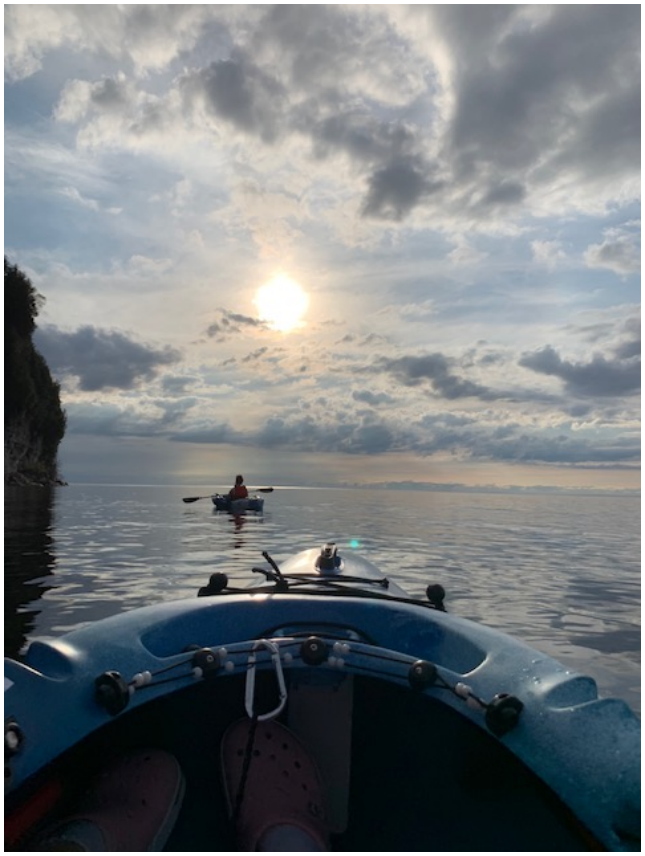
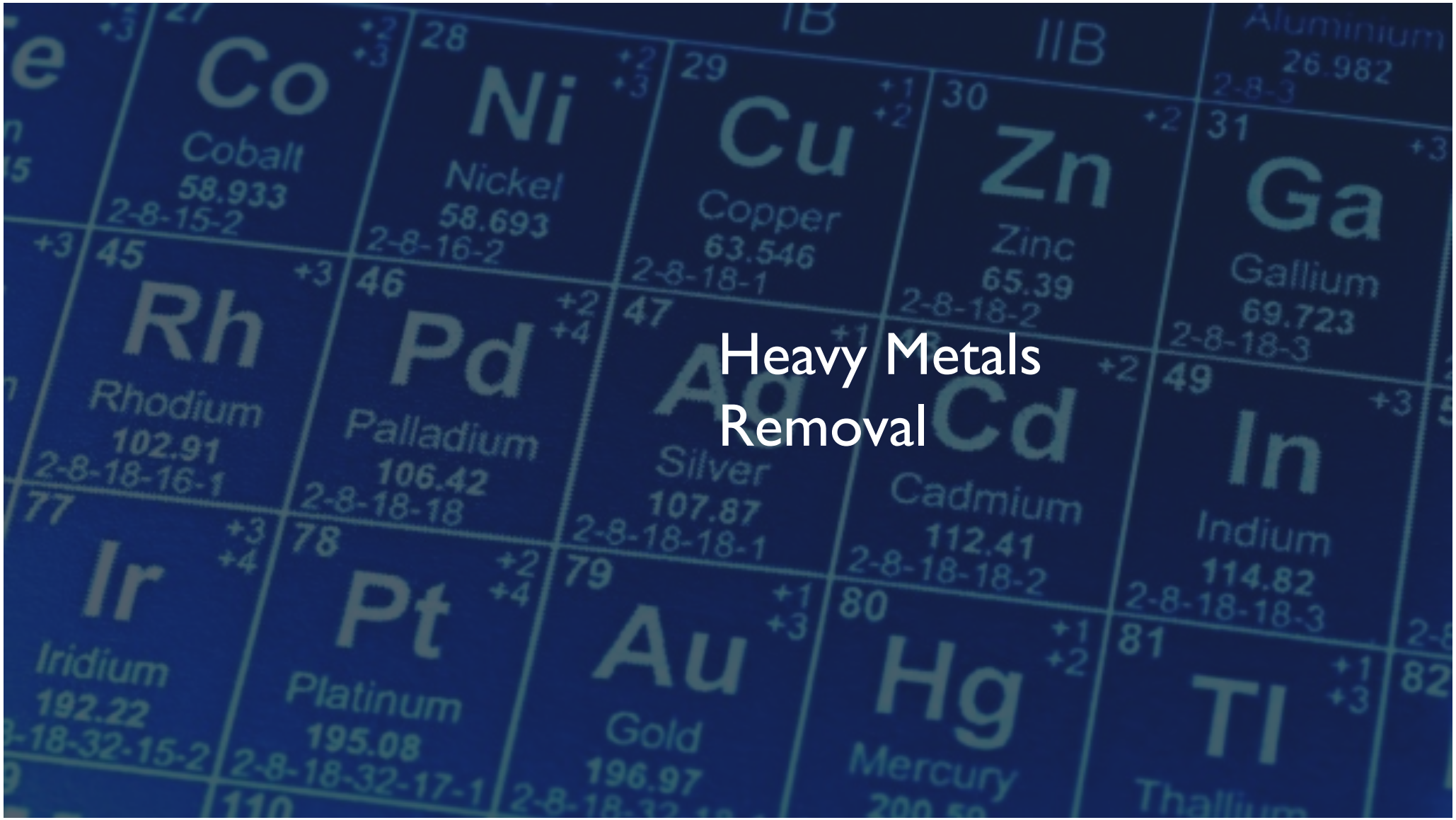
AWT

ASSOCIATION OF WATER TECHNOLOGIES

Training Seminars




Heavy Metals
Removal

INDUSTRIAL WASTEWATER 101

pH ADJUSTMENT

What does pH stand for?

