Industrial Wastewater Treatment

Presented by

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Neutralization

- In an aqueous solution, hydrogen ions ($H+$ or H_3O^+) react with Hydroxide (OH^-) to make water molecules

- A salt is also formed

- Neutralization reactions are exothermic or emit heat to its surroundings

- Can you dilute and acidic or basic wastewater by adding water?

METALS PRECIPITATION

CHEMICAL CONVERSION

- Required before precipitation:
  - Hexavalent chromium (Cr^{+6}) reduction
  - Treatment of any chelating agents must also happen prior to attempting precipitation
    - Cyanide (CN^-) destruction

Oxidation-Reduction Potential

- ORP is related to the concentration of oxidizers or reducers in a solution and their strength.

- It provides an indication of the solution's ability to oxidize or reduce another material.

- Addition of an oxidizer will raise the ORP value, while the addition of a reducer will lower the ORP value.

- The greater the concentration of an oxidizer or reducer in the solution, the faster the reaction.

ORP (cont.)

- For most purposes, water is generally considered "neutral" with regards to its ORP value.

- Water is actually a very weak oxidizer, due to dissolved oxygen.

- Well water or city-supplied water will generally have an ORP value of between 200 and 250 mV, a range that is considered the "zero" point (or standard potential).

ORP (cont.)

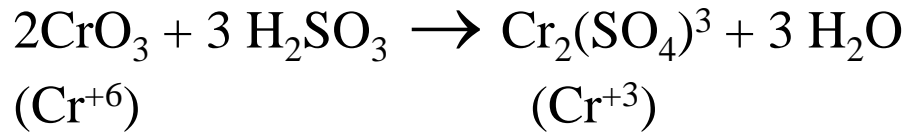| Oxidant	Oxidation Potential (Volts)	Oxidation Potential (reference chlorine)
Fluorine	3.05	2.25
Ozone	2.07	1.52
Hydrogen Peroxide	1.78	1.31
Potassium Permanganate	1.68	1.25
Chlorine Dioxide	1.57	1.15
Chlorine	1.36	1.0
Bromine	1.07	0.79

Hexavalent Chromium Reduction

- Chromium exists in several valence states
  - Chromium (III)
  - Chromium (VI)
- Trivalent state (chromium III) will form $Cr(OH)_3$, a hydroxide precipitate.
- Hexavalent chromium (chromium VI) persists as an ion even when the pH is increased by the addition of a hydroxide precipitant.

Hexavalent Chromium Reduction (cont.)

- Hexavalent chromium removal is done in two steps.

- First hexavalent chromium is reduced to its trivalent state.

  - This reduction is commonly done by adding sulfur dioxide (SO_2), sodium bisulfite ($NaHSO_3$), Ferrous Sulfate ($FeSO_4$) or sodium metabisulfite ($Na_2S_2O_5$) at pH 2.5.

    $$2CrO_3 + 3\ H_2SO_3 \longrightarrow Cr_2(SO_4)^3 + 3\ H_2O$$

    (Cr^{+6}) (Cr^{+3})

 H_2SO_3 is sulfurous acid, generated by sulfites at low pH

Hexavalent Chromium Reduction (cont.)

- An oxidation-reduction potential (ORP) meter can monitor the the reaction. Since a reducing agent is being added the ORP drop must be determined experimentally usually ~+250 mV. A color change from yellow to green occurs as chromium is reduced.

- Second step is hydroxide precipitation at pH 7.5 to 8.5 followed by flocculation.
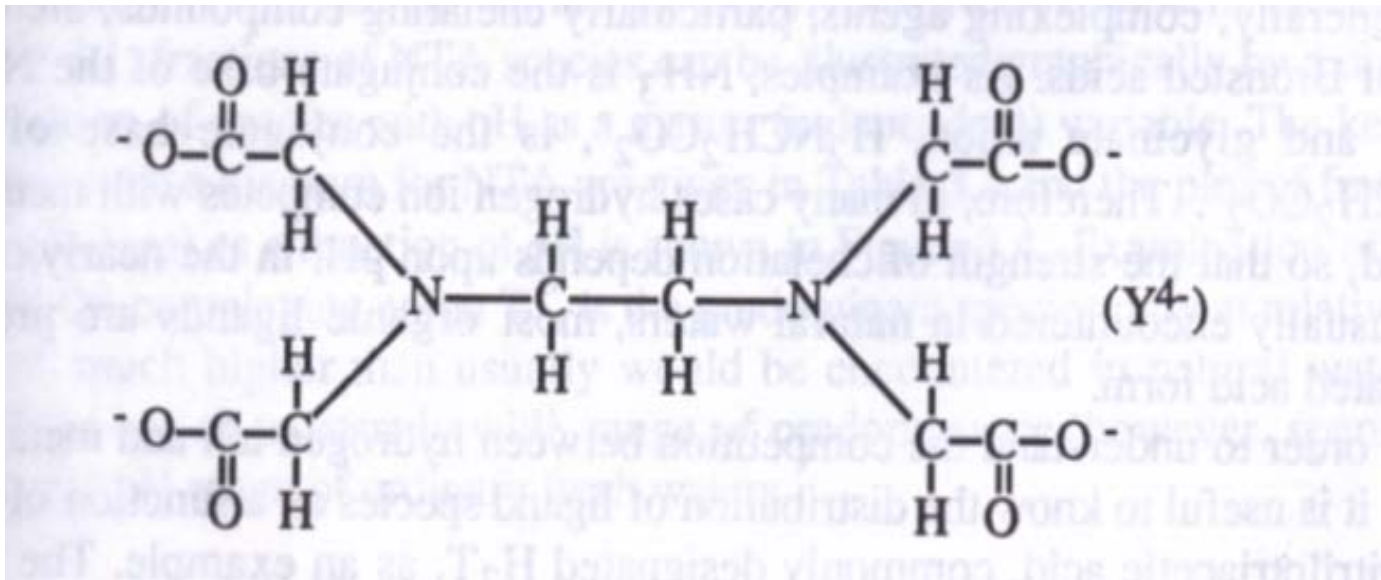
$$Cr_2(SO_4)_3 + 6NaOH \longrightarrow 3Na_2SO_4 + 2Cr(OH)_3$$
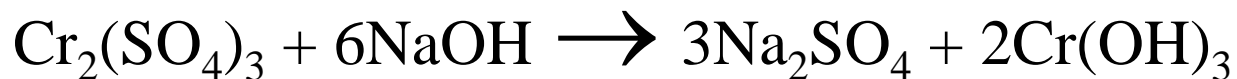
Chelating Agent

