g. in multi-metal solutions):
  - CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-} (depends on the cation)
  - HS^-, S^{2-} (reduced condition)

- Three types of important precipitates in water:
  - Sulfide, carbonate and hydroxide

- "Soluble" vs. "insoluble" metals in general:
  - Soluble: metal compounds with Cl^-, SO_4^{2-}, except AgCl, HgCl, $PbSO_4$
  - Insoluble (in aqueous solutions < 100 mg/L): CO_3^{2-}, S^{2-}, OH^-

CHEMICAL PRECIPITATION

1. Add lime (CaO) or sodium hydroxide ($NaOH$) to waste stream:

$$Cd^{2+} + Ca(OH)_2 \rightarrow \underline{Cd\,(OH)_2} \downarrow + Ca^{2+}$$

- NaOH is easier to handle but is very corrosive.
- Hydroxide will form flocs and settle in clarifier.

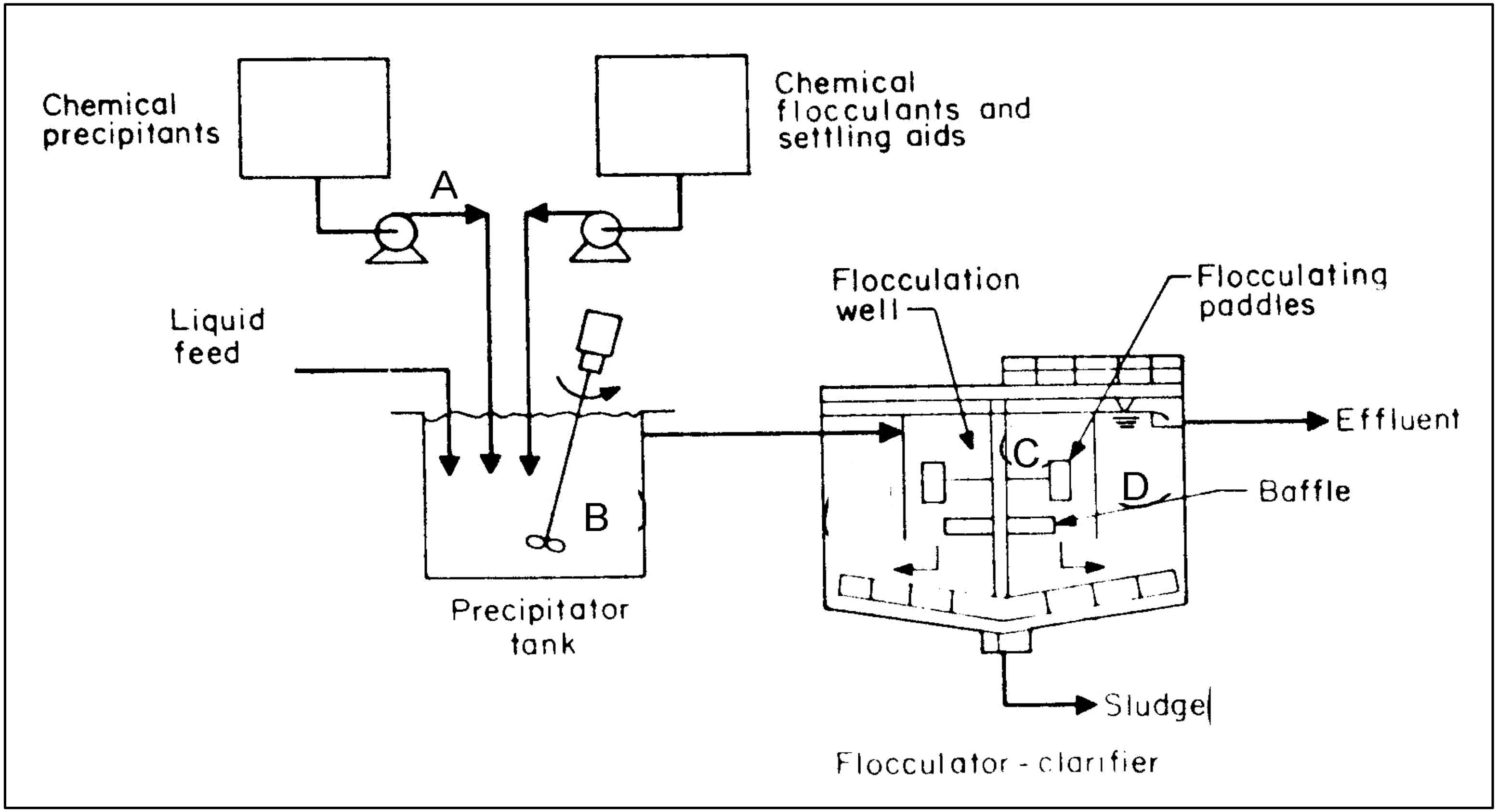
2. Use of sulphide in the form of Na_2S

- Metal removal as sulphide salt has low solubility limit

$$Cu^{2+} + Na_2S \rightarrow \underline{CuS} \downarrow +2Na+$$

- At low pH, reaction will proceed to the left (acid dissolves precipitate; thus, require pH > 8 for safe sulphide precipitation.

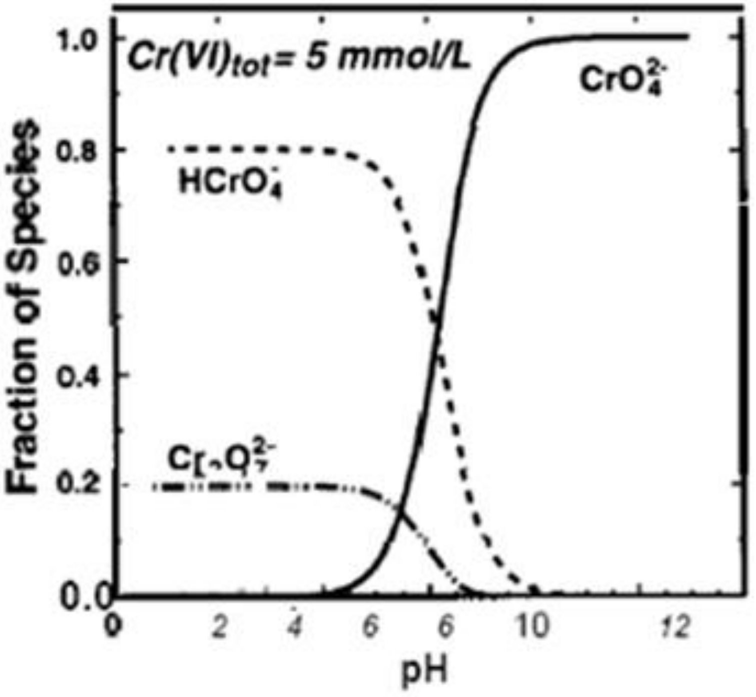
CHEMICAL PRECIPITATION: Basic Principles



- Add chemical precipitants to waste stream
- Mix thoroughly
- Allow solid precipitates to form flocs by slow mixing
- Allow flocs to settle in clarifier

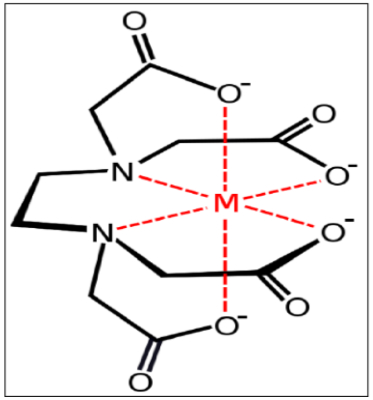
HEAVY METAL REMOVAL

Speciation of Metals in Aqueous Systems



- Metals in different species (speciation):
  1. Free metal ions (e.g., Cu^{2+}, Cr^{3+}) are virtually <u>not</u> existing.
  2. Complexed metal ions with inorganic or organic ligands (e.g., $Fe(H_2O)_6^{2+}$, $FeCN(H_2O)_5^{+}$) are in dissolved phase and soluble in water.
  3. Metal precipitates (e.g., PbS, AgCl) are in solid phase and <u>not</u> soluble in water

HEAVY METAL REMOVAL



Effects of Complexation

- If a complexing agent is present during the process of chemical precipitation, this will *lower the efficiency of precipitation* reactions as metals become more solubilized in water.
- **Synthetic Chelating Agents**
  - EDTA (sodium ethylene diamine tetra acetate): used as a cleaning and solubilizing agent for the decontamination of metal-contaminated equipment
  - NTA (nitrile tri acetic acid): used as a detergent phosphate substitute
  - Polyphosphate ($H_4P_2O_7$, $H_5P_3O_{10}$): used:
    - In water treatment ("sequester or capture" of Ca^{2+} to prevent scaling of $CaCO_3$ in water pipes and boilers),
    - In water softening, and
    - As detergent builders.

HEAVY METAL REMOVAL

Factors Affecting Solubility

1. Temperature

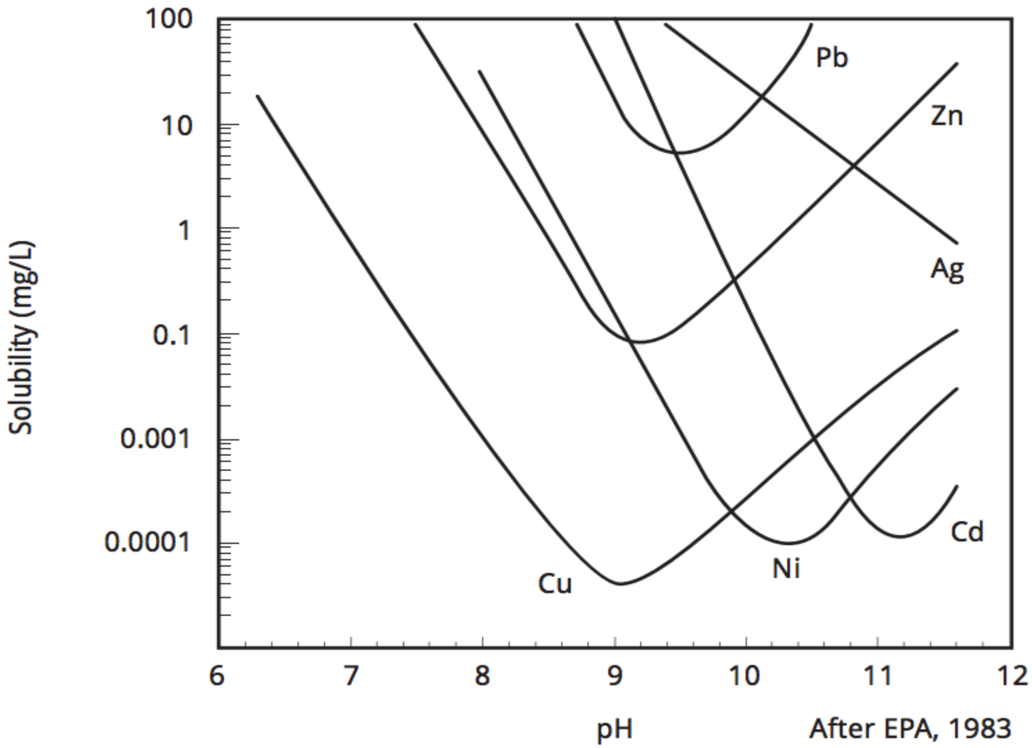
- In general, solubility of metal precipitates increases with increasing T, due to the *enthalpy needs of crystal dissolution.* However, some salts, e.g. $CaCO_3$, $CaSO_4$ and $FePO_4$ behave differently due to other reasons such as increase of CO2 solubility with decreasing temperature.