In chemistry, **pH** is a numeric scale used to specify the acidity or basicity of an aqueous solution. It is approximately the negative of the base 10 logarithm of the molar concentration, measured in units of moles per liter, of hydrogen ions. More precisely it is the negative of the base 10 logarithm of the activity of the hydrogen ion.[1] Solutions with a pH less than 7 are acidic and solutions with a pH greater than 7 are basic. Pure water is neutral, at pH 7 (25 °C), being neither an acid nor a base. Contrary to popular belief, the pH value can be less than 0 or greater than 14 for very strong acids and bases respectively.[2] *(SOURCE WIKIPEDIA)*

Potential of Hydrogen

INDUSTRIAL WASTEWATER 101

pH ADJUSTMENT

INDUSTRIAL WASTEWATER 101
pH ADJUSTMENT

Fundamentals of pH

$H_20 \leftrightarrow H^+ + OH^-$

Water ↔ Hydrogen ion + Hydroxide ion

- The balance of the H^+ and OH^- determines the pH of water
  - $H^+ > OH^-$ = acidic solution
  - $H^+ < OH^-$ = basic (alkaline) solution
  - $H^+ = OH^-$ = neutral solution

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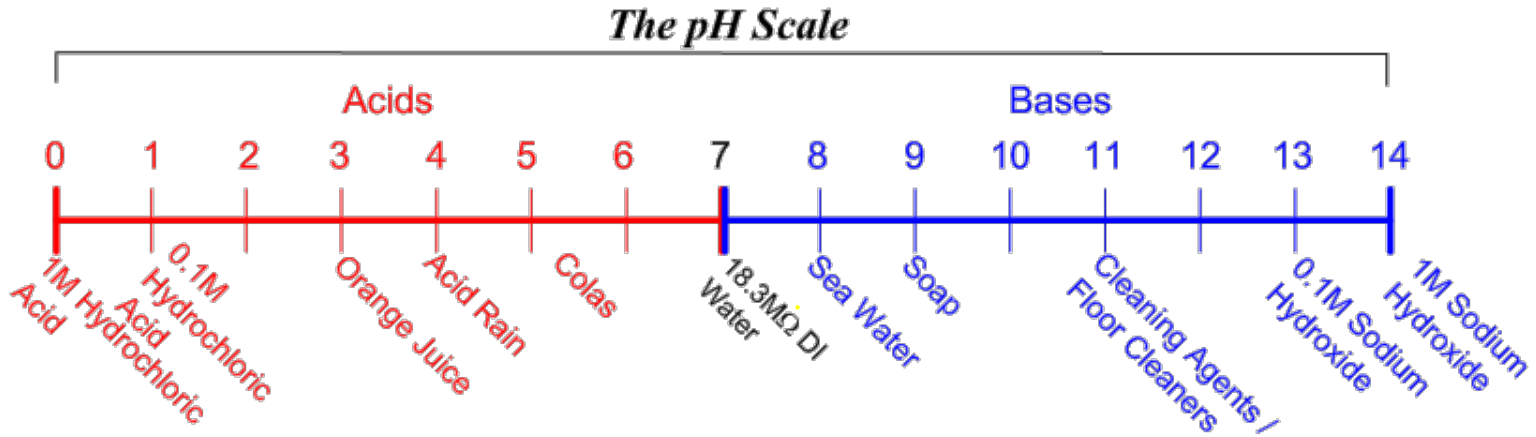
pH ADJUSTMENT



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pH ADJUSTMENT

- **pH Neutralization Reagents**
- Sulfuric Acid
- Hydrochloric acid (muriatic)
- Calcium hydroxide (lime)
- Magnesium hydroxide
- Sodium hydroxide (caustic)
- Sodium carbonate (soda Ash)