- Polyphosphate ($P_2O_7^{-4}$) bonds at two sites with calcium:
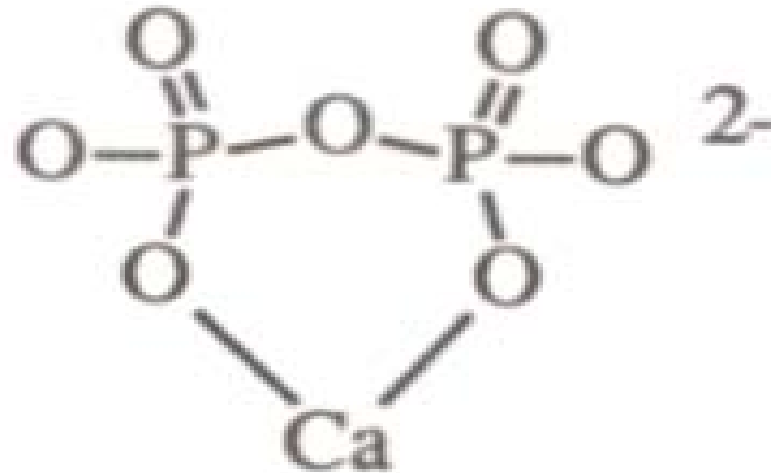
Chelating Agent (cont.)

- Ethylenediaminetetraacetate (EDTA) can chelate with more metals:

Chelating Agent (cont.)

- Many other chelating agents exist
  - Cyanide

Treating Chelating Agents

- Polyphosphate ($P_2O_7^{-4}$) – acid hydrolyze to orthophosphate (PO_4^{-3}) (another possible chelate) and precipitate with ferric iron or aluminum.

- EDTA, NTA, others – depends on metal chelated and pH solubilities but generally pH adjustements.

Cyanide Destruction

- Cyanide (CN^-) destruction is important in metal removal because cyanide complexes with metals. Once the cyanide-metal bond is broken the metal is free to precipitate under the appropriate pH.

- Cyanide destruction is an important pretreatment parameter because cyanide may destroy the active organisms in the treatment process or may pass-through a POTW.

- Cyanide destruction is typically a two-step process.

Cyanide Destruction (cont.)

- First step involves converting cyanide (CN^-) to cyanate (CNO^-) with sodium hypochlorite when pH is adjusted 10 or greater.
  - Note do Hexavalent Chromium treatment after cyanide treatment

    $NaCN + Cl_2 \rightarrow CNCl + NaCl$

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

  - Requiring approximately 30 minutes, an ORP meter and a color change from green to blue may monitor the reaction endpoint. An ORP between +325 and +400 indicates a complete reaction .
  - pH is important because Cyanogen chloride (CNCl) is volatile at low pH and is a lachrymator (tear gas).

Cyanide Destruction (cont.)

- Second, decreasing the pH with acid to 8.5 converts cyanate to carbon dioxide and nitrogen.

$$2 \, NaCNO + 4NaOH + 3Cl_2 \rightarrow 2CO_2 + 6NaCl + N_2 + 2H_2O$$
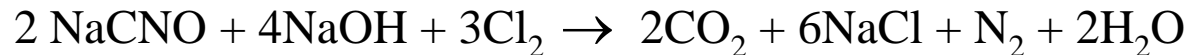
- The second step requires about 10 minutes. An ORP reading of +600 to +800 signals a complete reaction.

- The exact amount of chemicals needed for these reactions is determined experimentally (jar test).

- Other methods for cyanide destruction include ozone treatment, heat/pressure, electrolysis, and hydrogen peroxide.

HYDROXIDE PRECIPITATION/ COAGULATION

- Conventional heavy metals removal is by chemical precipitation of the metal as metal hydroxides followed by coagulation of the metal particles into larger, heavier, flocculated particles (floc).

- This frequently used method has proven reliable and can be inexpensive and highly selective. Generally, a properly designed and operated plant can reduce metal concentrations to 10^{-5} to 2.1 mg/L.

HYDROXIDE PRECIPITATION/ COAGULATION (cont.)

- Typically, heavy metals are dissolved under acid conditions and precipitated under alkaline conditions.

- Maintaining an alkaline pH throughout the process until sludge is removed is key. Sodium hydroxide (NaOH, caustic soda), calcium hydroxide [$Ca(OH)_2$, hydrated lime or CaO, quicklime] or magnesium oxide [$Mg(OH)_2$, hydrated magnesium hydroxide] are commonly added to increase pH and to provide hydroxide ions.
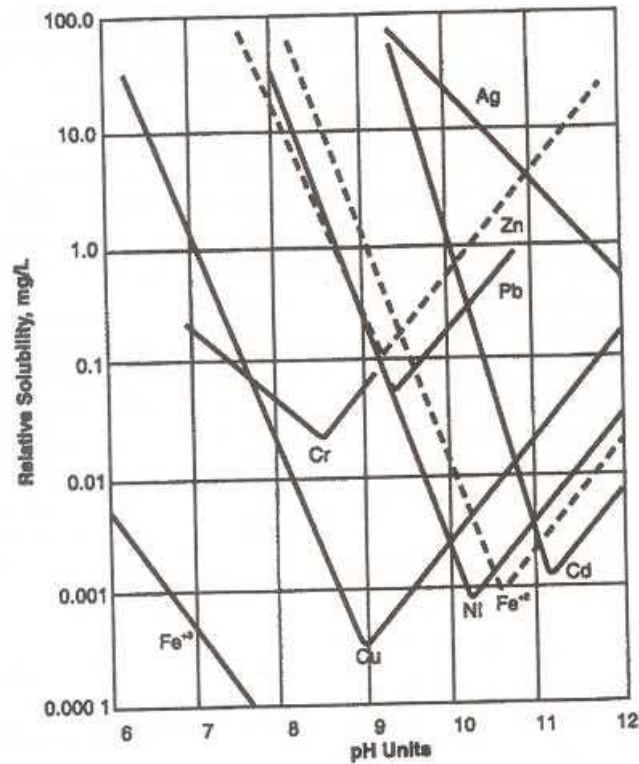
HYDROXIDE PRECIPITATION/ COAGULATION (cont.)