2. Common ion effect

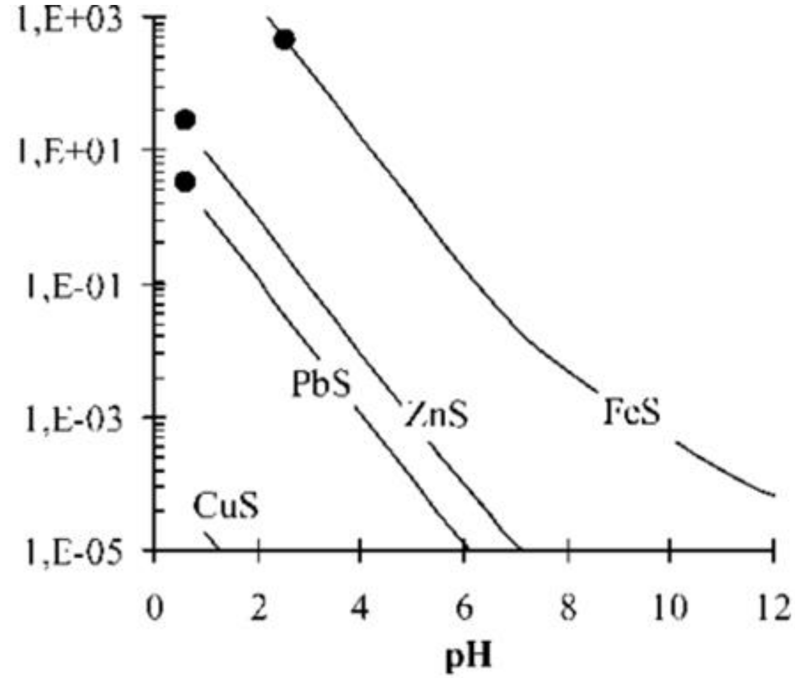
- When a solution contains an ion that is the same as one of the ions which result from the dissolution of the solid, the solubility of the solid will be less than that when the solid dissolves in pure water. e.g. solubility of AgCl (s) in NaCl $<$ solubility of AgCl (s) in water

3. Complexation

- Complexation will increase solubility: e.g. Complexation of Cd with OH^- (or Cl^-) will increase the solubility of $Cd(OH)_2$ (s). Thus, absence of complexing agents will favor metal precipitation.

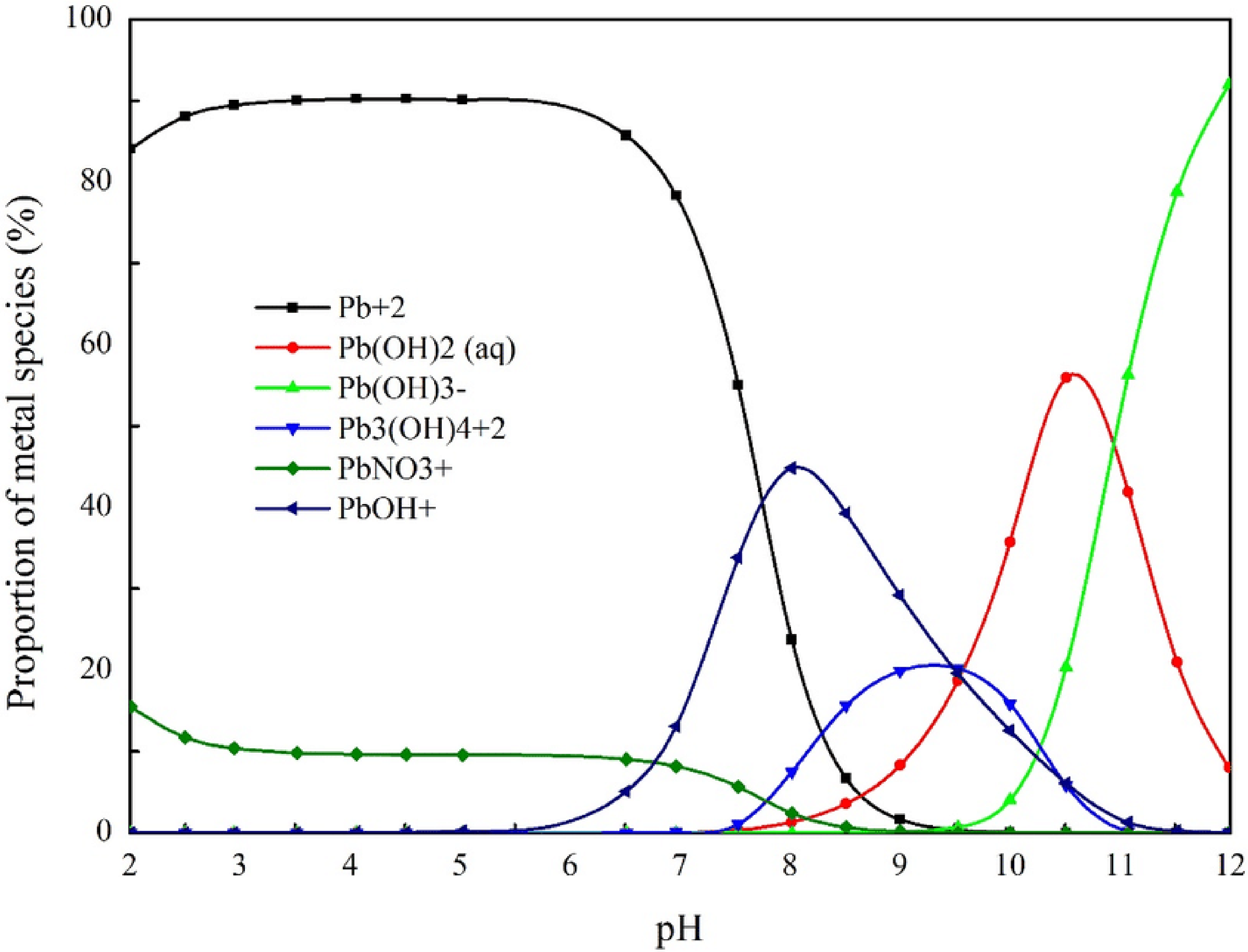


Solubility of
Metal Hydroxides
in Water vs. pH



Solubility of
Metal Sulfides
in Water vs. pH

Example of metal speciation in aqueous solutions: Pb



HEAVY METAL REMOVAL
Efficiency of Chemical Precipitation

	pH		Dosage (mM)		Heavy metal			
Situation	NaOH	Na_2S	NaOH	Na_2S	Cu	Cr	Pb	Zn
Na_2S	—	5	—	150				
Removal (%)					99.4	99.2	100	99.9
[Metal] $(mg \cdot L^{-1})^{a}$					0.1	0.05	0	0.03
$NaOH + Na_2S$	4	7	260	0.81				
Removal (%)					99.7	99.9	100	99.7
[Metal] $(mg \cdot L^{-1})^{a}$					0.05	0.007	0	0.1
$NaOH + Na_2S$	5	8	270	0.72				
Removal (%)					99.7	99.9	100	99.9
[Metal] $(mg \cdot L^{-1})^{a}$					0	0.06	0.008	0.07

Typical Effluent Concentrations Obtainable Through Chemical Precipitation

Heavy Metal	Achievable Concentration (mg/liter)	Precipitating Agent
Cadmium	0.3	Soda Ash
Trivalent Chrome	0.5	Caustic, Lime
Copper	0.5	Caustic, Lime
Iron	1.0	Caustic, Lime
Nickel	0.5	Soda Ash
Zinc	0.5	Caustic, Lime

HEAVY METAL REMOVAL

CHROMIUM REDUCTION & PRECIPITATION PROCESS

- For CHROMIUM waste treatment, HEXAVALENT chromium (Cr^{6+}) must first be reduced to the TRIVALENT state (Cr^{3+}) and then precipitated (generally with Lime).
- The reducing agents commonly used for chromium waste are FERROUS SULFATE and SODIUM METABISULFATE.

FEROUS SULFATE as reducing agent

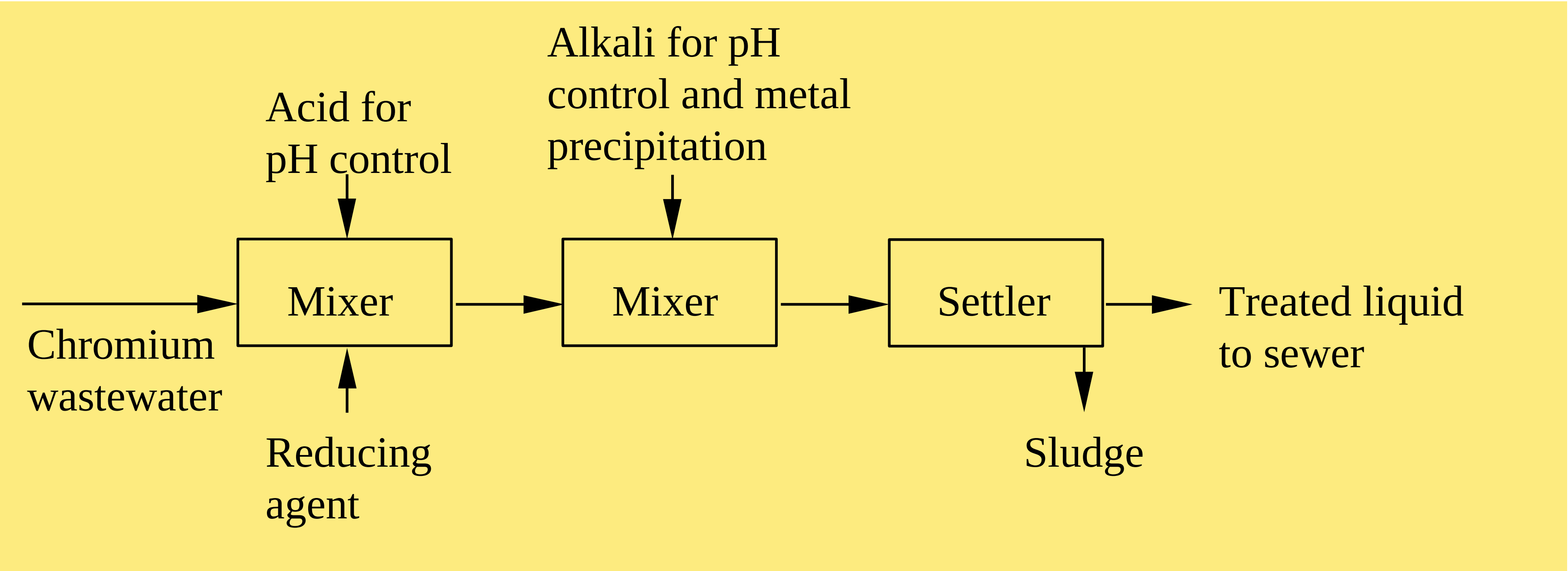
- Ferrous ion reacts with Cr^{3+} in oxidation-reduction reaction, reducing the chromium to a trivalent state and oxidizing the ferrous ions to the ferric state (this reaction occurs rapidly at pH level below 3, i.e. in acid medium).

HEAVY METAL REMOVAL

Chromium Reduction & Precipitation Process

$$Cr^{6+} + Fe^{2+} + H^{+} \rightarrow Cr^{3+} + Fe^{3+}$$

$$Cr^{3+} + 3OH^{-} \rightarrow Cr(OH)_3 \downarrow$$



CHEMICAL PRECIPITATION

TABLE 4.10
Summary of trivalent chromium treatment results

Method	pH	Chromium, mg/l	
		Initial	Final
Precipitation	7–8	140	1.0
	7.8–8.2	16.0	0.06–0.15
	8.5	47–52	0.3–1.5
	8.8	650	18
	8.5–10.5	26.0	0.44–0.86
	8.8–10.1	—	0.6–30
	12.2	650	0.3
Precipitation with sand filtration	8.5	7400	1.3–4.6
	8.5	7400	0.3–1.3
	9.8–10.0	49.4	0.17
	9.8–10.0	49.4	0.05

HEAVY METAL REMOVAL

Iron Oxidation & Precipitation Process

- In aerated water, oxidation of the ferrous iron into ferric iron occurs before Fe^{3+} precipitates as iron hydroxide, $Fe(OH)_3$, thus allowing a *natural removal* of dissolved iron by settling:

$$4\ Fe + 3\ O_2 \rightarrow 2\ Fe_2O_3$$

$$Fe_2O_3 + 3\ H_2O \rightarrow 2Fe(OH)_3$$

- The form of iron in water depends on the water pH and redox potential.