INDUSTRIAL WASTEWATER 101

pH ADJUSTMENT

HEAVY METALS REMOVAL

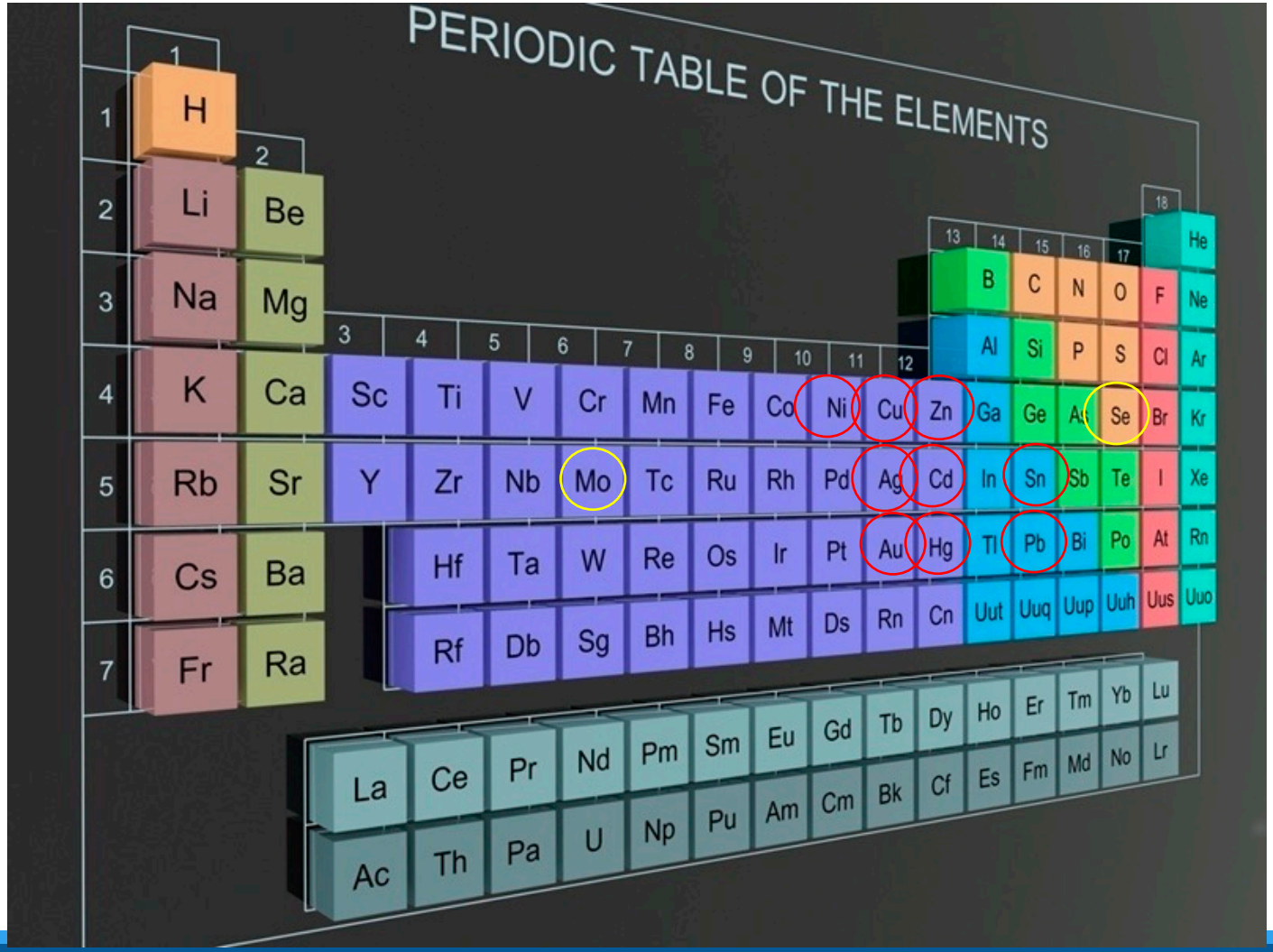
TOPICS

- What are heavy metals?
- Where do they come from?
- Why are they regulated?
- How do we remove heavy metals?
- Treatment chemicals
- Treatment equipment options
- Designing a chemical program

INDUSTRIAL WASTEWATER 101
ORGANIC TREATMENT

WHAT ARE HEAVY METALS?

A **toxic heavy metal** is any relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts. SOURCE WIKIPEDIA


PERIODIC TABLE OF THE ELEMENTS
H
Li Be
Na Mg
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Rf Db Sg Bh Hs Mt Ds Rn Cn Uut Uuq Uup Uuh Uus Uuo
B C N O F Ne
Al Si P S Cl Ar
He
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

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HEAVY METALS REMOVAL

WHERE DO THEY COME FROM?

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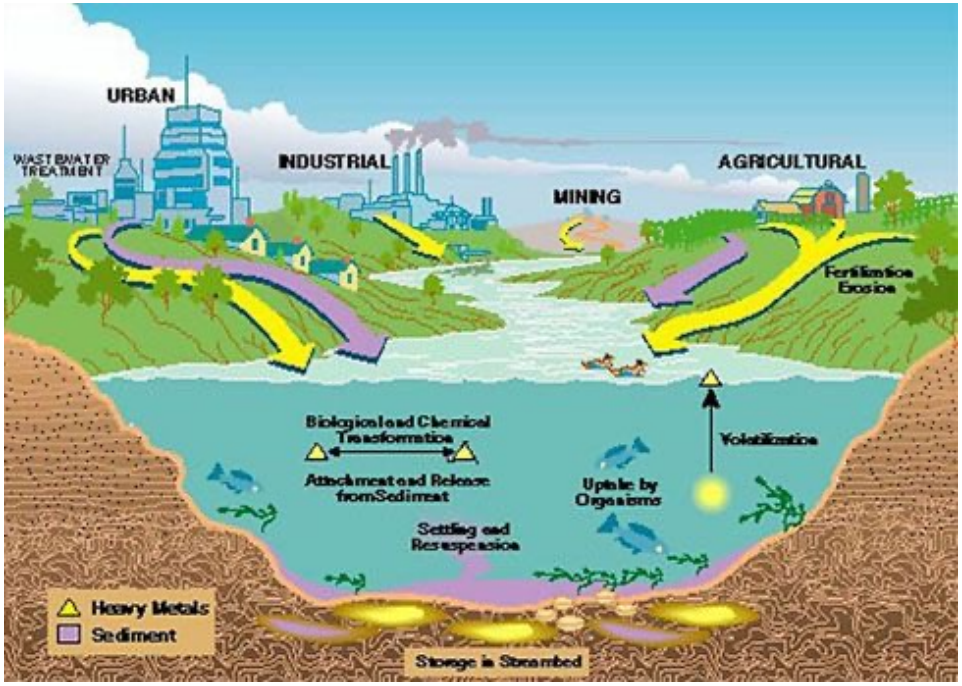
HEAVY METALS REMOVAL

WHY ARE THEY OF CONCERN?



Bioaccumulative:

Sediments

↓

Zooplankton

↓

Fish

↓

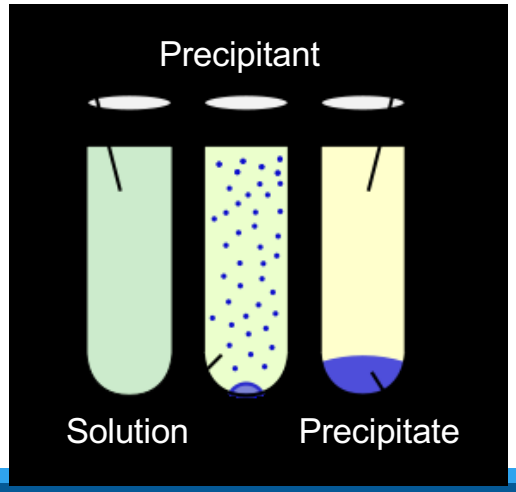
Birds
People

INDUSTRIAL WASTEWATER 101
HEAVY METALS REMOVAL

HOW DO WE REMOVE HEAVY METALS?