- Addition of enough excess hydroxide ions to drive the precipitation reaction to completion. The heavy metal ions in solution react with the hydroxide ions to form solid particles. For example, with copper:
  - Cu^{+2} (aq) + 2NaOH $\rightarrow$ $Cu(OH)_2$ (solid) + 2Na$^+$
  - Cu^{+2} (aq) + $Ca(OH)_2$ $\rightarrow$ $Cu(OH)_2$ (solid) + Ca^{+2}
- The typical pH at which a particular metal is least soluble (that is, most likely to precipitate) is a characteristic of the specific metal.

HYDROXIDE PRECIPITATION/ COAGULATION (cont.)

- This pH will vary depending on many factors:
  - Presences of chelating agents, surfactants, other ions, temperature, etc.

- For example, if copper is the only cation in a deionized water solution, its minimum solubility, theoretically, is at pH 8.9.

- Minimum solubility is the point at which no more copper will precipitate, not the point at which <u>all</u> copper precipitate.

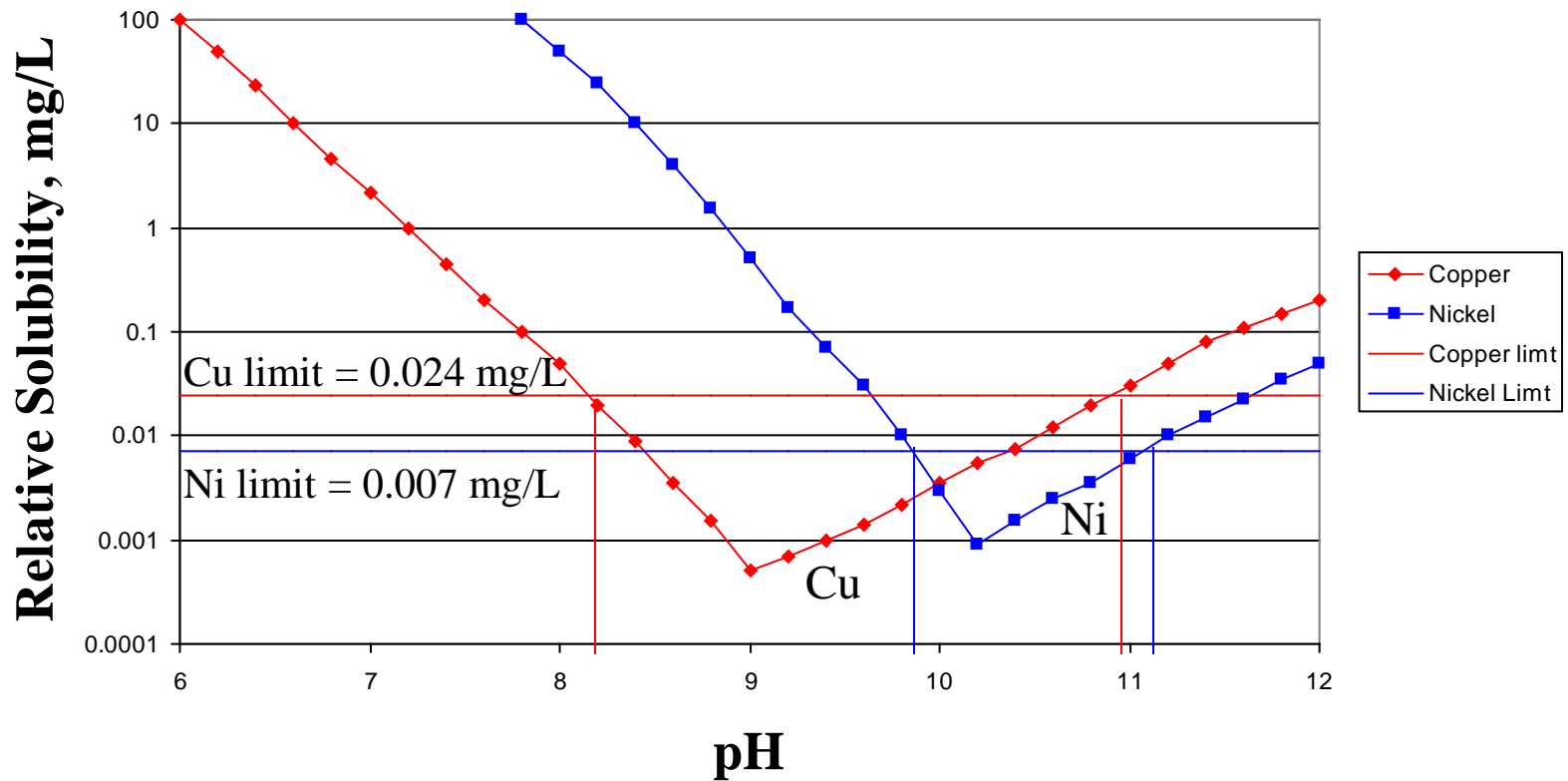# HYDROXIDE PRECIPITATION/ COAGULATION (cont.)

Relative solubilities of metal hydroxides versus pH (U.S. EPA, 1980).

HYDROXIDE PRECIPITATION/ COAGULATION (cont.)

- However, copper in a solution containing a mixture of copper, zinc, chromium, nickel, and iron might have a minimum solubility at pH 9.5. In this same solution, however, zinc might be least soluble at pH 8.5, chromium III and nickel at pH 10, and iron at pH 9.

- Laboratory experimentation or jar testing is necessary to determine both the pH at which most metals are least soluble and the probability that the resulting concentrations are low enough to satisfy the regulatory limits.

HYDROXIDE PRECIPITATION/ COAGULATION (cont.)