1. Oxidation Process (Aeration): **$Fe^{2+} \rightarrow Fe^{3+}$**

   at pH > 6.0 (fast reaction ≤ 10 min)

2. Precipitate: **Fe^{3+} as $Fe(OH)_3$**

   at pH 7.0 – 7.5

Chemical Precipitation

Table 6–3
Inorganic chemicals used most commonly for coagulation and precipitation processes in wastewater treatment

Chemical	Formula	Molecular weight	Equivalent weight	Availability	
				Form	Percent
Alum	$Al_2(SO_4)_3 \cdot 18H_2O$[a]	666.5		Liquid	8.5 (Al_2O_3)
				Lump	17 (Al_2O_3)
	$Al_2(SO_4)_3 \cdot 14H_2O$[a]	594.4	114	Liquid	8.5 (Al_2O_3)
				Lump	17 (Al_2O_3)
Aluminum chloride	$AlCl_3$	133.3	44	Liquid	
Calcium hydroxide (lime)	$Ca(OH)_2$	56.1 as CaO	40	Lump	63–73 as CaO
				Powder	85–99
				Slurry	15–20
Ferric chloride	$FeCl_3$	162.2	91	Liquid	20 (Fe)
				Lump	20 (Fe)
Ferric sulfate	$Fe_2(SO_4)_3$	400	51.5	Granular	18.5 (Fe)
Ferrous sulfate (copperas)	$FeSO_4 \cdot 7H_2O$	278.1	139	Granular	20 (Fe)
Sodium aluminate	$Na_2Al_2O_4$	163.9	100	Flake	46 (Al_2O_3)

Example

- The K_{sp} for strontium chromate is 3.6**E**-5 and the K_{sp} for barium chromate is 1.2**E**-10. What concentration of **potassium chromate** will precipitate the maximum amount of either the **barium or the strontium chromate** from an equimolar 0.30 M solution of **barium and strontium ions** without precipitating the other?
- **Solution**
- Let **x** be the concentration of chromate to precipitate Sr^{2+}, and

  y be that to precipitate Ba^{2+}.
- According to the definition of K_{sp} we have,

$$SrCrO_{4(s)} = Sr^{2+} + CrO_4^{2-}, \quad K_{sp} = 3.6E\text{-}5$$

0.30 **x**

x = 3.6**E**-5 / 0.30 = 1.2**E**-4 M

$$BaCrO_{4(s)} = Ba^{2+} + CrO_4^{2-}, \quad K_{sp} = 1.2E\text{-}10$$

0.30 **y**

y = 1.2**E**-10 / 0.30 = 4.0**E**-10 M

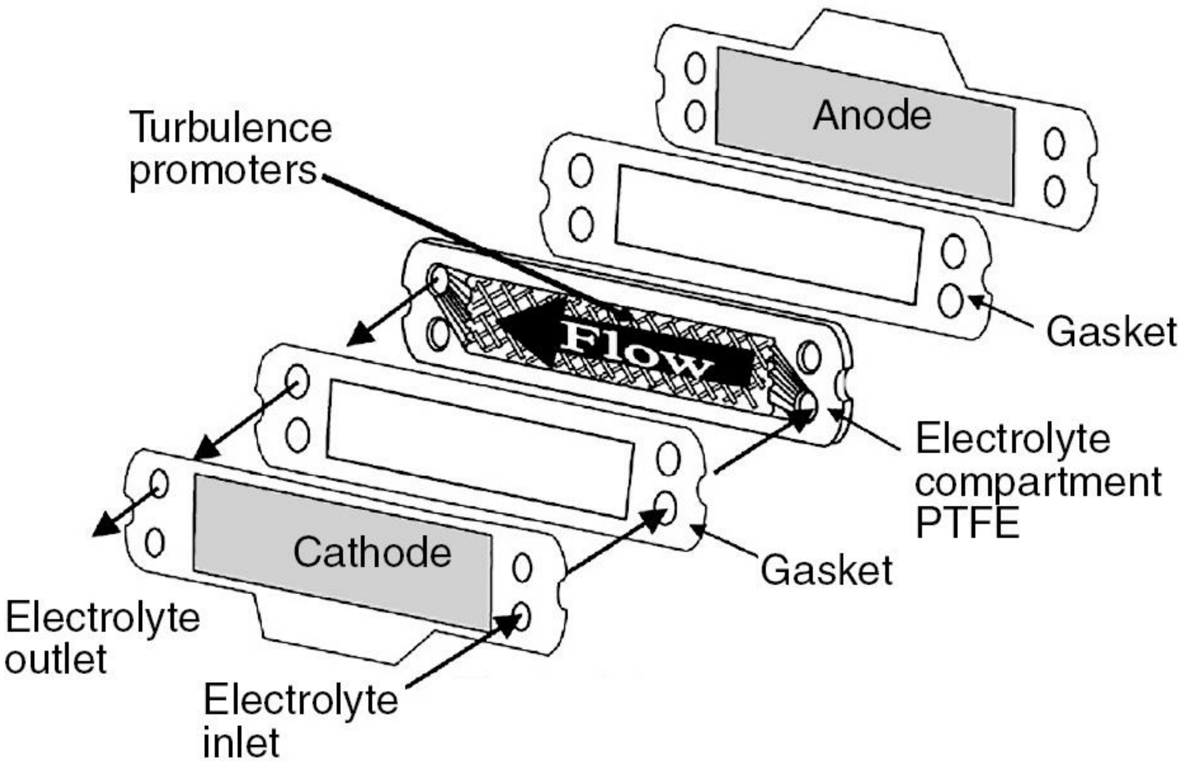
- The K_{sp}'s for the two salts indicate **$BaCrO_4$** to be much less soluble, and it will precipitate before any **$SrCrO_4$** precipitates. If chromate concentration is maintained a little less than 1.2**E**-4 M, Sr^{2+} ions will remain in the solution.

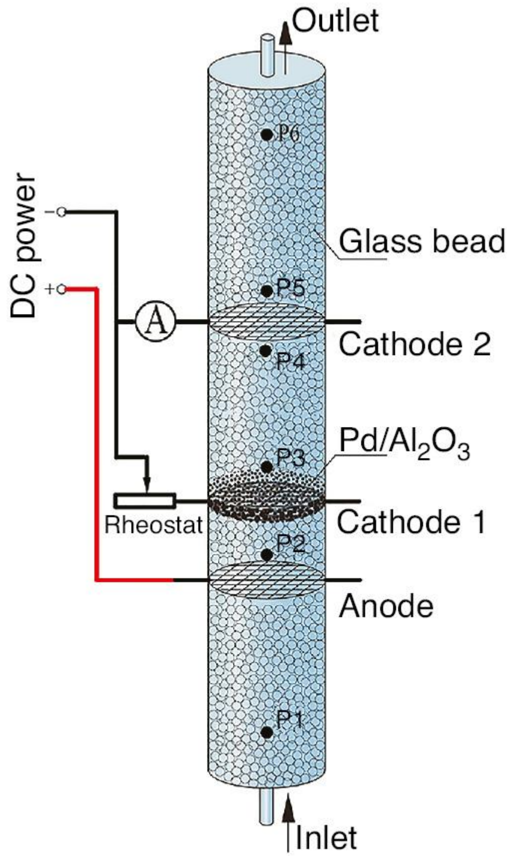
Electrolytic Heavy Metals Removal

- Waste waters containing heavy metal ions - generated in metallurgical and electroplating industries and in the manufacture of printed circuit boards.
- Conventional purification (use of hydroxide) precipitation gives voluminous metal hydroxide sludge that has to be disposed of.
- For complexed metal ions in alkaline solutions: Hydroxide precipitation is not a viable method.
- Cathodic removal of heavy metal ions is an attractive alternative process, where metal can be recovered in its pure metallic form.
- Electrochemical methods compete with a number of other technologies including evaporation, precipitation, ion exchange and solvent extraction to offer solutions to the needs of the many industries involved.
- Electrochemical methods, however, are uniquely capable of recovering pure metal for recycle.

Electrolytic Heavy Metals Removal

- This method is limited to those ions which reduce to the metal at potentials less negative than water reduction, which is now an unwanted, competing reaction leading to loss of current efficiency.
- Even so, many heavy and transition metals including Ag, Au, Pt, Cu, Ni, Hg, Cd, Pb, Zn, Ni, Co and As can be removed.





CHEMICAL PRECIPITATION FOR PHOSPHORUS REMOVAL

- Phosphorus may remain in excess after biological treatment since only 1:100 P:BOD is needed by microorganisms.
- Phosphorus is taken out to prevent excess growth of algae.
- Most phosphates are in the form of (HPO_4^{2-}), or soluble orthophosphate

- Usually accomplished with chemical precipitation:

  (salts addition)
    - Ferric chloride: $FeCl_3$
    - Alum: $Al_2(SO_4)_3.14H_2O$
    - Lime: CaO or $Ca(OH)_2$

CHEMICAL PRECIPITATION FOR PHOSPHORUS REMOVAL

Phosphate precipitation with aluminum:

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

Phosphate precipitation with iron:

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

$$\mathbf{FeCl_3 + HPO_4^{2-} = FePO_{4\,(s)} + HCl}$$

$$\mathbf{Al_2(SO_4)_3 \cdot 14H_2O + 2HPO_4^{2-} = 2AlPO_{4\,(s)} + 2H^+ + 3SO_4^{2-}}$$

- Effective range for alum or ferric chloride is pH 5.5 to 7.0
- If insufficient alkalinity, need to add lime to neutralize H^+

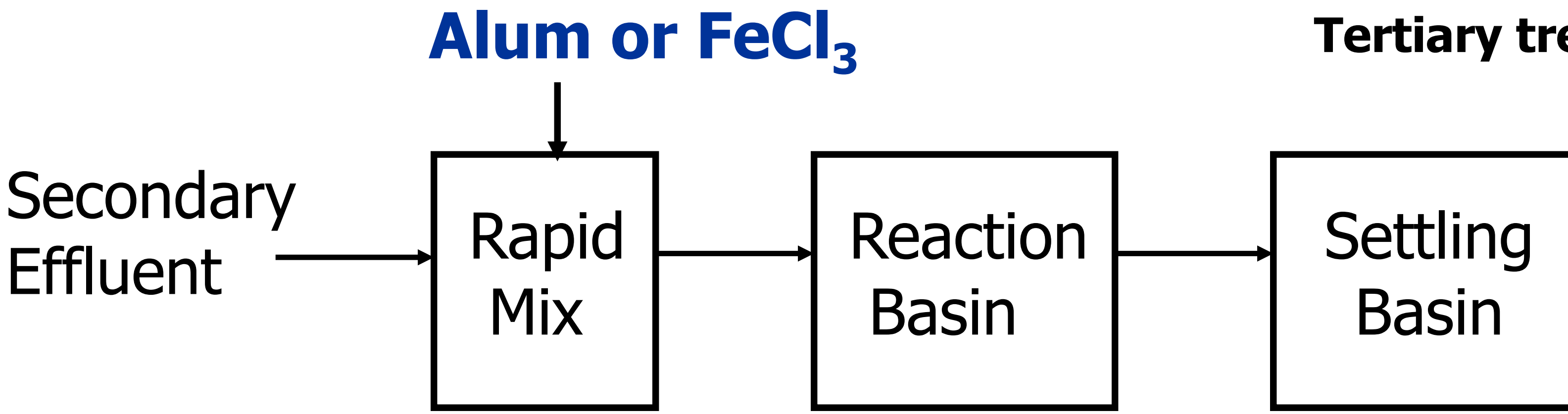
Phosphorus Removal by Lime

1. Calcium is added in the form of lime $Ca(OH)_2$.
2. Quantity of lime required to precipitate P is dependent of wastewater alkalinity.
3. As the pH value of the wastewater increases > 10, excess calcium ions will then react with the phosphate, to precipitate in *hydroxylapatite* form:

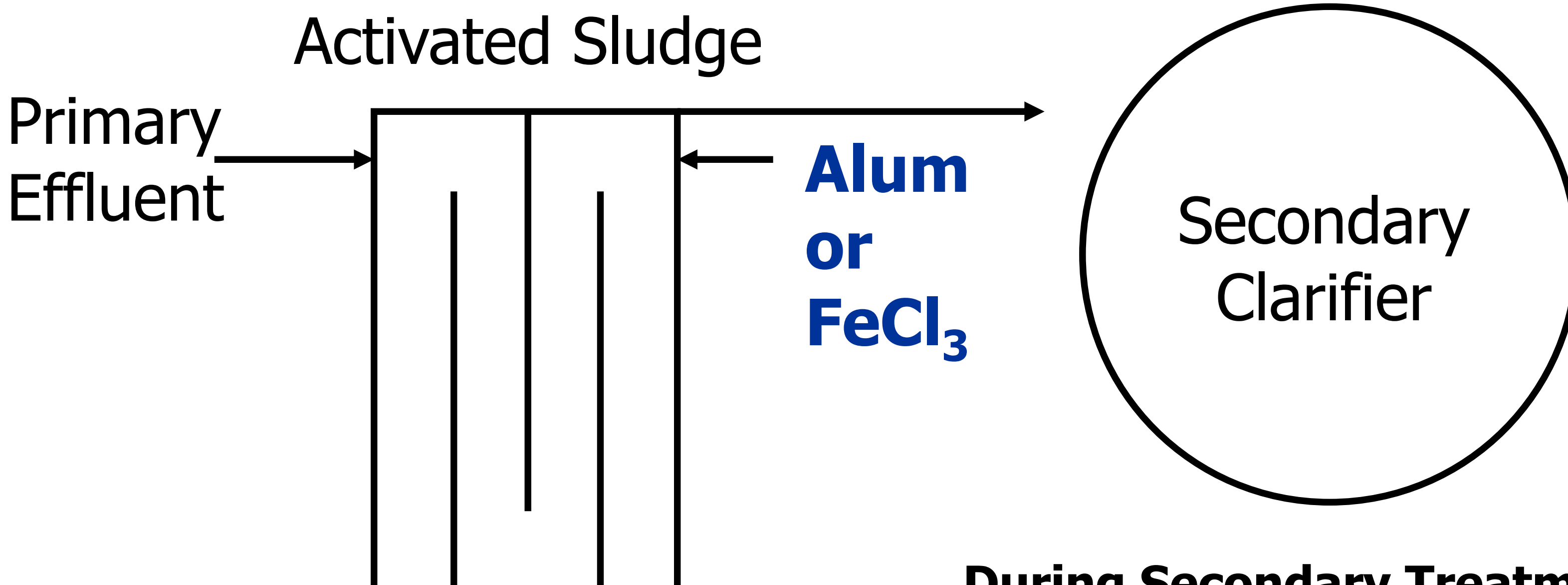
$$5\ Ca^{2+} + 3\ PO_4^{3-} + OH^- \leftrightarrow Ca_5(PO_4)_5(OH)_{(s)}$$

4. Amount of lime required depends on pH of water rather than amount of phosphate present
5. Neutralization may be required to lower the pH before further treatment or disposal.
6. Solubility product: $K_{sp}=10^{-55}$ (very insoluble)

Phosphorus Removal

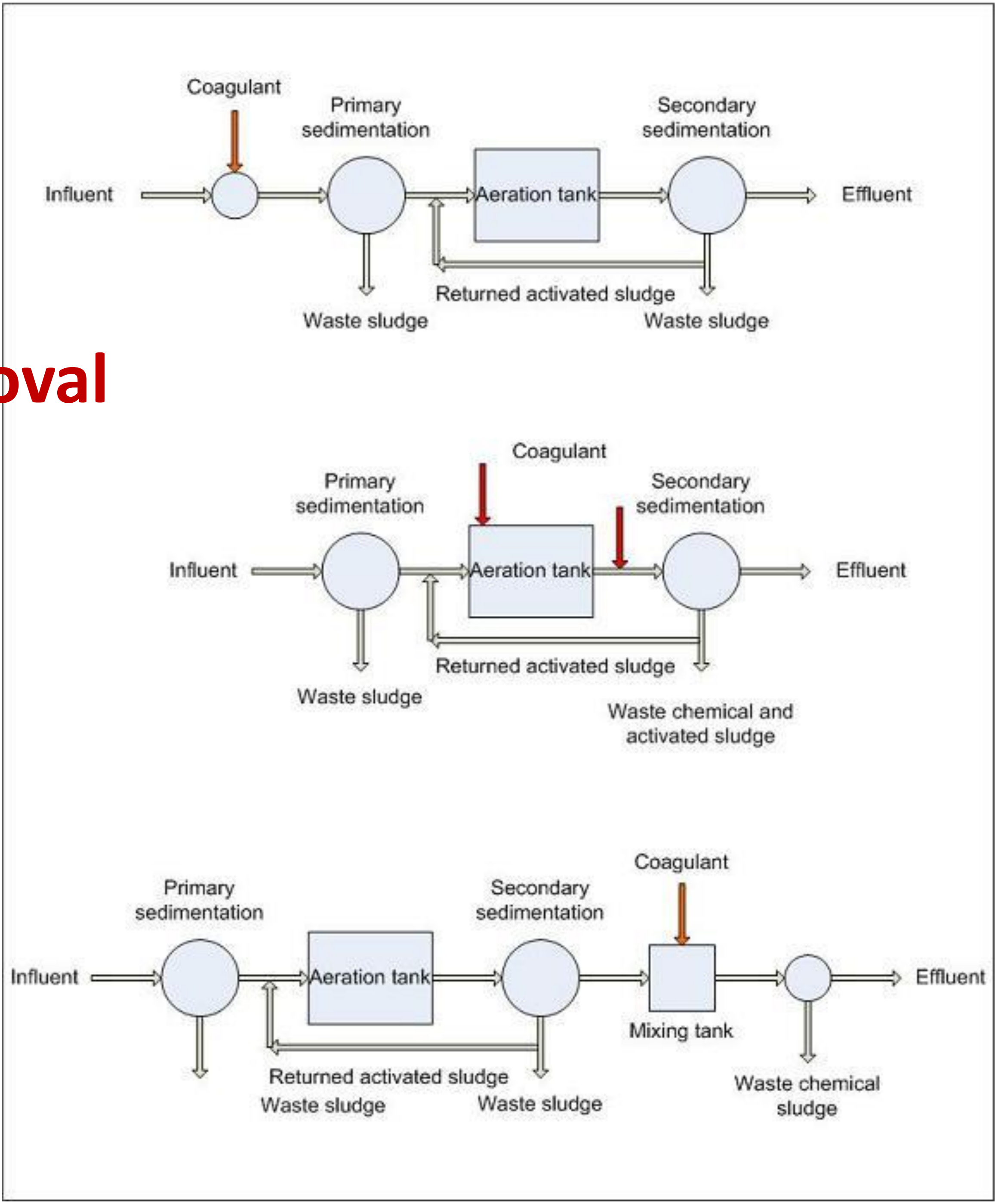


Tertiary treatment



During Secondary Treatment

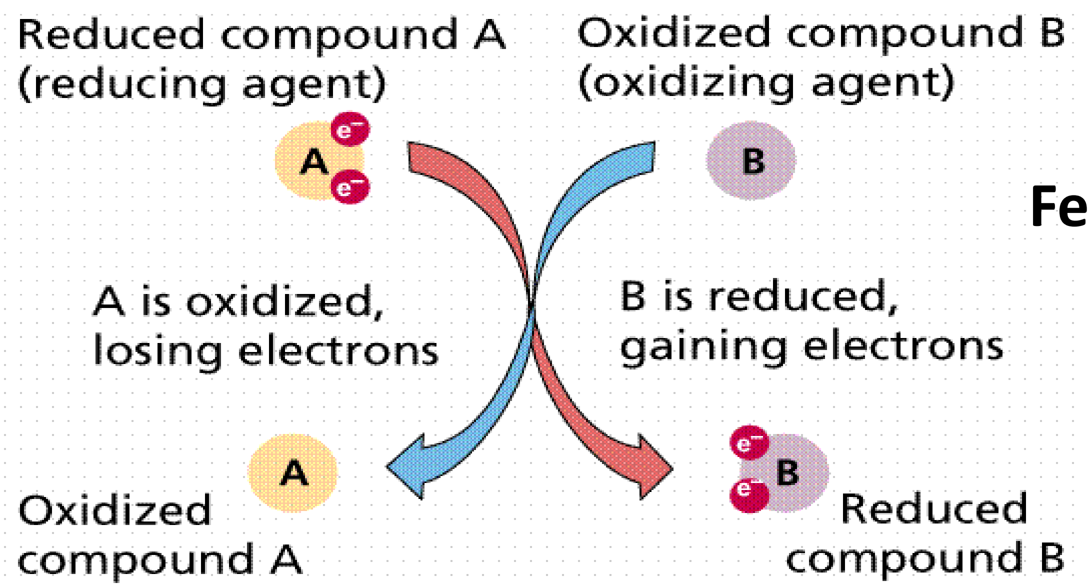
Phosphorus Removal



REDOX: Oxidation-Reduction

Oxidation-Reduction: the exchange of electrons

1. loss of electrons is oxidation
2. gain of electrons is reduction
3. a reducing agent gives up electrons and is oxidized
4. an oxidizing agent accepts electrons and is reduced



$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

$$Cu^{2+} + 2e^- \leftrightarrow Cu \quad E^\circ = 0.34 \text{ volt}$$

$$Zn + 2e^- \leftrightarrow Zn^{2+} \quad E^\circ = -0.763 \text{ volt}$$

REDOX: Reduction Oxidation

REDOX Process:

1. Changing oxidation state of pollutants to render them non-toxic or available for precipitation (e.g. **Cr^{+6}** to **Cr^{+3}**).

$$Cr^{6+} + Fe^{2+} + H^{+} \rightarrow Cr^{3+} + Fe^{3+}$$

$$Cr^{3+} + 3OH^{-} \rightarrow Cr(OH)_3 \downarrow$$

2. Redox reactions are usually monitored and controlled by oxidation/reduction probes (ORP) which read out in *millivolts.*

REDOX Reactions *can either Chemical or Electrochemical*

- **Common Applications** in wastewater:
  1. Chromium reduction (Chemical or Electrochemical).
  2. Cyanide oxidation/destruction (Chemical or Electrochemical).
  3. Recovery of valuable metals, e.g. Au, Ag, Pt, Cr, Zn, Ni (Electrochemical by precipitation on electrolytic cell cathode).

Chemical Reduction for Chromium

Hexavalent chromium Cr^{+6}

- Orange or yellow
- Used for chrome plating, chrome conversion coating and etching with chromic acid
- Extremely toxic
- Very low discharge limits *(JS202: total chrome = 0.1 ppm)*
- Prefers to pick up O^{-2} and form chromates which act like an anion and will <u>not</u> precipitate out as a metal hydroxide

Trivalent Chromium Cr^{+3}

$$Cr^{6+} + Fe^{2+} + H^{+} \rightarrow Cr^{3+} + Fe^{3+}$$

$$Cr^{3+} + 3OH^{-} \rightarrow Cr(OH)_3 \downarrow$$

- Blue or blue-green
- Reduced form of Cr^{+6}
- Much less toxic
- Precipitates well as metal hydroxide [$Cr(OH)_3$]

Redox Application:
Chemical Reduction for Chromium

Cr (VI) Reducing Agents

1. Sulfur dioxide gas, SO_2 :

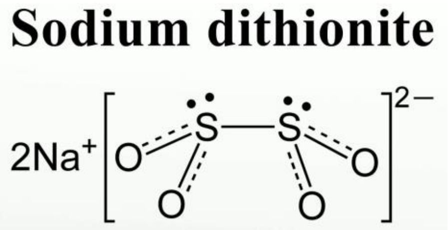
$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$3H_2SO_3 + 2H_2CrO_4 \rightarrow Cr_2(SO_4)_3 + 5H_2O$$

2. Sodium metabisulfite,

$$2H_2CrO_4 + 3NaHSO_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3NaHSO_4 + 5H_2O$$

3. Sodium dithionite,



$$Na_2S_2O_4 + 2H_2CrO_4 + 2H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 4H_2O + Na_2SO_4$$

4. Ferrous Sulfate (FeSO4).

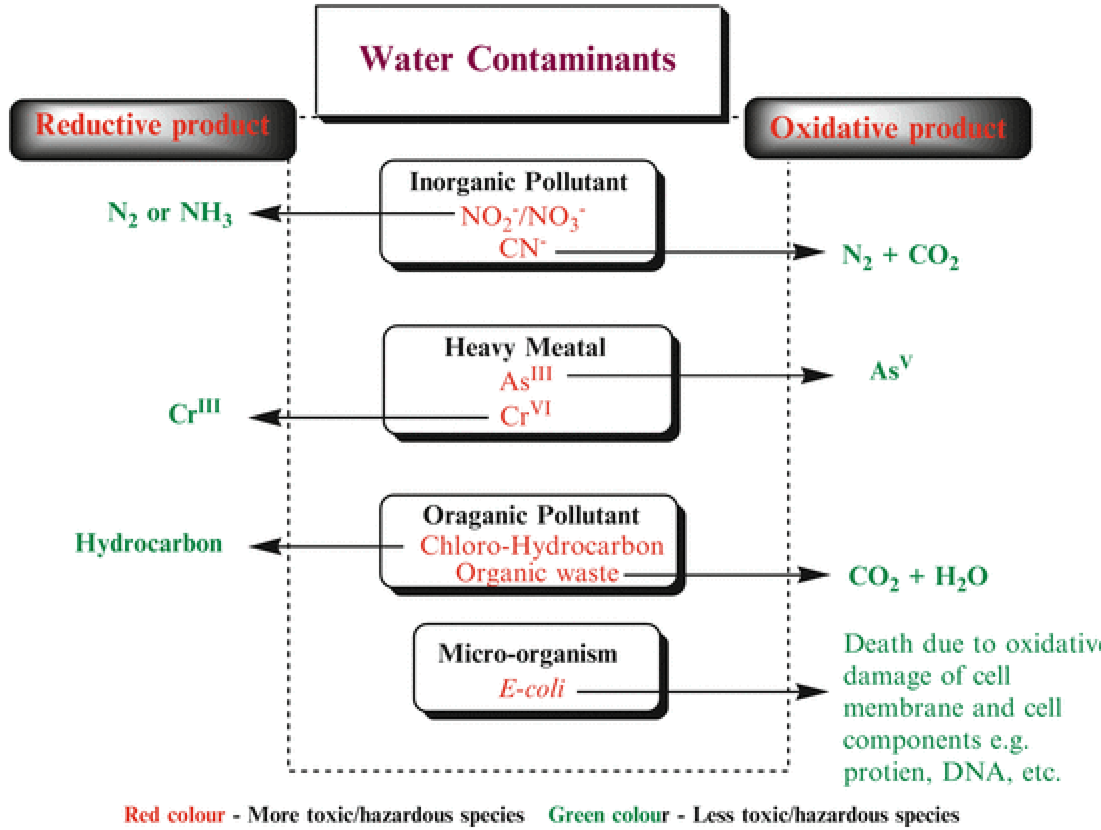
Redox Application:
Cyanide Destruction by Alkaline Chlorination

- Cyanide is used in electroplating because it dissolves metals easily due to complexing.