1. THEY MUST BE PRECIPITATED OUT OF SOLUTION

PRECIPITATION IS THE CREATION OF A SOLID FROM A SOLUTION. WHEN THE REACTION OCCURS IN A LIQUID SOLUTION, THE SOLID FORMED IS CALLED THE 'PRECIPITATE'. THE CHEMICAL THAT CAUSES THE SOLID TO FORM IS CALLED THE 'PRECIPITANT'. SOURCE WIKIPEDIA



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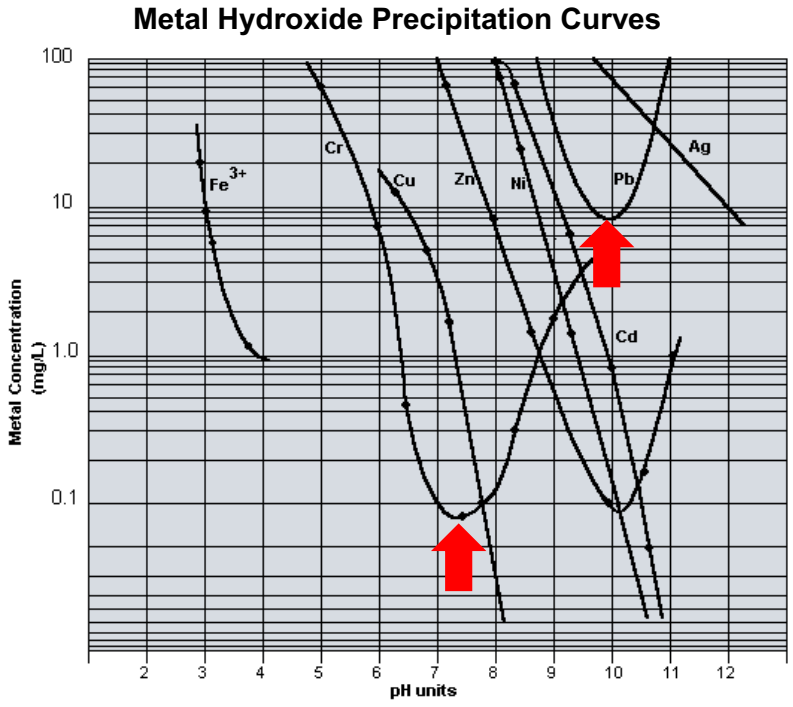
HEAVY METALS REMOVAL

HOW DO WE REMOVE HEAVY METALS?

1. THERE ARE (2) METHODS TO PRECIPITATE HEAVY METALS



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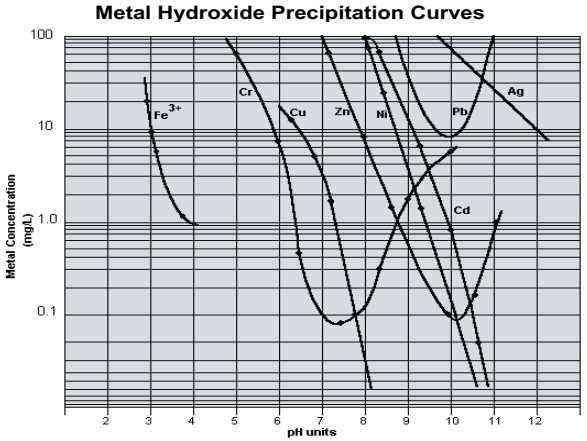
HEAVY METALS REMOVAL

HOW DO WE REMOVE HEAVY METALS?

HYDROXIDE PRECIPITATION

1. Utilizes the solubility constant (K_{sp}) for precipitation
2. Requires caustic, lime or an alkaline source. *Hint: NaOH/KOH Winter blend.*
3. Each metal has an optimum pH of minimum solubility



Some metals are amphoteric and pH is critical!!!!

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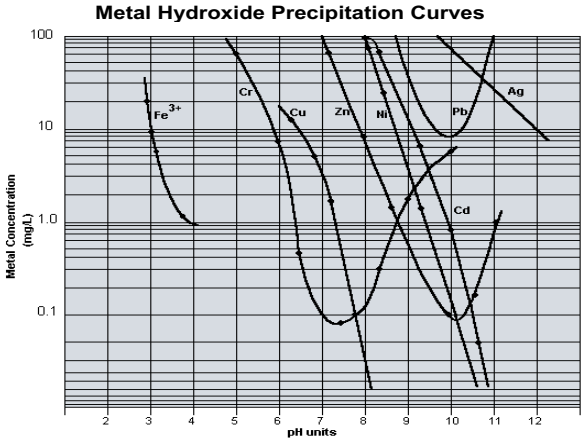
HEAVY METALS REMOVAL

HOW DO WE REMOVE HEAVY METALS?

HYDROXIDE PRECIPITATION

1. Advantages
    1. Least expensive
    2. Bulk removal

2. Disadvantages
    1. Metals can re-solubilize
    2. Creates voluminous sludge
    3. Various pH points may be needed
    4. Limited in meeting newer discharge limits.
    5. Need a pH controller and probe.