HYDROXIDE PRECIPITATION/ COAGULATION (cont.)

- Once the appropriate pH is chosen and the metal hydroxides have precipitated, the next step is to coagulate the tiny particles into flocs.

- The heavier the flocs, the quicker they settle.

- Thus, a coagulant/flocculent aid may be added to enhance flocculation of particles, improving sedimentation.

- This process typically is accomplished using commercially available polymers.

SULFIDE PRECIPITATION/ COAGULATION

- When lower metals concentrations are required in wastewater discharges or if the metals are complexed with chelating agents such as cyanide or ammonia, sulfide or carbonate precipitation may be an effective treatment.

- Additionally, metal hydroxides tend to redissolve as pH increases, while metal sulfides continue to precipitate with increasing pH.

Precipitation Comparison

Solubility of metal ion, mg/L

Metal	As hydroxide	As carbonate	As sulfide
Cadmium (Cd^{++})	2.3×10^{-5}	1.0×10^{-4}	6.7×10^{-10}
Chromium (Cr^{+3})	8.4×10^{-4}	-	No precipitate
Cobalt (Co^{++})	0.22	-	1.0×10^{-8}
Copper (Cu^{++})	2.2×10^{-2}	-	5.8×10^{-18}
Iron (Fe^{++})	0.89	-	3.4×10^{-5}
Lead (Pb^{++})	2.1	7.0×10^{-3}	3.8×10^{-9}
Manganese (Mn^{++})	1.2	-	2.1×10^{-3}
Mercury (Hg^{++})	3.9×10^{-4}	3.9×10^{-2}	9.0×10^{-20}
Nickel (Ni^{++})	6.9×10^{-3}	0.19	6.9×10^{-8}
Silver (Ag^{+})	13.3	0.21	7.4×10^{-12}
Tin (Sn^{++})	1.1×10^{-4}	-	3.8×10^{-8}
Zinc (Zn^{++})	1.1	7.0×10^{-4}	2.3×10^{-7}

SULFIDE PRECIPITATION/ COAGULATION (cont.)

- The heavy metal ions in solution react with the sulfide ions to form solid particles.

    Cu^{+2} (aq) + Na_2S → CuS (solid) + $2Na^+$

- Two distinct sulfide precipitation processes

    – Insoluble sulfide precipitation (ISP) uses ferrous sulfide as the sulfide source. The main advantage of ISP over soluble sulfide is that ferrous sulfide (FeS) is relatively insoluble - no detectable hydrogen sulfide odor.

    – Soluble sulfide precipitation uses a water-soluble reagent such as sodium hydrosulfide (NaSH·2HOH) or sodium sulfide (Na_2S).

SULFIDE PRECIPITATION/ COAGULATION (cont.)

- The use of sulfides in metal precipitation requires more care. Excess sulfides in an alkaline solution form hydrogen sulfide (H_2S), an odorous gas lethal at low concentrations.

- In an acidic solution a larger quantities of H_2S is formed.

- The cost of sulfide precipitation usually is higher.

- Sulfide treatment also requires continuous operator attention to control the toxicity hazards.

Iron Coprecipitation

- $FeCl_3 + H_2O \longrightarrow Fe(OH)_3$ (solid) $+ 3Cl^- + 3H^+$
- $As(III) + Fe(OH)_3$ solid $\leftrightarrow As(III)/Fe(OH)_3$ solid
- Coprecipitation of arsenate with ferric iron
- Ferric iron coprecipitation is particularly useful in the mining industry
- 50% removal of arsenite (as(IV) at a pH of 7.0
- Iron dosage 4 to 8 times higher than that of arsenic

Treatment of Organic Compounds

Introduction

- Four Standard Methods Used in Surface and Groundwater Treatment for the removal Volatile Organic Compounds (VOC)
  - Activated Carbon (GAC)
  - Chemical Oxidation
  - Reverse Osmosis (RO)
  - Air Stripping
- GAC and RO
  - Not Effective in removing low-molecular weight organics such as trihalomethanes (THMs)
- Incomplete Oxidation can produce other organics
- Micro, Nono and Ultrafiltration