- Complexed cyanides not amenable to chlorination (Requires extra efforts: heat, stronger oxidizers, etc)
  - Iron cyanide, $Fe(CN)_6^{-4}$ and Cobalt cyanide

- Complexed cyanide amenable to chlorination:
  - Very slowly: nickel cyanide $Ni(CN)_4^{-2}$
  - Slowly: copper cyanide, $Cu(CN)_3^{-2}$, gold cyanide, silver cyanide, $Ag(CN)_2^{-1}$
  - Readily: sodium cyanide, NaCN, potassium cyanide, KCN, cadmium cyanide, $Cd(CN)_4^{-2}$ and zinc cyanide, $Zn(CN)_4^{-2}$

Cyanide Destruction Reactions



Oxidation Reaction	Chemical Equation	pH	ORP
(1) Cyanide → Cyanate	$NaCN + 2NaOH + Cl_2 \rightleftharpoons NaCNO + 2NaCl + H_2O$	10-11.5	(+) 250mV-400mV
(2) Cyanate → Carbon Dioxide & Nitrogen	$2NaCNO + 4NaOH + 3Cl_2 \rightleftharpoons 6NaCl + 2CO_2 + N_2 + 2H_2O$	8.5-9	(+) 300mV-600mV

Cyanide Destruction Reactions

- **First stage**
  - Raise pH (10.5-11.5) with sodium hydroxide and add chlorine (as sodium hypochlorite):

$$NaCN + NaOCl + H_2O \rightarrow CNCl + 2NaOH \rightarrow NaCNO + NaCl + H_2O$$

Rapid rxn; pH must be above 10 & ORP* = 500-600 mV

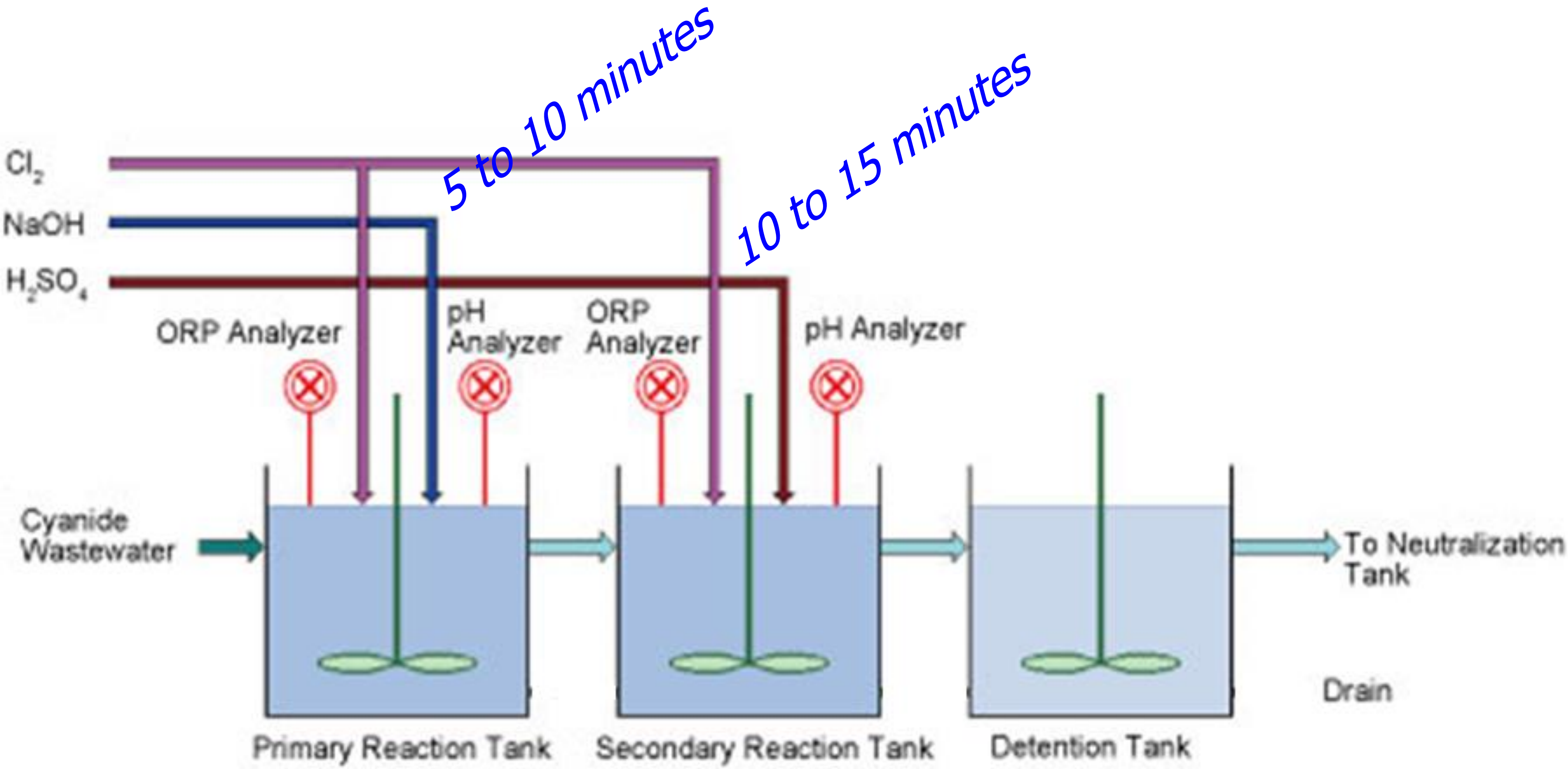
- **Second stage**
  - Lower pH (8.5-9.5) with sulfuric acid and add more chlorine:

$$2NaCNO + NaOCl + H_2O \rightarrow 2CO_2 + N_2 + 3NaCl + 2NaOH$$

Slow rxn; pH must be between 8.5-9.5 & ORP* = 650-850 mV

** oxidation/reduction probes reading*

Cyanide Destruction Process



- The full reaction requires 7.2 kg of NaOCl / kg of CN
- Sufficient retention time to react properly depending on concentration & flow of system
- NaOCl usually supplied as 15% solution

REDUCTION/OXIDATION REACTIONS

Purpose: Use pH and ORP controls to add chemicals which oxidize or reduce pollutants.
Design Conditions: Mixed, vented tanks, pH and ORP controls, redundant systems.

CHEMICAL POLLUTANT	pH CONTROL	ORP CONTROL	CHEMICALS USED	HRT (1) (minutes)
Cyanide				Retention Time
1st Stage	>10.5	350 mv	Sodium Hypochlorite	40-60
2nd Stage	8.5-9.0	600 mv	Sodium Hypochlorite	40-60
			Alternative Oxidants	
			Ozone/UV	
			Hydrogen Peroxide	
			Chlorine Dioxide	
Phenols	6.0-9.0	400-600 mv	Ozone/UV	10-20
			Hydrogen Peroxide/	
			Ferrous Sulfate	
			Potassium Permanganate	
			Chlorine Dioxide	
Chromium VI	<2.5	250-300 mv	Sodium Sulfite	10-20
			Ferrous Sulfate	

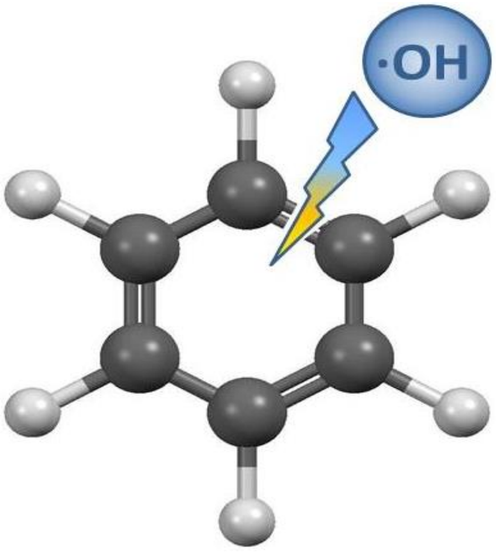
Cyanide Process Safety

1. Physiology:
   - Cyanide enters the blood stream via inhalation, ingestion (swallowing /absorption) and skin absorption.
   - It is picked up by the hemoglobin molecule in the red blood cells instead of oxygen.
   - Thus, it blocks the blood cells from picking up and distributing oxygen to the body cells, causing *cell death*.
2. Cyanide is *quickly fatal.*
3. Self-contained breathing apparatus needed.
4. Labels for pipes, tanks, etc. are important.

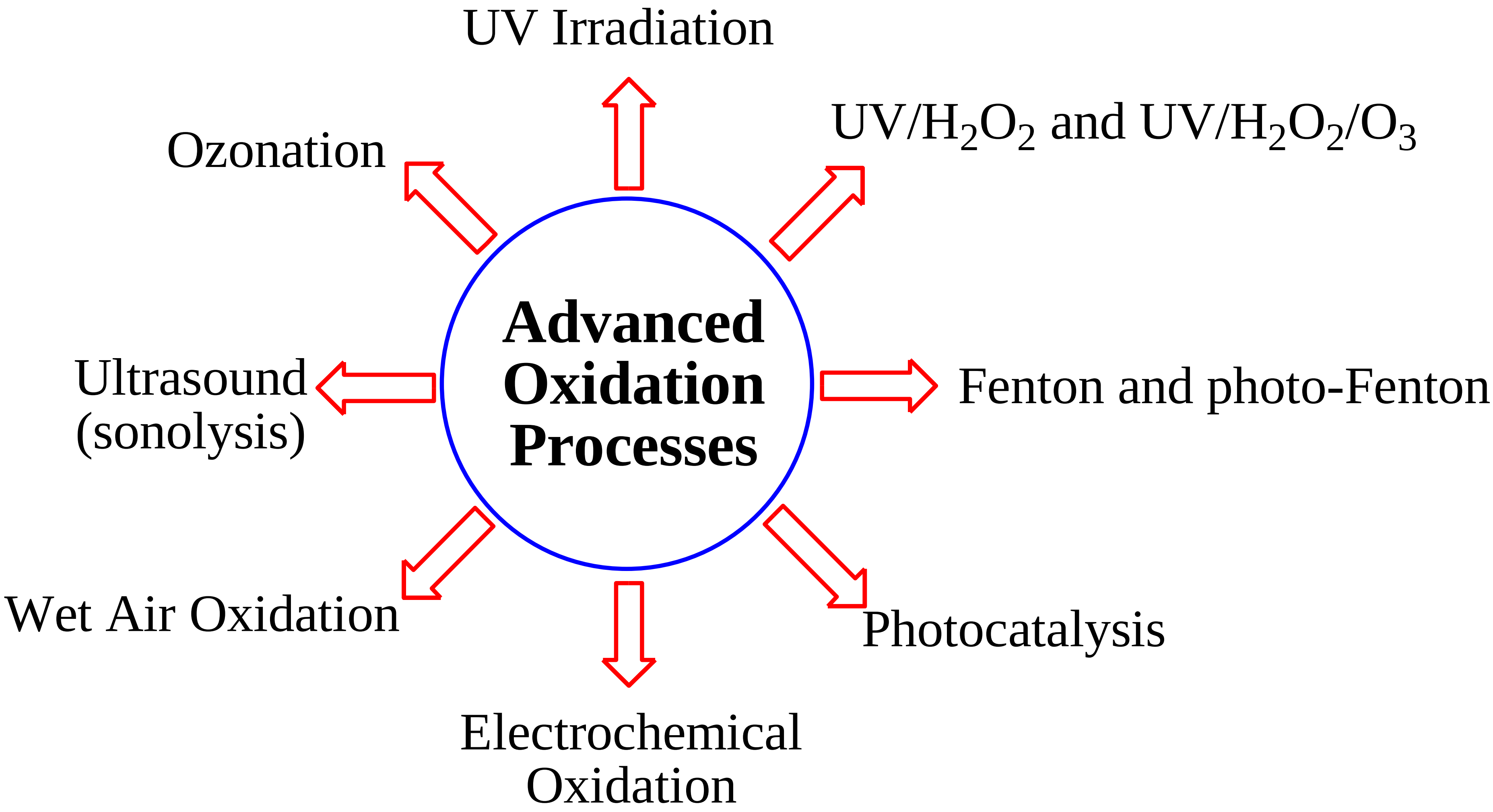
Advanced Oxidation Process (AOPs)