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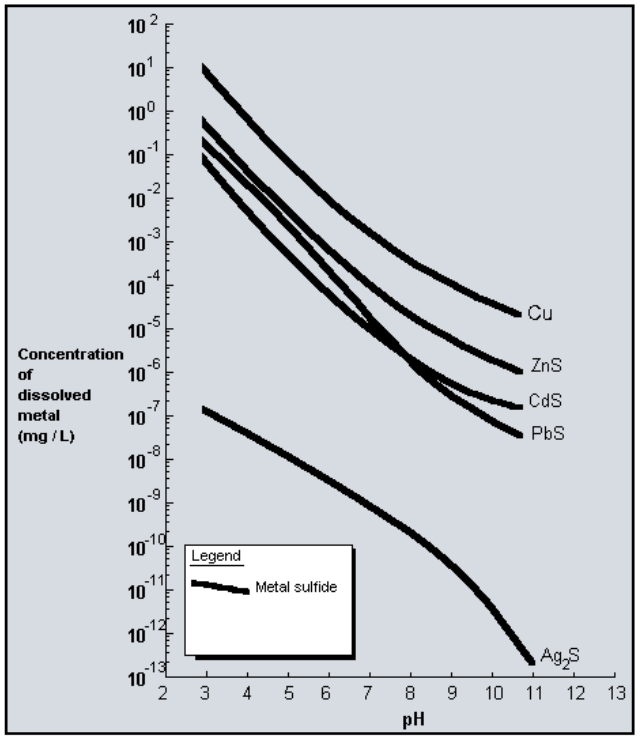
HEAVY METALS REMOVAL

- HOW DO WE REMOVE HEAVY METALS
  1. THERE ARE (2) METHODS TO PRECIPITATE HEAVY METALS

Method #2 Sulfide

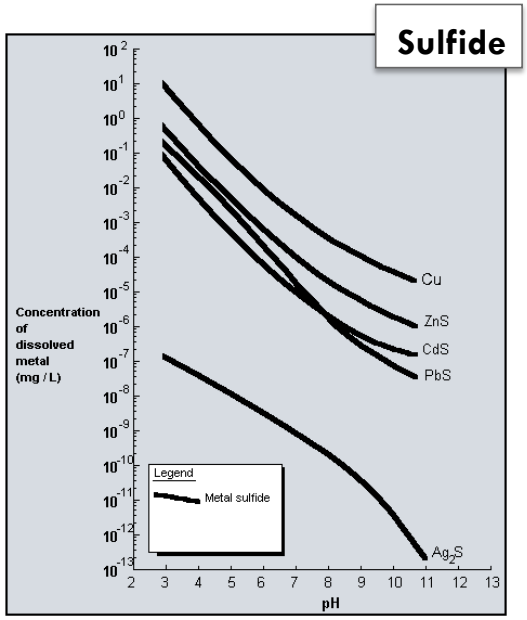


INDUSTRIAL WASTEWATER 101
HEAVY METALS REMOVAL

HOW DO WE REMOVE HEAVY METALS?

SULFIDE PRECIPITATION

1. Utilizes the solubility constant of the metal (K_{sp}) to precipitate it from water.
2. All metals form an insoluble sulfide salt.
3. Two types of sulfide
    1. Inorganic
    2. Organic



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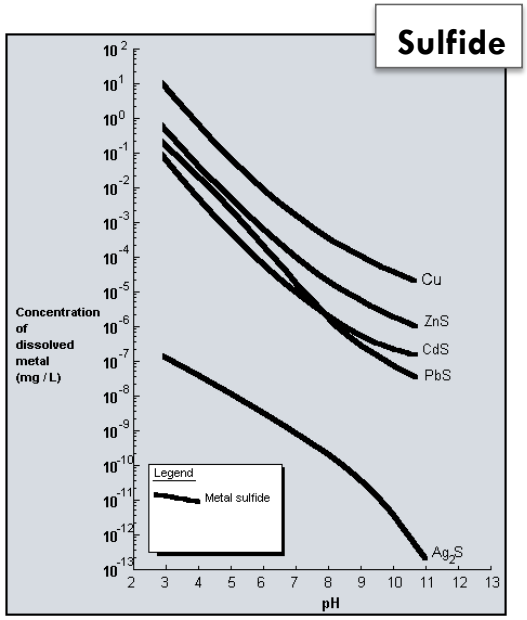
HEAVY METALS REMOVAL

HOW DO WE REMOVE HEAVY METALS?

INORGANIC SULFIDE PRECIPITATION

1. Advantages:
    1. Less pH dependent.
    2. Creates less, more compact sludge than hydroxide
    3. Metal complexes less likely to re-solubilize
2. Disadvantages:
    1. Slightly more expensive than hydroxide precipitation
    2. Environmental "odor" concerns
    3. Handling concerns



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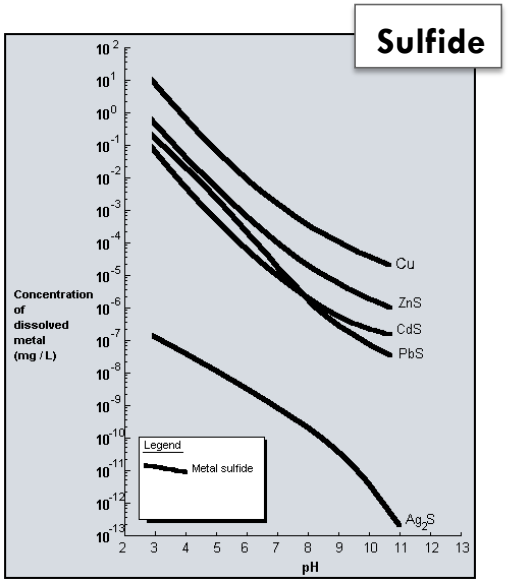
HEAVY METALS REMOVAL

HOW DO WE REMOVE HEAVY METALS?

ORGANIC SULFIDE PRECIPITATION

1. Advantages:
    1. Chelant breaker
    2. Complex metals at pH <7.
    3. Creates less sludge than hydroxide
    4. pH "independent"
    5. Metals complexes will not re-solubilize.
2. Disadvantages:
    1. Slightly more expensive than hydroxide precipitation
    2. Environmental "odor" concerns
    3. Handling concerns



INDUSTRIAL WASTEWATER 101
HEAVY METALS REMOVAL

HOW DO WE REMOVE HEAVY METALS?