Dissolved oil (organics) in water
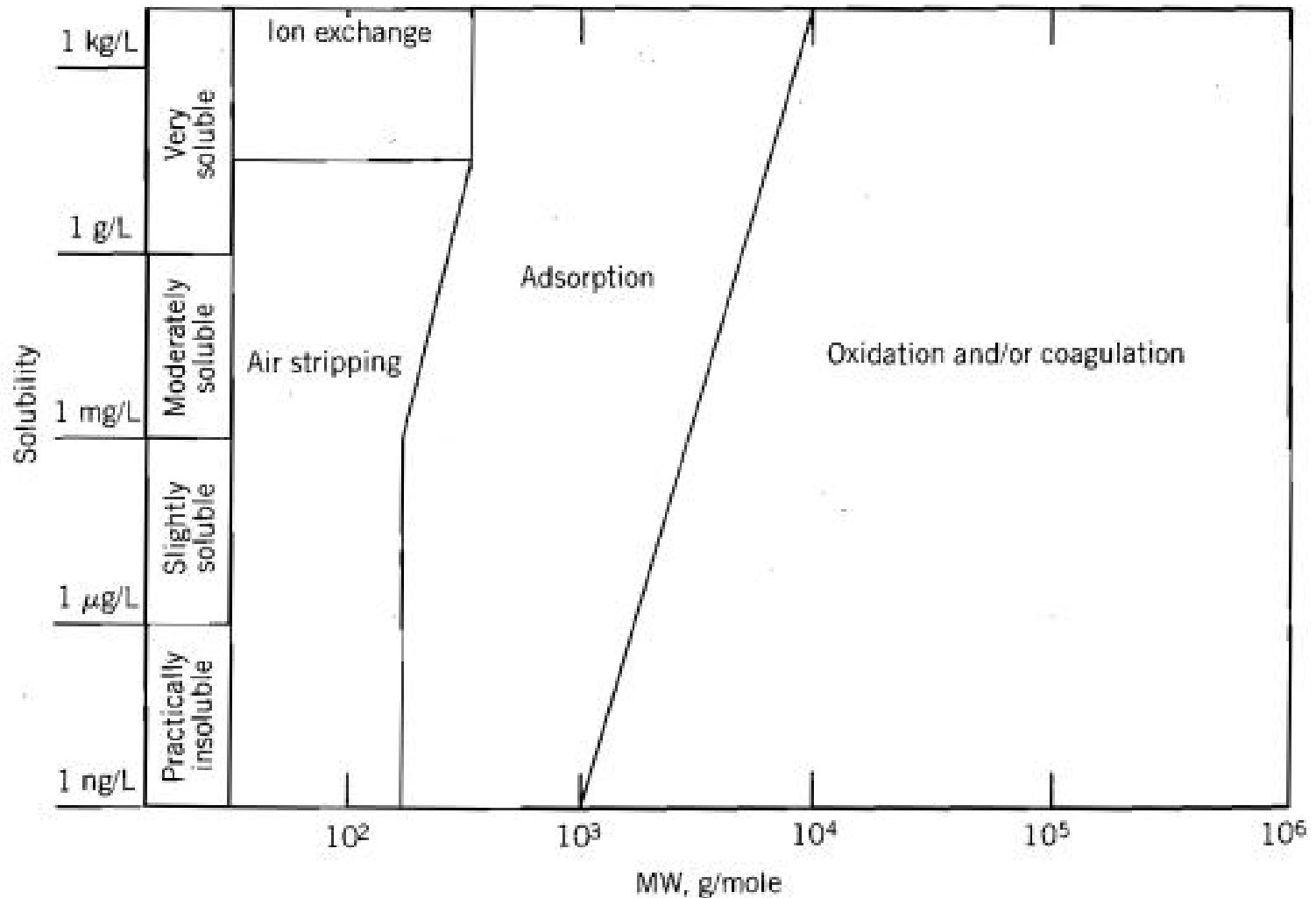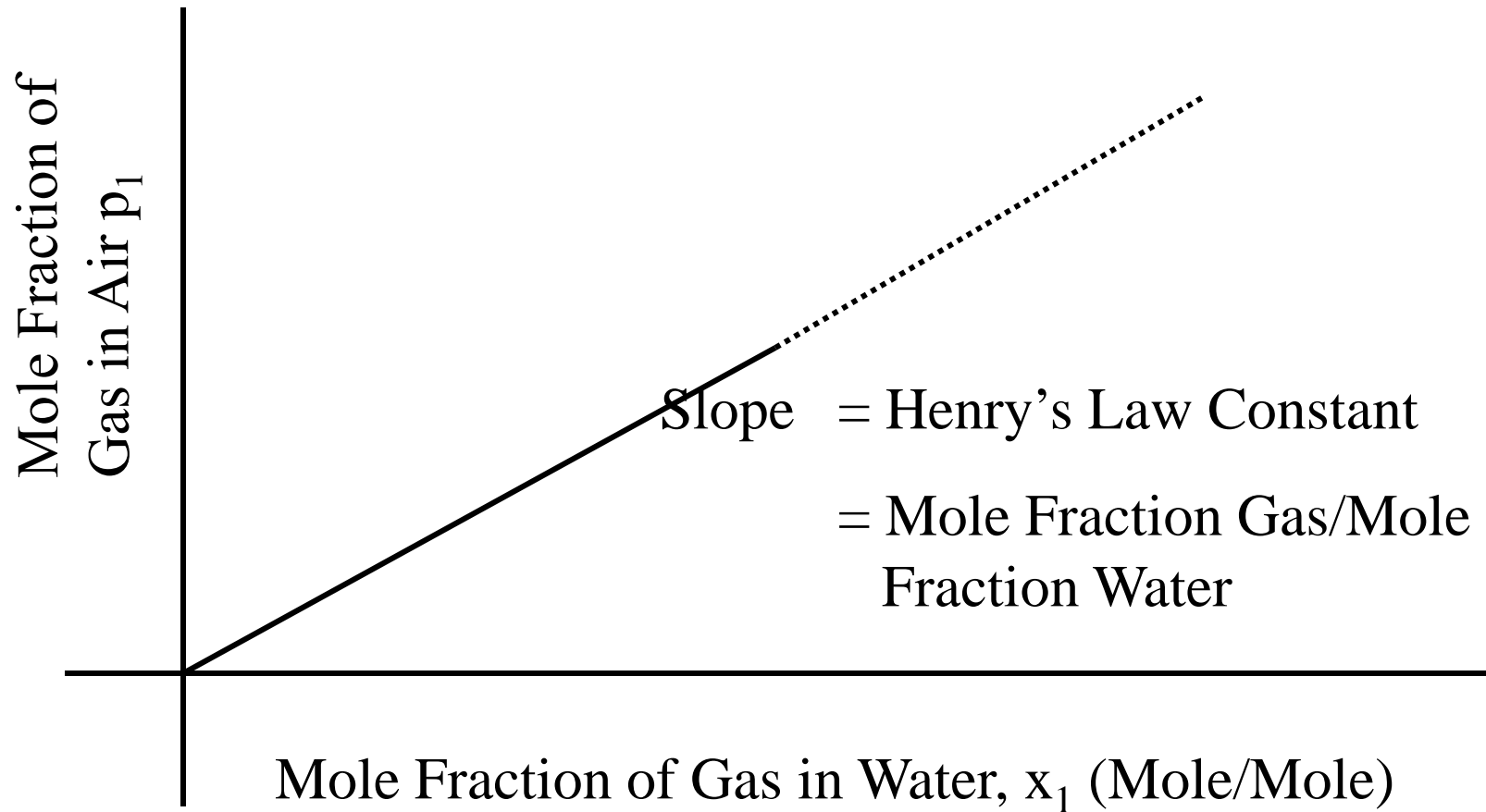
Air Stripping

- Air Stripping is the Best Available Technology (BAT) for removal of organics with boiling points <200°C

- Strips CO_2, Ammonia, H_2S, Taste & Odor & VOC

- Used extensively since the 1970's for VOC removal

Introduction

- Air stripping is similar to evaporation.
- Chemicals which evaporate quicker than water will "strip"
- A chemical's ability to "evaporate" is measured by its vapor pressure.
- Air Stripping uses the principle that molecules of dissolved gas move freely between gas &liquid until equilibrium is reached.
- In dilute solutions this movement is dictated by Henry's Law