- Advanced oxidation processes (AOPs) have been defined as near-ambient temperature processes that involve the generation of highly reactive radical intermediates, especially the **hydroxyl radicals.**
- AOPs include several types of reaction processes:

1. *Wet air oxidation (WAO) or Subcritical oxidation,*
2. *Electrochemical oxidation,*
3. *Supercritical water oxidation,*
4. *Oxidation with ozone and hydrogen peroxide,*
5. *Fenton reaction.*



ADVANCED OXIDATION PROCESSES



Advanced Oxidation Process (AOPs)

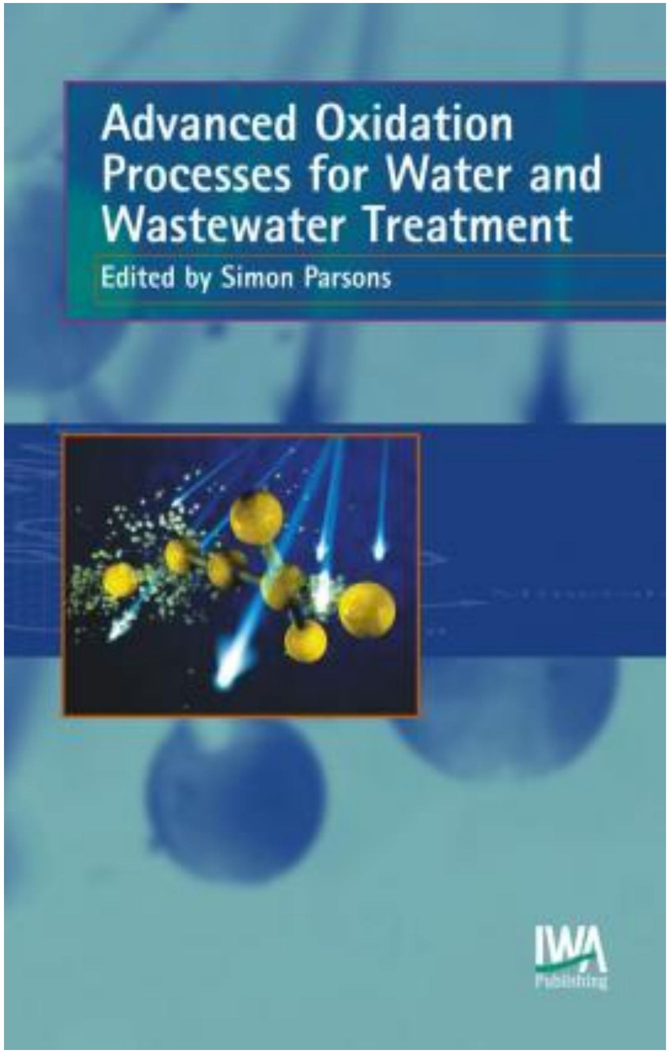
- **In the past, ChemOx have been used:**
  1. To reduce concentrations of residual organics,
  2. To remove ammonia,
  3. for control of odors, and
  4. for disinfection purposes (kill pathogenic microorganisms).

- **In addition, currently, ChemOx processes are recommended:**
  1. For improving treatability of refractory organics,
  2. To eliminate toxic compounds affecting microbial growth & aquatic flora.
  3. To remove toxic organic compounds, e.g. phenols and other priority pollutants that may threaten health,
  4. To remove or modify inorganic toxic constituents, e.g. Mn(II), Fe(II), S^{2-}, CN^-, SO_3^{2-}

Advanced Oxidation Process (AOPs)

Common oxidizing agents

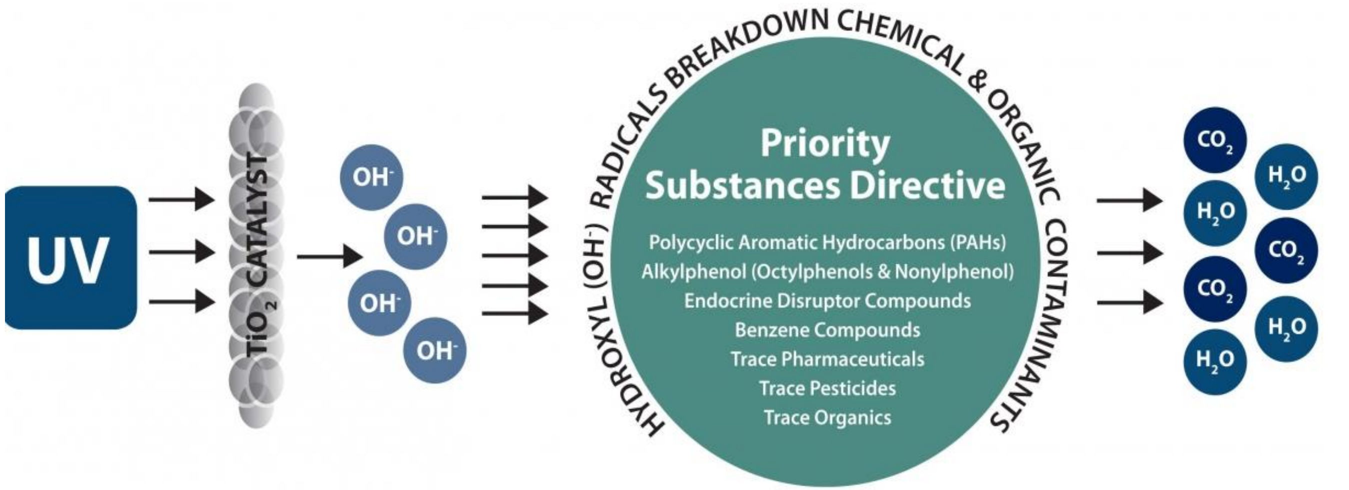
1. Hydrogen peroxide
2. Nitric acid and Nitrates
3. Chlorites, chlorate, perchlorate and other analogous halogen compounds
4. Hypochlorite and similar compounds such as bleach
5. Fluorine and other halogens
6. Ozone
7. Nitrous oxide (N_2O)
8. Silver oxide
9. Permanganate salts
10. Gaseous oxygen at high T & P.



ADVANCED OXIDATION PROCESSES

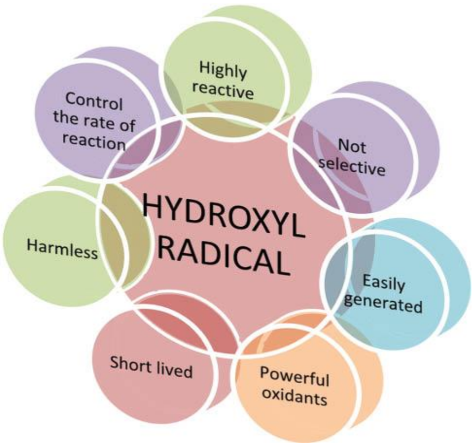
- Several methods are available for generating **.OH radicals**
- These include both non-photochemical and photochemical methods:

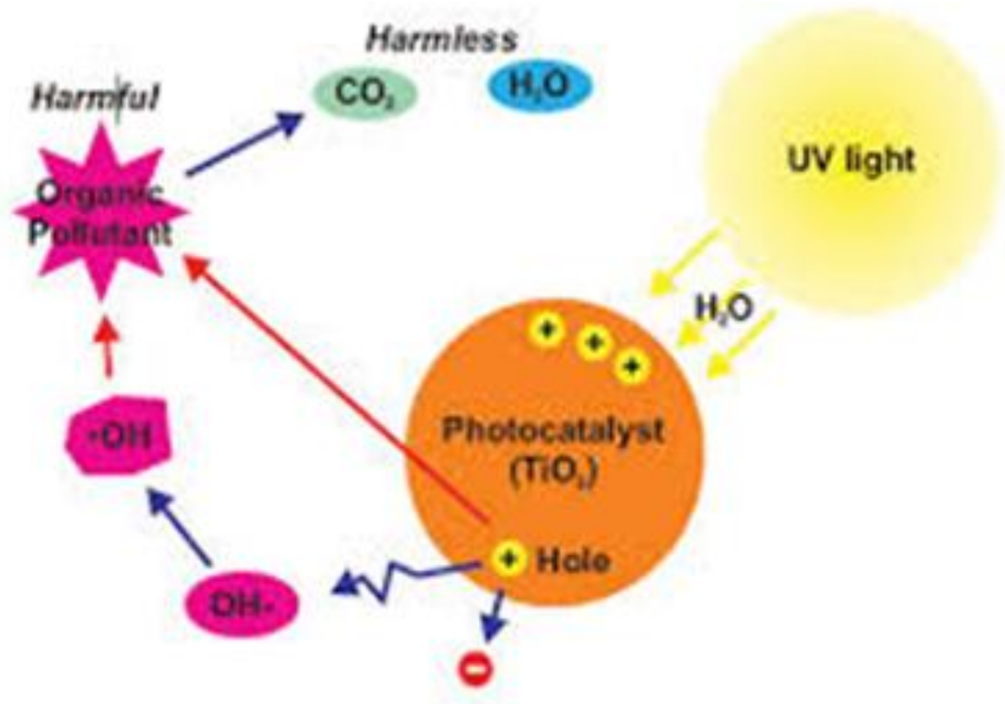
1. Ozonation at elevated pH (>8.5)
2. Ozone + hydrogen peroxide (O_3/H_2O_2)
3. Ozone + catalyst (O_3/CAT)
4. O_3/UV
5. H_2O_2/UV
6. O_3/H_2O_2/UV
7. Fenton system (H_2O_2/Fe^{2+})
8. Photo-Fenton/Fenton- like systems
9. Photocatalytic oxidation (UV/TiO_2)



Established AOPs Technologies

1. Wet Air Oxidation: O_2 @ high T and P
2. UV-Based Processes
   a) UV/H_2O_2
   b) UV/O_3
   c) $UV/H_2O_2/O_3$





Advanced Oxidation Process (AOPs)