1. WHAT ABOUT METALS THAT HAVE MORE THAN ONE VALENCE STATE?

In chemistry, **polyvalence** or **multivalence** refers to atoms or molecules that exhibit more than one valence (chemistry). Source Wikipedia

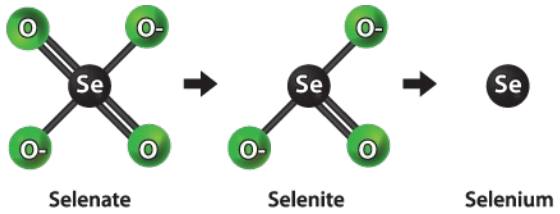
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
-	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	+1	**+2**
+3	+3	+3	**+3**	+3	**+3**	**+3**	+3	**+2**	-
-	**+4**	+4	+4	+4	+4	+4	+4	-	-
-	-	**+5**	+5	+5	-	-	-	-	-
-	-	-	**+6**	+6	+6	-	-	-	-
-	-	-	-	**+7**	-	-	-	-	-

INDUSTRIAL WASTEWATER 101
HEAVY METALS REMOVAL

HOW DO WE REMOVE HEAVY METALS?

1. WHAT ABOUT METALLOIDS LIKE SELENIUM?

1. Multivalent metaloids such as Selenium exist in (2) valence states Selenium Se^{+6} and Se^{+4}.
2. Zero valent iron (ZVI) can be used to reduce Selenium to insoluble Selenite.[2]
3. Ion exchange and RO are non-chemical alternatives.



[2] Source: Evaluation of Treatment Techniques for Selenium Removal, Kyle Smith DOW Water solutions

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HEAVY METALS REMOVAL

- HOW DO WE REMOVE HEAVY METALS

  IS THERE ANY GOOD WAY TO REMOVE MOLYBDENUM?

1. Polyvalent Molybdenum exists in 6 valence states. $Mo^{+6+5+4+3+2+0}$
2. Removal of molybdate ions from water is possible using zeolite coated with magnetite nanoparticles. [1]
3. In some instances evaporation is the only method of disposal.

[1] Source: **Removal of molybdate anions from water by adsorption on zeolite-supported magnetite,** Verbinnen B

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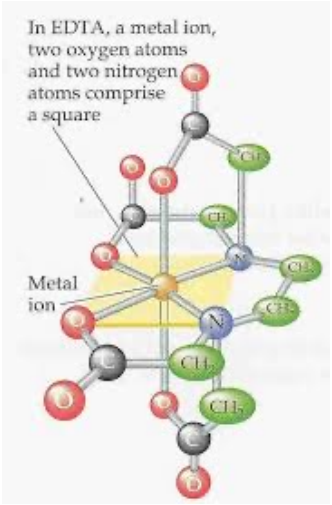
HEAVY METALS REMOVAL

HOW DO WE REMOVE HEAVY METALS?

1. WHAT ABOUT CHELANTS?

Chelation is a type of bonding of ions and molecules to metal ions. Usually these ligands are organic compounds, and are called chelants, chelators, chelating agents, or sequestering agents. Source Wikipedia

1. EDTA – Ethylenediaminetetracetate
2. Sodium Gluconate
3. Ammonia
4. Phosphorus (Hypophosphite)



HEAVY METALS REMOVAL

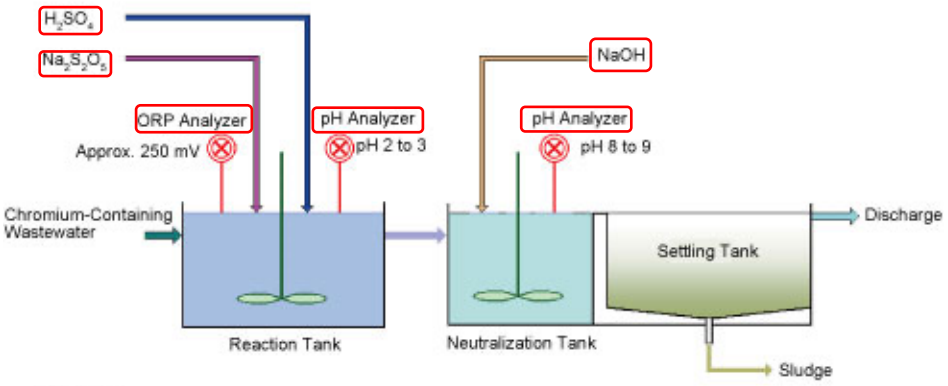
HOW DO WE REMOVE HEAVY METALS?

1. WHAT ABOUT TREATING METALS LIKE HEXAVALENT CHROME (Cr^{+6})?

The treatment of hexavalent chrome Cr^{+6} is accomplished in 2-3 steps:

1. Chrome Cr^{+6} is reduced by adding sulfuric acid pH 2-3. Sodium bisulfite is adjusted using ORP -250 mV.
2. pH is raised to 8-9 and chrome^{+3} is precipitated.

The Cr^{+6} cannot be removed until it is reduced to Cr^{+3}



Reaction
Sodium metabisulfite

$$Na_2S_2O_5 + H_2O \rightarrow 2NaHSO_3$$
$$2H_2CrO_4 + 3NaHSO_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3NaHSO_4 + 5H_2O$$
$$Na_2Cr_2O_7 + 3NaHSO_3 + 5H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 5NaHSO_4 + 4H_2O$$
$$Cr_2(SO_4)_3 + 6NaOH \rightarrow 2Cr(OH)_3 + 3Na_2SO_4$$

HEAVY METALS REMOVAL

HOW DO WE REMOVE HEAVY METALS?

WHAT ABOUT ELECTROLESS METAL PLATING COMPOUNDS?

Electroless metal plating compounds like Ni, Cu contain high levels of sodium hypophosphite and ammonia. *High, Mid and Low Phos products are typically available.*

1. Spent electroless metal plating baths can be plated out on steel wool in a process called "electrowinning"
2. If there is sufficient flow volume spent baths might also be metered slowly into a continuous flow waste stream.
3. Sludge generated from electroless plating processes may also be recycled if metals content is sufficient.