Equilibrium Distribution of Gas – Liquid Phase

Mole Fraction of Gas in Air p_1

Slope = Henry's Law Constant

= Mole Fraction Gas/Mole Fraction Water

Mole Fraction of Gas in Water, x_1 (Mole/Mole)

Equilibrium Distribution

- Straight line portion is called Henry's Law Region
    - $C_g = H_u \, C_w$
    - C_g, C_w = Gas/Liquid conc. (mg/L)
    - H_u = Dimensionless Henry's Const
    - Larger H = Better Stripping
        Vinyl chloride – 1245

        TCE -648

        Benzene – 309

        MTBE -32

        Acetone - 2.4
- When no chemical reaction takes place, then a material balance can be:
    - Gas lost by water = Gas gained by Air

Introduction

- Counter current flow is best, Why?
  - Clean air (0 contaminate concentration) enters at the bottom where contaminate concentration in water is lowest.
  - As it moves up the column concentrations get higher

Types of Contactors for VOC Removal

- Packed Tower

- Tray Tower

- Diffused bubble aeration

- Spray towers

- Surface Aerators

Packed Tower

- Most Efficient
- High interfacial contact
- Not tolerant of solids
- Difficult to clean
- Tall stuctures
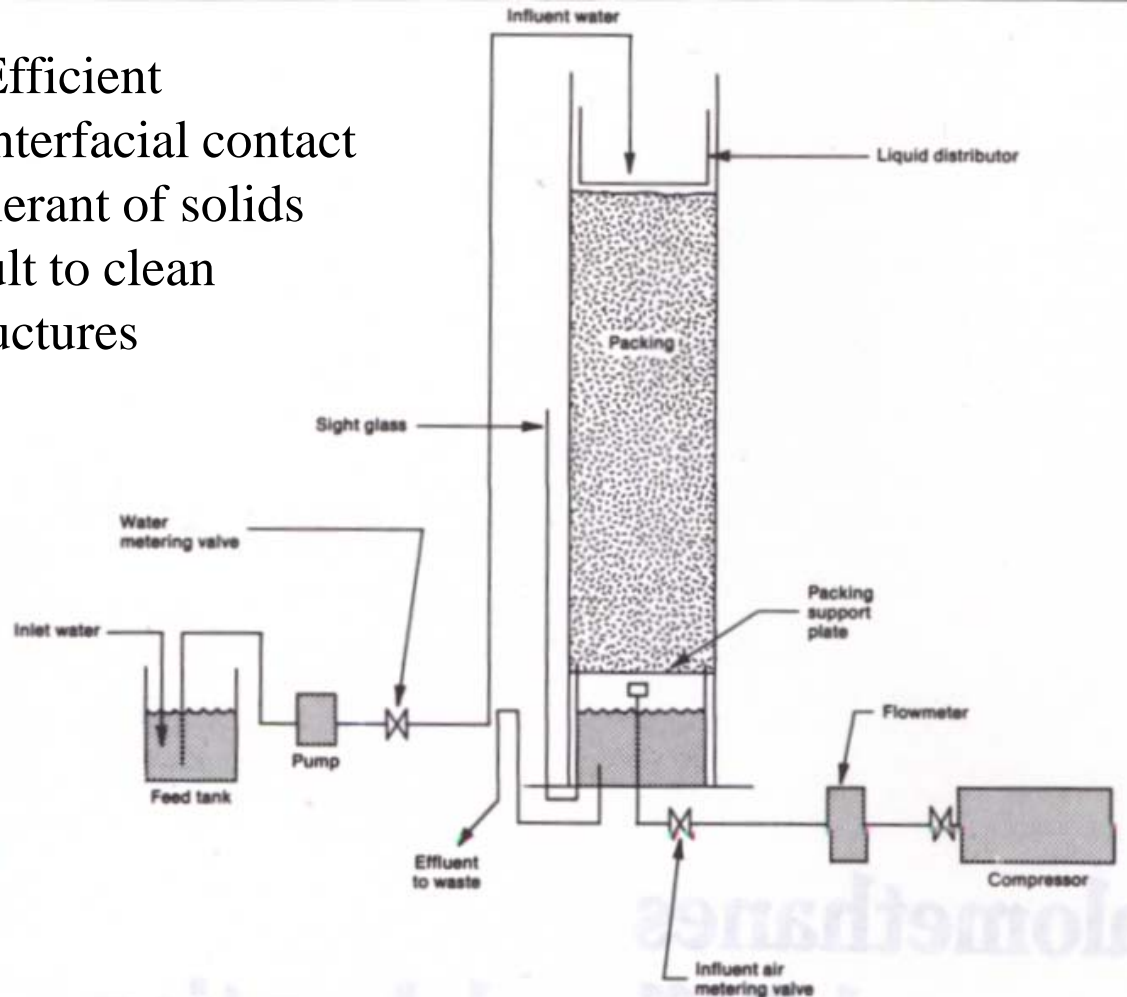
Lockheed Martin's Packed Air Stripping Towers

Waste Water 2-20-01-C-1-27

Tray Tower

- More tolerant of solids
- Easier access for cleaning
- Smaller
- Less interfacial contact
- Less Efficient

Operating Air Strippers

- Usually air to water ratios
  - 100-200 cfm air:cfm water
  - Or 10 – 20 cfm air:gal of water
- Tower Plugging
  - Solids
  - Scale-forming chemicals
  - Biological growth
  - Remove prior to tower or occasionally remove fouling
- No Surfactants

Activated Carbon

- Adsorption is a process where dissolved compounds adhere to the surface of an adsorbent solid.

- How carbon is made
  - Carbon is made from charring almond, coconut, walnut hulls, wood or coal
  - Heating the material to red heat without enough oxygen to combust
  - Then activated by exposure to an oxidizing gas at high temperature

Introduction

- Activated carbon is a good adsorbent due to its high surface area to volume ratio

- One gram of a activated carbon will have a surface area of 1,000 square meters.