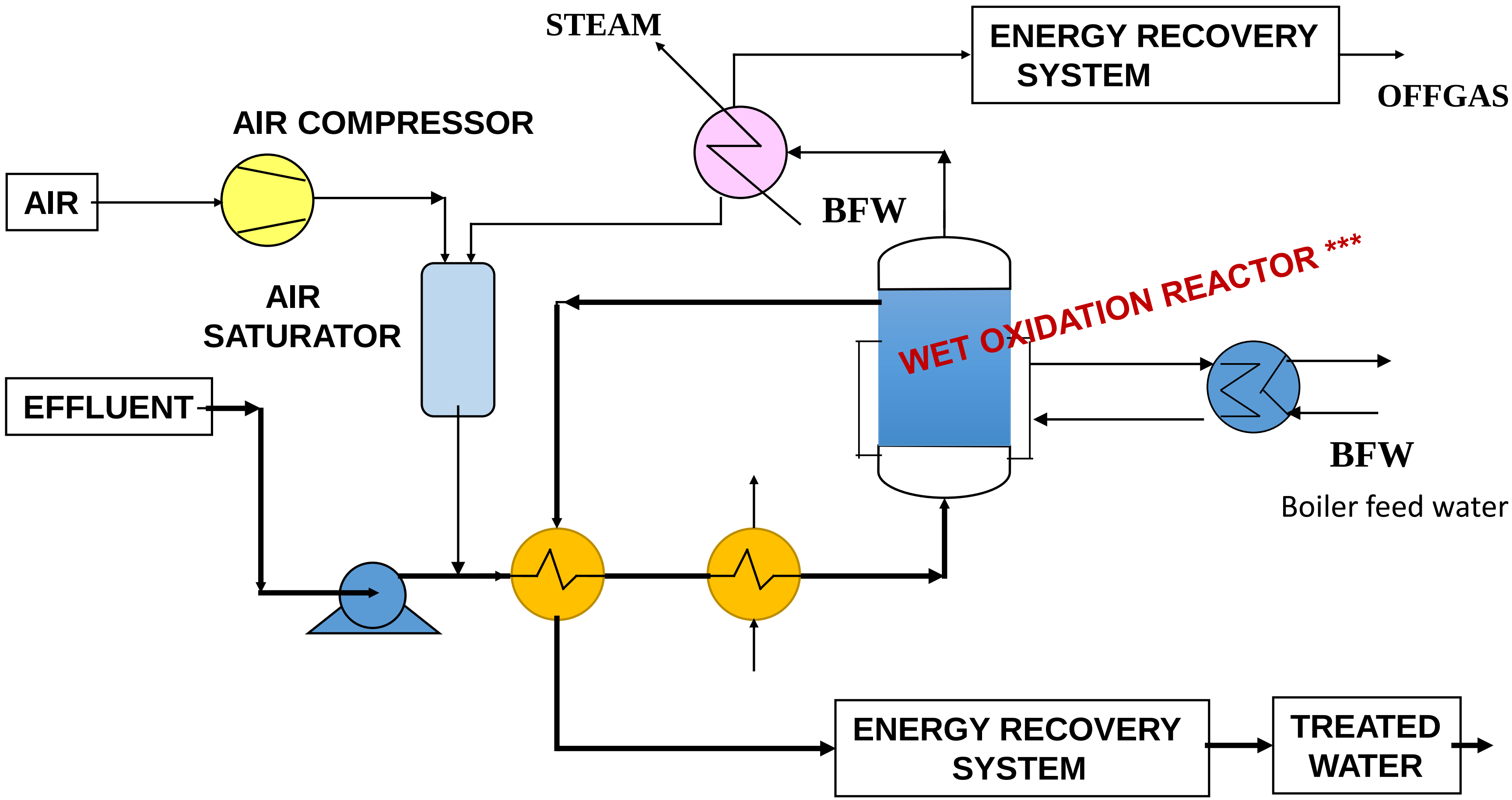
- **AOPs** have gained growing attention as an emerging clean and efficient technology for air and water treatment. The **major advantages** of this technology are:
  1. It can completely or partially destroy complex organics at room temperature by converting them into various harmless intermediates and end products, *such as carboxylic acids, carbon dioxide and halide ions.*
  2. It can handle concentrated waste COD 10,000-500,000 mg/L, toxic chemicals & priority pollutants in presence of high TDS.

- The major oxidants of **AOPs** are **hydroxyl radicals and ozone** which can react with organic compounds at very high reaction rates.
- In particular, **hydroxyl radicals** can attack most organics non-selectively at a reaction rate constant as high as 10^9 M^{-1} sec^{-1} through:
  - hydrogen atom abstraction or
  - by addition of the hydroxyl radical.

1. Wet Air Oxidation (WAO)

1. WAO is a well established technology for wastewater treatment, particularly for the treatment of *toxic and highly concentrated wastewaters.*
2. WAO is a chemical oxidation process involving organics or oxidizable inorganic components in an aqueous liquid phase:
    1. *at high temperatures (125-320°C) and*
    2. *at high pressures (0.5-20 MPa), 5-200 atm*
    3. *using a gaseous source of oxygen (normally air).*
3. WAO has been demonstrated to mineralize various organic compounds to carbon dioxide, water and other inorganic end products such as *ammonia, nitrate, nitrogen, chloride, sulfate and phosphate.*
4. The oxidation capability of WAO is greatly enhanced if catalysts and oxidants such as *ozone and hydrogen peroxide* are present .

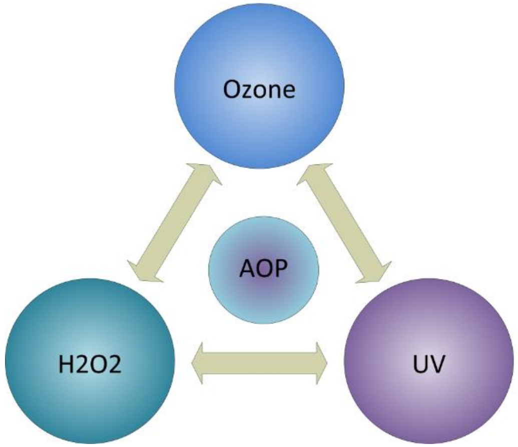
1. Wet Air Oxidation (WAO)



Typical Continuous Wet Oxidation System

***Bubble column

2. UV- based AOPs



- Apply oxidation by **OH·** radical.
- Used for <u>low</u> concentrations of compounds resistant to air stripping, e.g. trichloromethane.

- Different ways to get hydroxyl radicals (OH.):
  1. UV effect on H_2O_2:

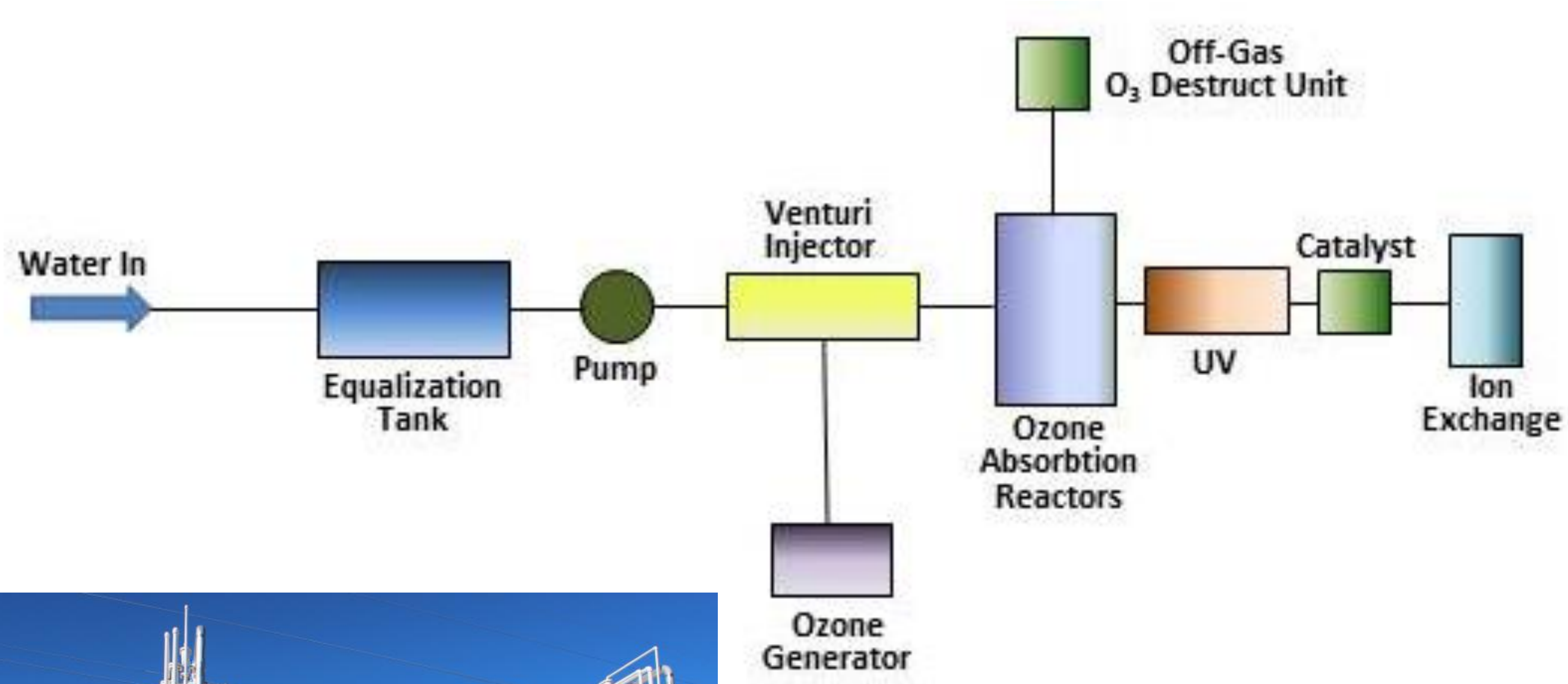
     $H_2O_2 \rightarrow 2OH\cdot$
  2. UV effect on ozone, O_3:

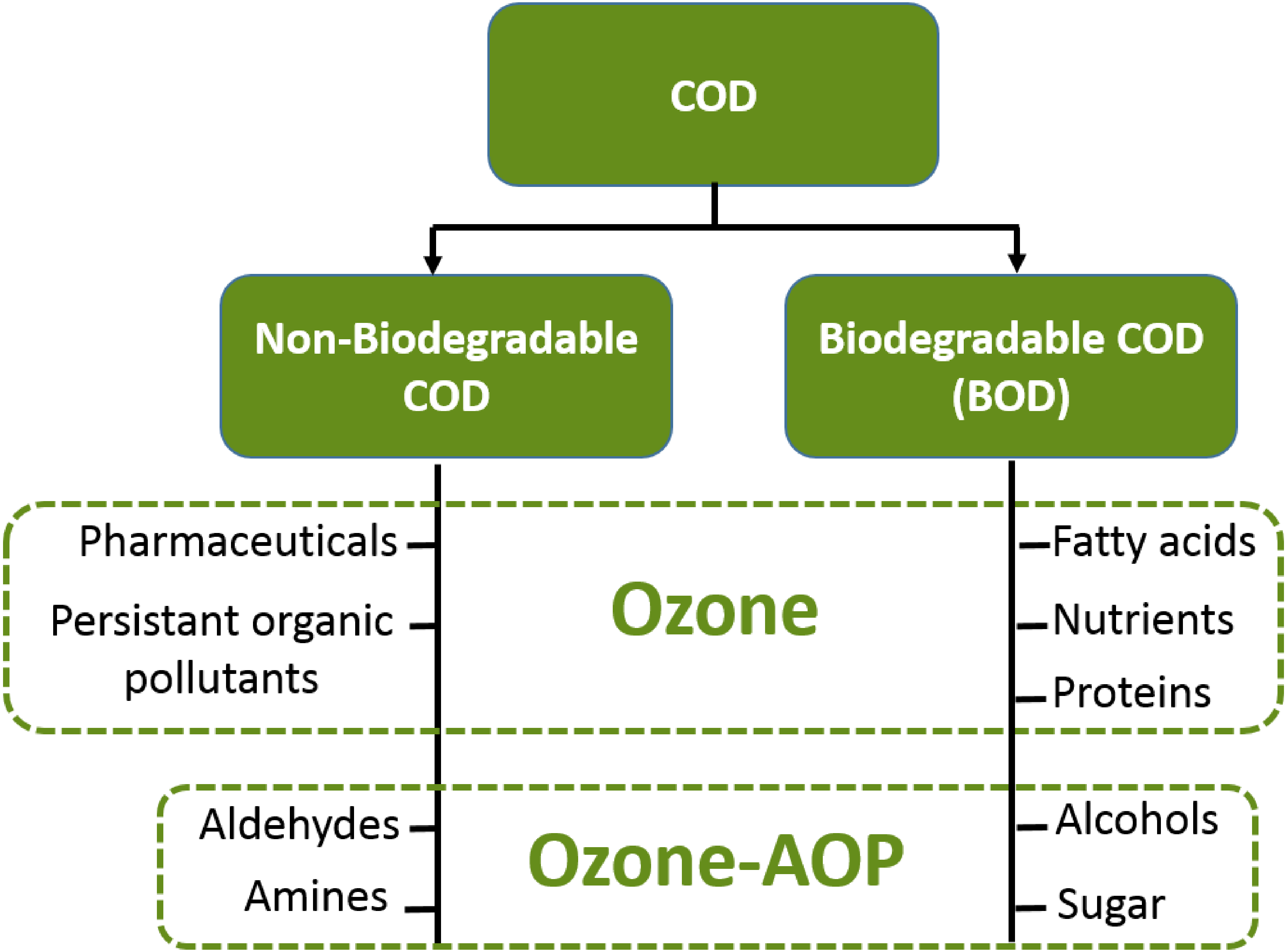
     $O_3 \rightarrow O_2 + O$

     $O + H_2O \rightarrow H_2O_2 \rightarrow 2OH\cdot$

     $H_2O_2 + 2O_3 \rightarrow 2\ HO\cdot + 3\ O_2$
  3. UV effect with mixture of H_2O_2 and O_3.