INDUSTRIAL WASTEWATER 101

HEAVY METALS REMOVAL

TREATMENT EQUIPMENT OPTIONS?

HEAVY METALS REMOVAL

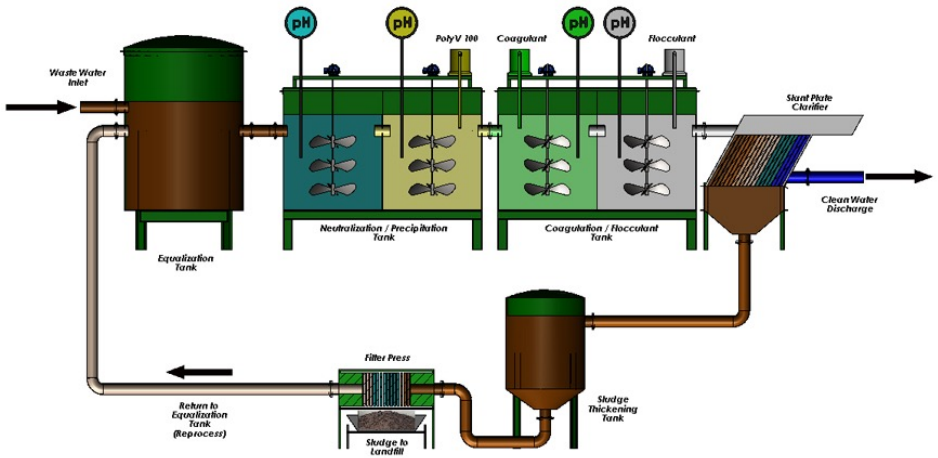
TREATMENT EQUIPMENT OPTIONS?

CONTINUOUS FLOW

1. Usually considered for larger flow volumes >10,000 GPD.
2. Addition of H+/OH- controlled by pH meter / controller.
3. Chemicals are metered in with pumps.
4. Seeding the system is an option.

Minimum 10 min. residence time for pH adjust is ideal

Typical Process Flow of a Continuous Sedimentation System

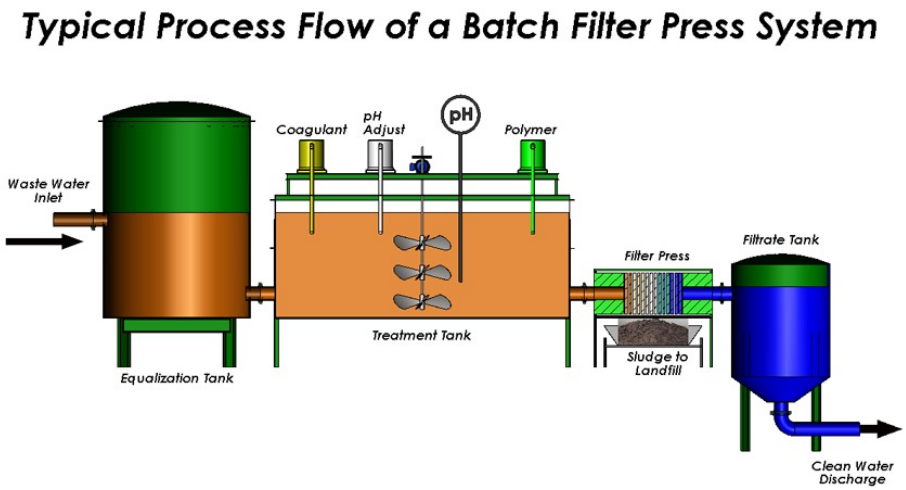


HEAVY METALS REMOVAL

WHAT ABOUT TREATMENT EQUIPMENT?

BATCH TREATMENT

1. Usually preferred for lower flows <10,000 GPD.
2. Either a holding tank and reaction tank, or two reaction tanks.
3. Reaction tanks serve also as clarifiers.
4. Allows for maximum control of effluent quality.



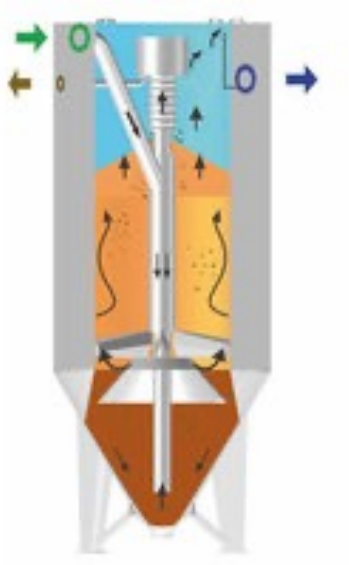
INDUSTRIAL WASTEWATER 101
HEAVY METALS REMOVAL

WHAT ABOUT TREATMENT EQUIPMENT?

SAND FILTER

In some cases it may be advantageous to have a sand filter prior to discharge:

1. Capable of removing insoluble metal hydroxides. "Solids carryover"
2. Filter can be cleaned and solids removed during backwash cycle.
3. Allows for improved control of effluent quality especially Total Suspended Solids (TSS).



Sand filters cannot remove <u>soluble</u> metals!!

INDUSTRIAL WASTEWATER 101

HEAVY METALS REMOVAL

WHAT ABOUT TREATMENT EQUIPMENT?

ION EXCHANGE RESIN

1. Ion exchange is used for recovery of precious metals
2. Specialized resin's are capable of removing troublesome metals.
3. It may also be used as a polish when discharging to surface waters requiring very low metals concentrations.

Ion Exchange Usage and Metal Concentrations	
Metal Levels	**Suggested technologies**
Above 300 ppm	RO, precipitation, most cases do not use resins
200 - 300 ppm	Cost analysis needed: Resins vs other technologies
Below 200 ppm	Resins are an economical solution
Below 1 ppm	Cost analysis needed: Resin vs trace contaminant removal media

HEAVY METALS REMOVAL

WHAT ABOUT TREATMENT EQUIPMENT?