- What it's made of can determine Contaminates, Strength

Activated Carbon
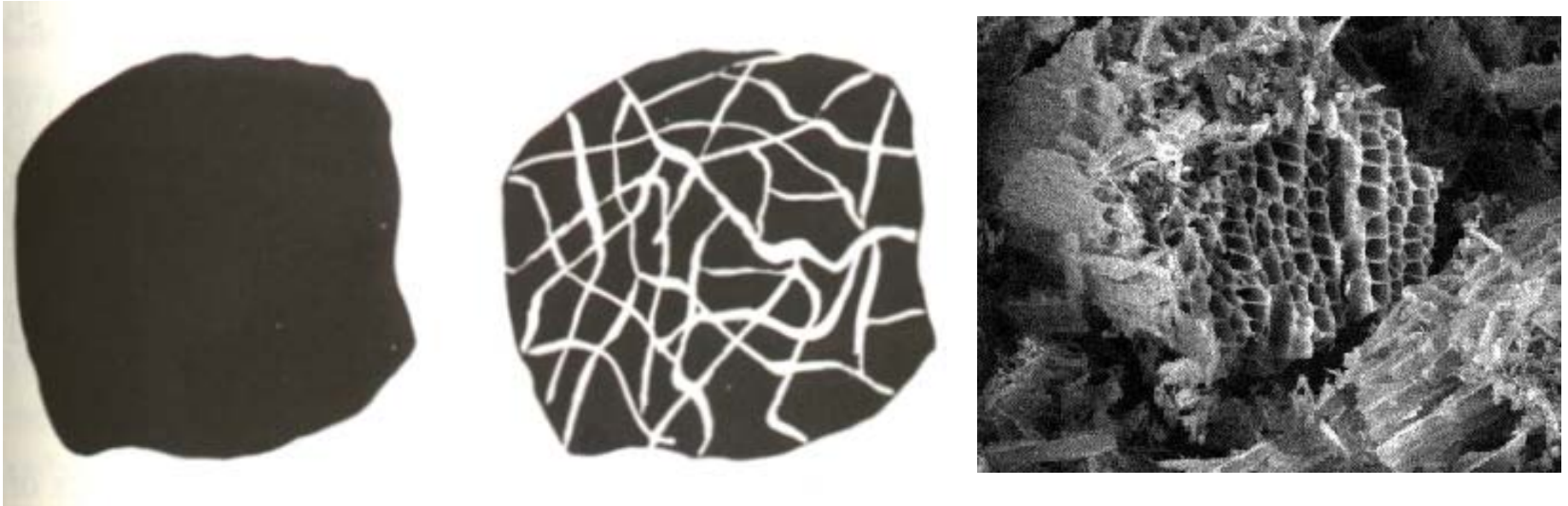
Sketch of activated carbon before and after activation and electron microscopic view of GAC

Carbon Specifications

- Iodine Number: Adsorptive rate of smaller Compounds
  - Content of Micropores 0 to 20 Å
  - Our Example: GAC 830+: 900 mg/g
- Molasses number: Ability to adsorb larger Compounds
  - Content of pores greater than 20 Å
  - Our Example: GAC 830+: 200 mg/g
- Abrasion number: Ability to withstand backwashing
- Ash content is an indication of plant/algal growth.

Activated Carbon Uses

- One of the major attributes of activated carbon treatment is its ability to remove a wide variety of toxic organic compounds to non-detectable levels (99.99%).

- Filtration

Activated Carbon Uses (cont.)

- What Types of Compounds Can and Cannot be removed by carbon
  - Readily adsorbed compounds:
    - $100 < MW < 10{,}000$
    - Aromatic compounds
    - Chlorinated compounds
    - Polynuclear aromatic
  - Poorly adsorbed compounds:
    - Low MW compounds
    - Sugars/starches
    - High MW compounds

Activated Carbon Uses

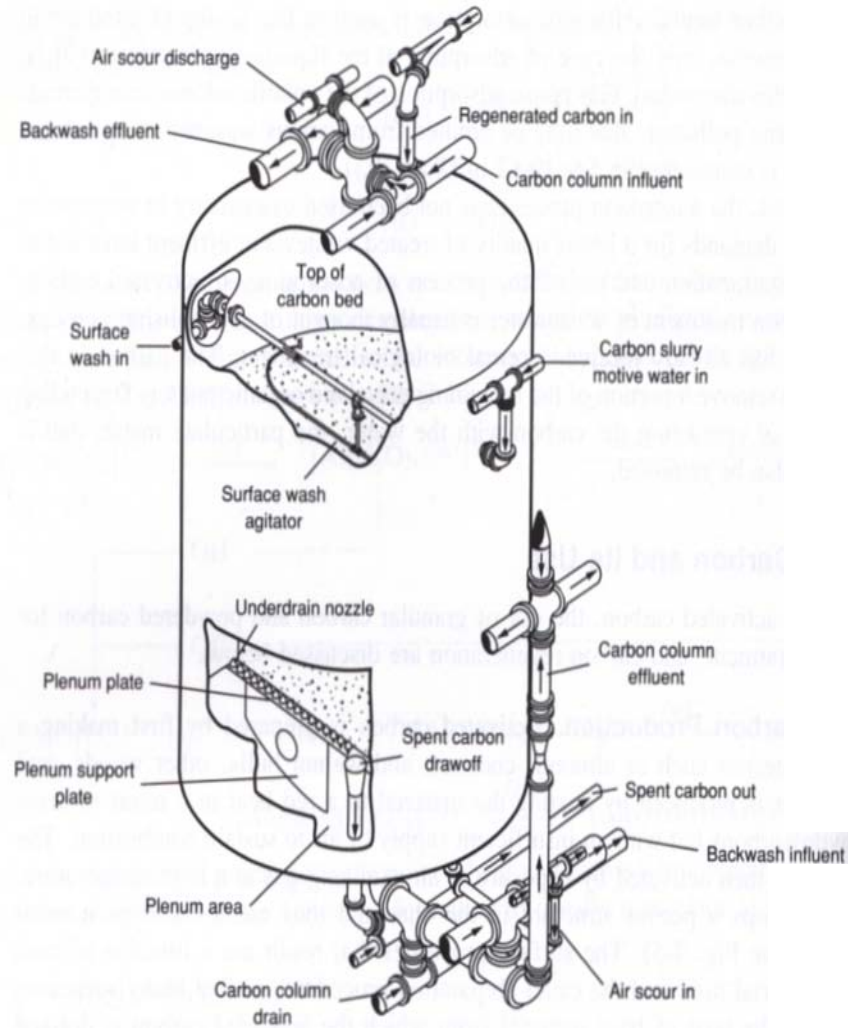| Compound | Molecular Weight | Adsorbability | |
		g compound/g carbon	Percent Reduction
Formaldehyde	30.0	0.018	9.2
Methanol	32.0	0.007	3.6
Acetaldehyde	44.1	0.022	11.9
Formic Acid	46.0	0.047	23.5
Ethanol	46.1	0.020	10.0
Acetone	58.1	0.043	21.8
Propanol	60.1	0.038	18.9
Isopropanol	60.1	0.025	12.6
Acetic Acid	60.1	0.048	24.0
Ethylene Glycol	62.1	0.136	6.8
Methyl Ethyl Ketone	72.1	0.094	46.8
Butanol	74.1	0.107	53.4
Isobutanol	74.1	0.084	41.9
Methyl Acetate	74.1	0.054	26.2
Benzene	78.1	0.080	95.0
Pyridine	79.1	0.095	47.3
Ethyl Acetate	88.1	0.100	50.5
Toluene	92.5	0.050	79.2
Phenol	94.0	0.161	80.6
Cyclohexanone	98.2	0.134	66.8
Methyl Isobutyl Ketone	100.2	0.169	84.8
Styrene	104.2	0.028	88.8
Benzaldehyde	106.1	0.188	94.0
Ethyl Benzene	106.2	0.019	84.3
Nitrobenzene	123.1	0.196	95.6
2-Ethyl Hexanol	130.2	0.138	98.5