2. UV-based AOPs




COD
Non-Biodegradable COD
Biodegradable COD (BOD)
Pharmaceuticals
Persistant organic pollutants
Ozone
Fatty acids
Nutrients
Proteins
Aldehydes
Amines
Ozone-AOP
Alcohols
Sugar

Advanced Oxidation Processes

Table 1.10. Oxidizable compouns by hydroxyl radicals (Bigda, 1995)

Compounds	
Acids	Formic, gluconic, lactic, malic, propionic, tartaric
Alcohols	Benzyl, *tert*-butyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol, propenediol
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal, isobutyraldehyde, trichloroacetaldehyde
Aromatics	Benzene, chlorobenzene, chlorophenol, creosote, dichlorophenol, hydroquinone, p-nitrophenol, phenol, toluene, trichlorophenol, xylene, trinitrotoluene
Amines	Aniline, cyclic amines, diethylamine, dimethylformamide, EDTA, propanediamine, n-propylamine
Dyes	Anthraquinone, diazo, monoazo
Ethers	tetrahydrofuran
Ketones	Dihydroxyacetone, methyl ethyl ketone

Table 1.11. Reaction rate constant (k, L mol^{-1} s^{-1})

Compounds	$OH^{\bullet}$
Chlorinated alkenes	10^9 to 10^{11}
Phenols	10^9 to 10^{10}
N-containing organics	10^8 to 10^{10}
Aromatics	10^8 to 10^{10}
Ketones	10^9 to 10^{10}
Alcohols	10^8 to 10^9
Alkanes	10^6 to 10^9

Compound + OH. → Products

(2nd order reaction)

Advanced Oxidation Processes (AOPs)

Comparing Removal Efficiencies of AOPs for Phenol

AOP	$[H_2O_2]_0$ (mol/L)	$PhOH_{60}$ removed at pH_{neut} (%)	$PhOH_{90}$ removed at pH_{neut} (%)	$PhOH_{60}$ removed at pH_{bas} (%)	$PhOH_{90}$ removed at pH_{bas} (%)
UV	-	5.6	8		
O_3	-	84.8	92.1	98.7	100
O_3/UV	-	87.7	94.6	88.2	93.5
O_3/H_2O_2	$0.58 . 10^{-4}$	84.8	92.8		
O_3/H_2O_2	$0.58 . 10^{-3}$	86.6	95.8	86.3	95.0
O_3/H_2O_2	$2.94 . 10^{-3}$	79.4	89.8	80.5	92.5
O_3/H_2O_2	$7.35 . 10^{-3}$	78.9	89.5		
O_3/H_2O_2	$1.47 . 10^{-2}$	70.3	80.9		
$O_3/UV/H_2O_2$	$0.58 . 10^{-3}$	70.5	76.9	70.9	83.6

Legend:

PhOH: phenol, C6H5OH / Contact Time: 60, 90 min /neutral pH (6.8-7.2) and basic pH (9.3-9.5)

Ref. spartanwatertreatment

Electrochemical Oxidation

- This is Electrochemical Oxidation of organic Pollutants for Wastewater Treatment
- A study on electro-oxidation for wastewater treatment goes back to the 19th century, when electrochemical decomposition of cyanide was investigated.
- Extensive investigation of this technology commenced since the late 1970s.
- During the last two decades, research works have been focused on:
  - the efficiency in oxidizing various pollutants on different electrodes
  - improvement of the electrocatalytic activity and electrochemical stability of electrode materials
  - investigation of factors affecting the process performance
  - exploration of the mechanisms and kinetics of pollutant degradation

Electrochemical Oxidation

Electrochemical oxidation of organic pollutants

Anode | **Cathode**

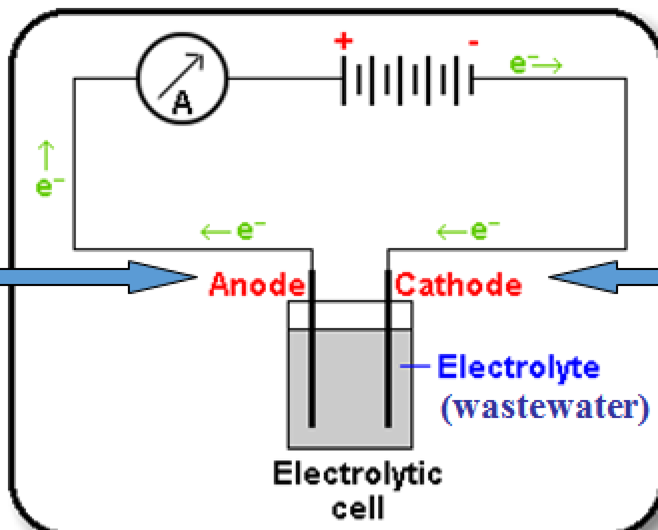
Oxidation:

$$R + H_2O \longrightarrow RO + 2H^+ + 2e^-$$

(main reaction)

$$H_2O \longrightarrow 1/2O_2 + 2H^+ + 2e^-$$

(side reaction)



Reduction:

$$2H^+ + 2e^- \longrightarrow H_2\uparrow$$

<u>Global reaction:</u>

$$R + H_2O \longrightarrow RO + H_2\uparrow \quad \text{(main reaction)}$$

$$H_2O \longrightarrow 1/2O_2\uparrow + H_2\uparrow \quad \text{(side reaction)}$$

Electrochemical Oxidation

- Oxidation of organics on BDD* electrodes.
- Investigated organic compounds include:

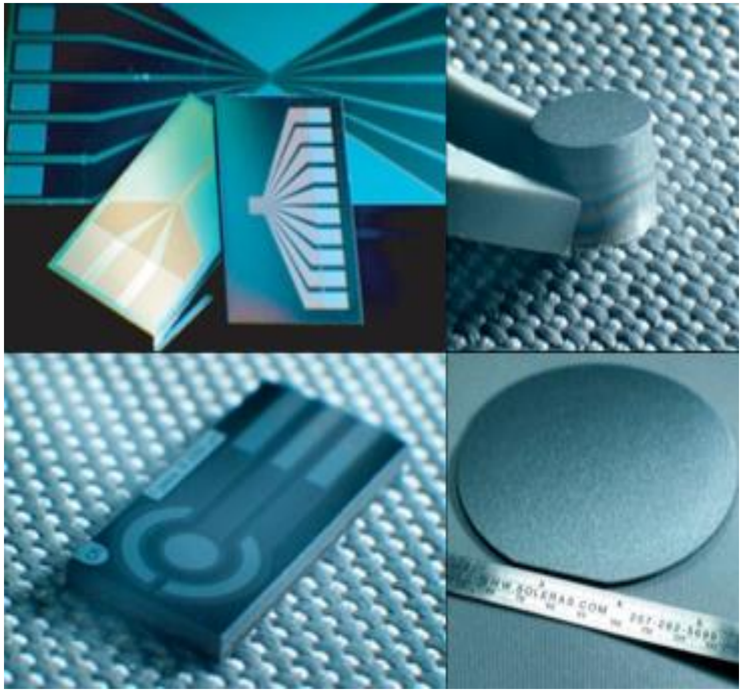
Carboxylic acids
Acetic, Formic, Maleic and **Oxalic**

Alcohols and ketones
Methanol, Ethanol, Isopropanol, Acetone

Phenolic compounds
Phenol, p-chlorophenol, β-naphthol

Aromatic acids
Benzoic acid, Benzene sulfonic acid, Nicotinic acid

Soluble polymers
Polyacrylic acid



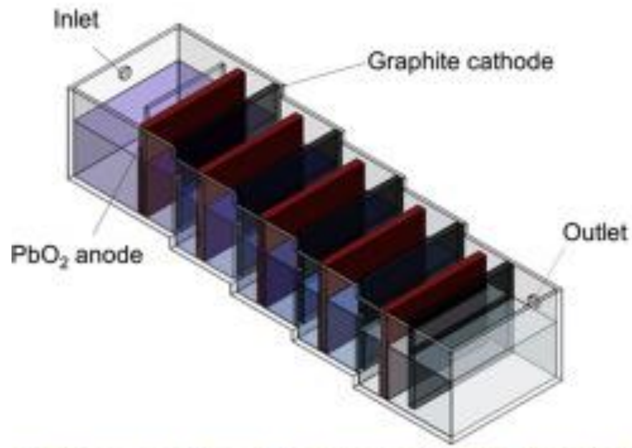
*boron-doped diamond

Electrochemical Oxidation

- Two mechanisms are thought to be responsible for organic matter electrochemical degradation, namely:
  a) Indirect oxidation in the liquid bulk
  b) Direct anodic oxidation at the surface of the anode electrode
- Indirect oxidation in the liquid bulk: it is mediated by the oxidants that are formed electrochemically. Such oxidants include:
  - chlorine and hypochlorite; hydrogen peroxide & ozone
- Electrochemical oxidation can occur directly at the anode through the generation of physically adsorbed hydroxyl radicals, HO•, or chemisorbed "active oxygen'' (oxygen in the oxide lattice, MOx+1).
- The pollutants are adsorbed on the anode surface and destroyed by the anodic electron transfer reaction.

Electrochemical Oxidation

- Electrochemical degradation mechanisms
- Indirect oxidation in the liquid bulk



Continuous Flow Electrochemical Oxidation

Wastewater	Energy consumption
Synthetic wastewater	9.2 kWh (kg COD)$^{-1}$ (90% COD removal)
Real textile industry wastewater	59.3 kWh (kg COD)$^{-1}$ (100% COD removal)

Treatment option	Cost of treatment
Continuous electrochemical oxidation	5.83 USD m^{-3}
Batch electrochemical oxidation	10.2 USD m^{-3}

- Reactions at the anode

$H_2O + M + Cl^- \rightarrow M[ClHO^\bullet] + H^+ + 2e^-$

$R + M[ClHO^\bullet] \rightarrow M + RO + H^+ + Cl^-$

$H_2O + M[ClHO^\bullet] + Cl^- \rightarrow M + O_2 + Cl_2 + 3H^+ + 4e^-$

$H_2O + Cl^- \rightarrow HOCl + H^+ + 2e^-$

$H_2O + M[ClOH^\bullet] + Cl_2 \rightarrow M + ClO_2 + 3H^+ + 2Cl^- + e^-$

$H_2O + M[HO\bullet] \rightarrow M + H_2O_2 + H^+ + e^-$

$O_2 + M[HO^\bullet] \rightarrow M + O_3 + H^+ + e^-$

R + oxidants $\rightarrow$ oxidation products

1. **Electrogenerated $OH^\cdot$ are the active oxidants involved in the electrochemical oxidation of organic pollutants.**
2. **The main side reaction in the electrochemical oxidation of organic pollutants is oxygen evolution.**

SLUDGE MANAGEMENT

- Sludge management is the process of processing and ultimate disposal of the residuals of wastewater treatment.

- **THICKENING**
  - Solids are combined from inorganic precipitates of metals formed by chemical treatment as well as oil from pre-treatment.
  - Gravity thickeners take advantage of the particulate's settling characteristics due to higher density of solids relative to water.
  - All thickening processes increase sludge solids concentrations from ~1.0% to ~5.0%.
  - The sludge is still pumpable at these concentrations.

SLUDGE MANAGEMENT

- **Dewatering**
  - Filter press
  - Centrifuge

- **Fixation and Stabilization**
  - Calcium and aluminum silicates
  - Cement

- **Ultimate Disposal**
  - Hazardous waste landfill