REVERSE OSMOSIS

1. Reverse osmosis is used when discharge limits cannot be met and water reuse is the only option.
2. It may also be used in regions where water is scarce and expensive.

iSPRING WATER

REJECTION RATES

ITEMS	REJECTION RATE
Aluminum	97 - 98%
AmeobicCysts	99%
Ammonium	85 - 95%
Arsenic	94 - 96%
Asbestos	99%
Bacteria	99+%
Barium	90 - 98%
Bicarbonate	95 - 96%
Boron	50 - 70%
Bromide	93 - 96%
Cadmium	96 - 98%
Calcium	96 - 98%
Chloride	94 - 95%
Chromate	90 - 98%
Chromium	96 - 98%
Copper	97 - 99%
Cryptosporidium	99%
Cyanide	90 - 95%
Detergents	97%

ITEMS	REJECTION RATE
Ferrocyanide	98 - 99%
Fluoride	94 - 96%
Giardia	99%
Hardness	93 - 97%
Herbicides	97%
Hydrocarbons	90+%
Insecticides	97%
Iron	98 - 99%
Lead	96 - 98%
Magnesium	96 - 98%
Manganese	96 - 98%
Mercury	96 - 98%
Nickel	97 - 99%
Nitrate	93 - 96%
PCBs	97%
Pesticides	90+%
Phosphate	99+%
Polyphosphate	98 - 99%
Potassium	92 - 97%

ITEMS	REJECTION RATE
Proteins	90+%
Protozoa	99%
Pyrogen	99+%
Radioactivity	95 - 98%
Radium	97%
Sediment	99%
Selenium	97%
Silica	85 - 90%
Silicate	95 - 97%
Silver	95 - 97%
Sodium	92 - 98%
Strontium	90 - 95%
Sulfur/Sulfate	97 - 98%
Sulphite	96 - 98%
TDS	95 - 99%
THMs	90+%
Trichlorethylene	90+%
Virus	99+%
Zinc	98 - 99%

INDUSTRIAL WASTEWATER 101

HEAVY METALS REMOVAL

TREATMENT CHEMICALS

INDUSTRIAL WASTEWATER 101

HEAVY METALS REMOVAL

TREATMENT CHEMICALS

Acids

CHEMISTRY	HANDLING	COST	SLUDGE
Hydrochloric Acid (Muriatic)	Worst	Moderate	Good
Sulfuric Acid	Better	Low	Better

Bases

CHEMISTRY	HANDLING	COST	SLUDGE
Calcium Hydroxide (Lime)	Worst	Low	High
Soda Ash	Better	Moderate	Medium
Sodium Hydroxide (caustic)	Bad	High	Medium

INDUSTRIAL WASTEWATER 101
HEAVY METALS REMOVAL

TREATMENT CHEMICALS

Coagulants

CHEMISTRY	DOSAGE	Ag	Au	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Aluminum Chloride	+++	++	++	++	++	++	+++	+++	+++	++++
Aluminum Chlorhydrate	++	++	++	++	++	++	++	+++	+++	+++
Aluminum Sulfate	+++	++	++	++	++	++	+++	++	+++	++
Calcium Chloride	++++	++	++	++	++	++	++	++	++	++++
DADMAC	+	+++	+++	+++	+++	+++	+++	+++	+++	+++
Ferric Chloride/Sulfate	+++	+++	+++	++	+++	++	+++	+++	+++	++++
Ferrous Chloride/Sulfate	+++	+++	+++	++	++++	++++	++	++	+++	++
Magnesium Chloride/Sulfate	++++	++	++	++	++	++	++	++	++	+++
Polyamine	+	+++	+++	+++	+++	+++	+++	+++	+++	+++
Sodium Aluminate	++	+	+	+	+	+	+	+	+	+

INDUSTRIAL WASTEWATER 101
HEAVY METALS REMOVAL

TREATMENT CHEMICALS

Precipitants

CHEMISTRY	DOSAGE	TOXICITY	HANDLING	COST	SLUDGE	EFFECTIVENESS
Hydroxide	++++	low	corrosive	$	+++++	limited
Calcium Polysulfide	+++	Low	None	$$	+++	+++
Dimethyldithiocarbamate (DTC, carbamate)	+++	High	Hazardous	$$$	+++	+++
Diethyldithiocarbamate (DEDTC)	+++	High	Hazardous	$$$	+++	+++
Organocarbamate (DTC w/anionic polymer)	+++	Low	None	$$$$	+++	+++
Sodium Sulfide/Hydrosulfide	++	Med	Hazardous	$$	+++	++++
Tri-mercapto-s-triazine (TMT)	+++	Low	None	$$$$$	++	+
Disodium trithiocarbonate (TTC)	+++	Low	None	$$$$	+++	+++
Polythicarbonate “Thiored”	+++	Low	None	$$$	++	+++

INDUSTRIAL WASTEWATER 101
HEAVY METALS REMOVAL

TREATMENT CHEMICALS

Flocculants

CHEMISTRY	MAKE-DOWN	AGING TIME	HANDLING	COST
Anionic Emulsion	Moderate	30 min.	Worst	Moderate
Anionic Dry	Somewhat Difficult	60 min.	Better	Low
Anionic Liquid	None	None	Best	High

Medium/medium high molecular weight, medium charge is industry standard

HEAVY METALS REMOVAL

DESIGNING A CHEMICAL PROGRAM

- Treatability Study
- Sludge Handling
- Metals mix and concentration
- Ability to recycle metals (Cu, Ni)
- Future expansion

REGULATORY AFFAIRS

- Maintain good working relationship with your Federal, State and Local Regulatory Agencies

EPA United States Environmental Protection Agency