Operating

- Adsorption depends on Detention time, pH, and what's being adsorbed

- Loading Rates
  - Hydraulic Loading rate
    - 2-10 gpm/ft2
  - Chemical Loading Rate
    - Depends on compounds and carbon
    - Chemical testing
- Carbon has a finite adsorption capacity
- When Saturated Breakthrough Occurs

Operating

- Breakthrough will release lower adsorbed compounds
- Carbon must be Regenerated or Disposed
- Valving is Extremely Important
- Pressure relief designed into the unit
- Pressure Gauges determine ΔP and unit P

GAC Column

Air scour discharge

Backwash effluent

Regenerated carbon in

Carbon column influent

Top of
carbon bed

Surface
wash in

Carbon slurry
motive water in

Surface wash
agitator

Underdrain nozzle

Carbon column
effluent

Plenum plate

Spent carbon
drawoff

Plenum support
plate

Spent carbon out

Backwash influent

Plenum area

Carbon column
drain

Air scour in

Lockheed Martin's GAC Column

Waste Water 2-20-01-C-1-25

Introduction

- Ion Exchange:
  - Ions are electrostatically attached to the surface of a resin
  - The preferred anions are exchanged for a similarly charged harmless ion
  - Metals recovered: Arsenic, cadmium, chromium, copper, gold, lead, molybdenum, nickel, radium, selenium, silver, uranium, zinc
  - Anions removed: Chromate, cyanide, nitrate, perchlorate, phosphate, sulfate

Resin Selectivity

- Selectivity Preference
  - E.g. Rohm and Haas, RH2103 resin:
  - 1. Ferrous Fe^{++}
  - 2. Cadmium cd^{++}
  - 3. Silver Ag^{++}

Types of Ion Exchange

- ## Cation Exchange
  - ### What are Cations?
    - Has an overall positive charge
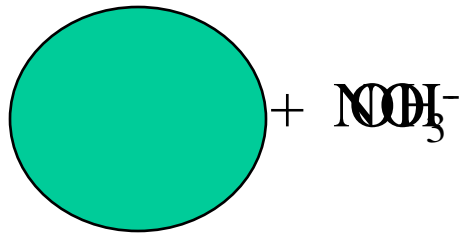
    $$M^{n+} + R^-H^+ \longrightarrow R^-M^{n+} + H^+$$

- ## Anion Exchange
  - ### What are Anions?
    - Has an overall negative charge

    $$H^+ + CrO_4^{2-} + R^+OH^- \longrightarrow R^+CrO_4^{2-} + H_2O$$

Anion Exchange Resin

$+$ NOOH$_3^-$

Cation Exchange Resin

$-$ HZn^{2+}
$-$ H$^+$
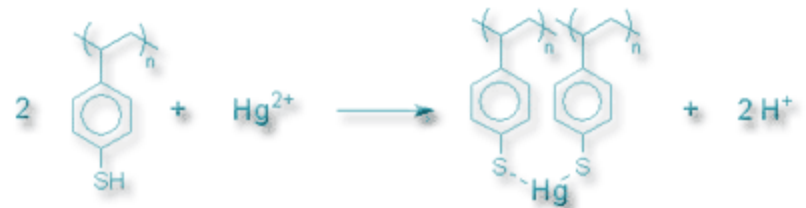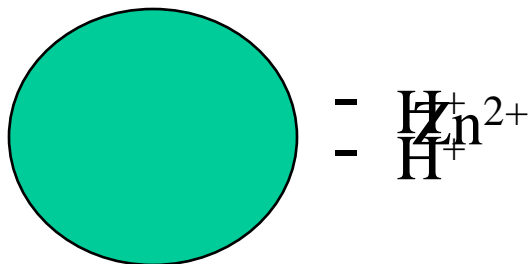
Waste Water 2-20-01-C-1-26

Operating

- Ion resins have a finite adsorption capacity
- Saturated Breakthrough Occurs
- Resin must be Regenerated or Disposed
  - Steam
  - Furnace
  - Acid or Caustic Wash
- Place a harmless ion back on the resin
- For metals, soak the column in concentrated acid
- The low pH solubilizes metals off the resin
- Remove the acid solution, now loaded with metals
- Neutralize and Precipitate the regeneration stream