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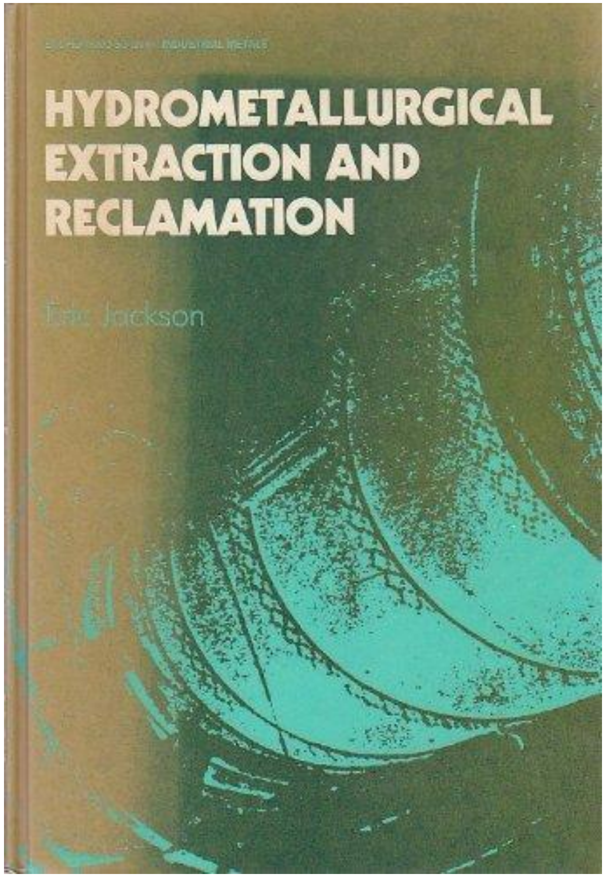

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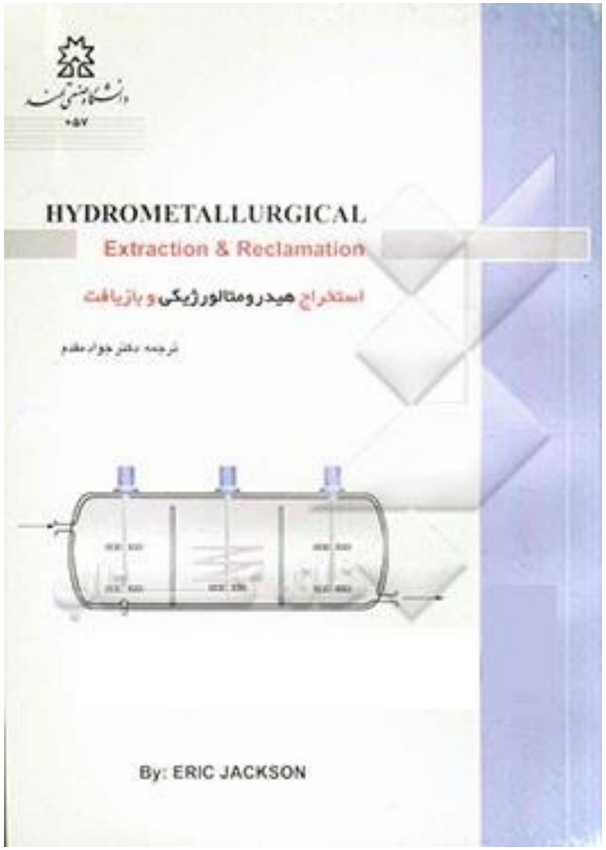

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HYDROMETALLURGICAL

Extraction & Reclamation

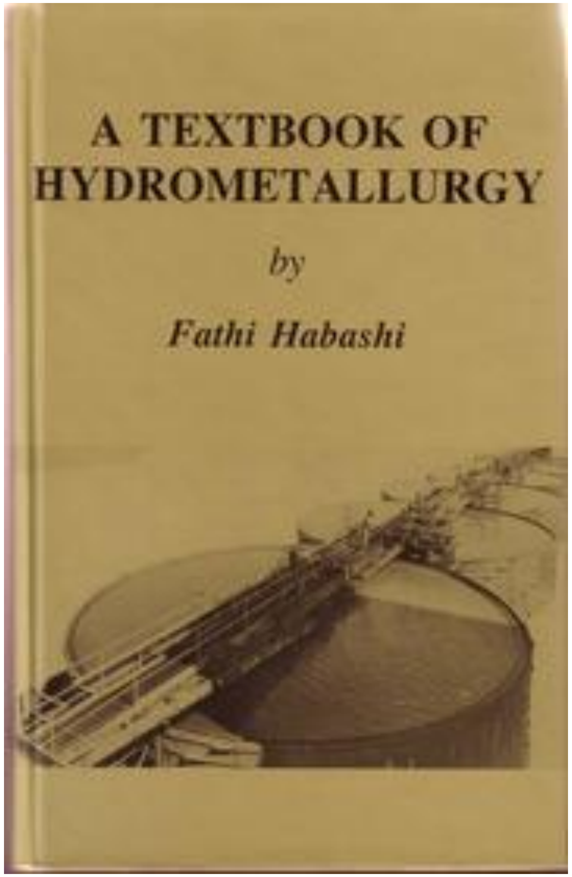
استخراج هیدرومتالورژیکی و بازیافت

ترجمه دکتر جواد مقدم

By: ERIC JACKSON

References:

A Textbook of Hydrometallurgy, Fathi Habashi, 1993



A TEXTBOOK OF
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by

Fathi Habashi

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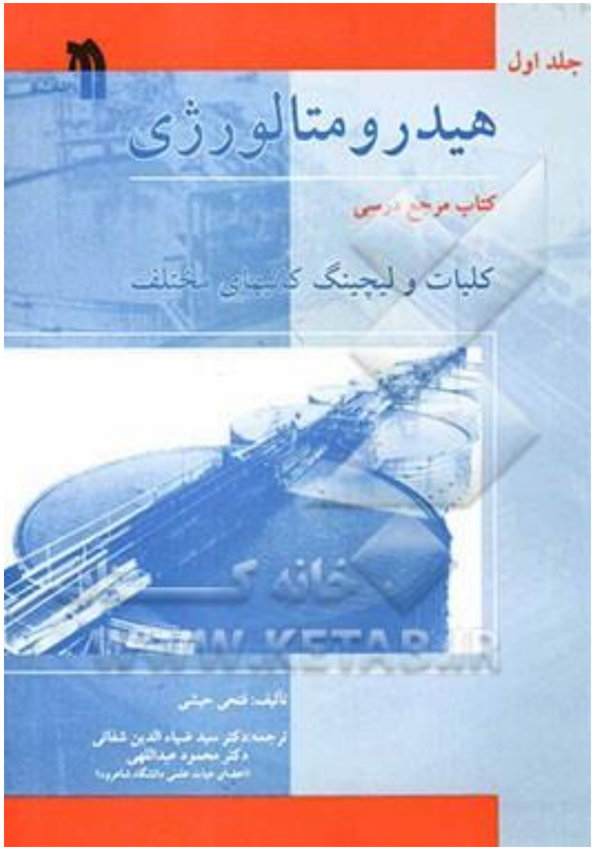

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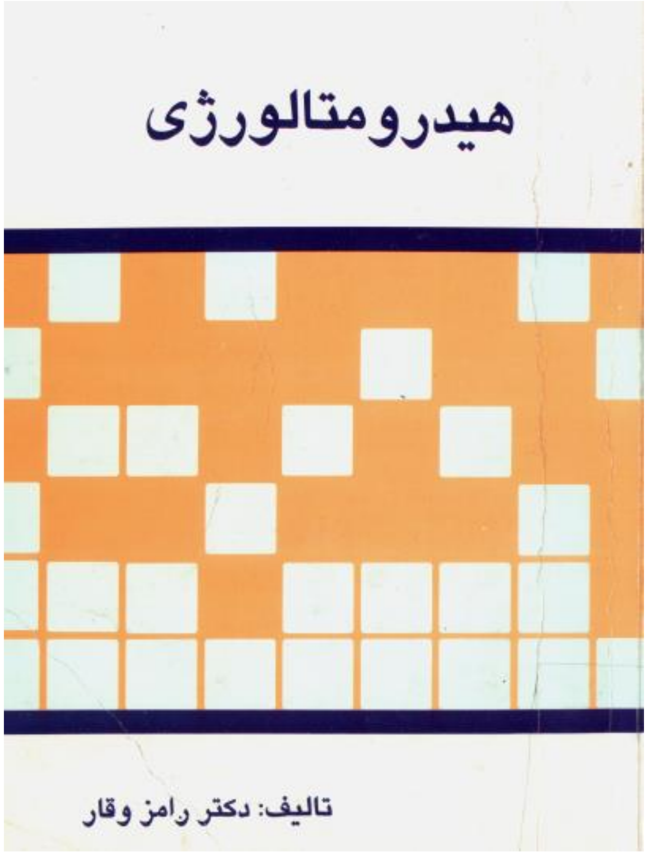

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تالیف: دکتر رامز وقار

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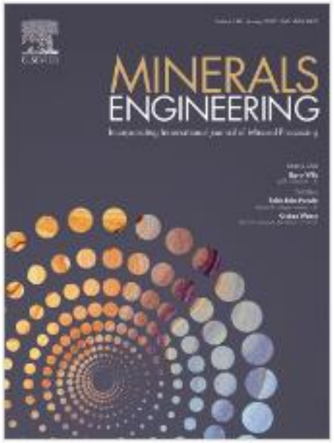


Extractive metallurgy branches:

1-Pyrometallurgy

2-Hydrometallurgy

3-Electrometallurgy

Definition of Hydrometallurgy:

Science and technology of extracting metals from ores and secondary resources by aqueous methods.

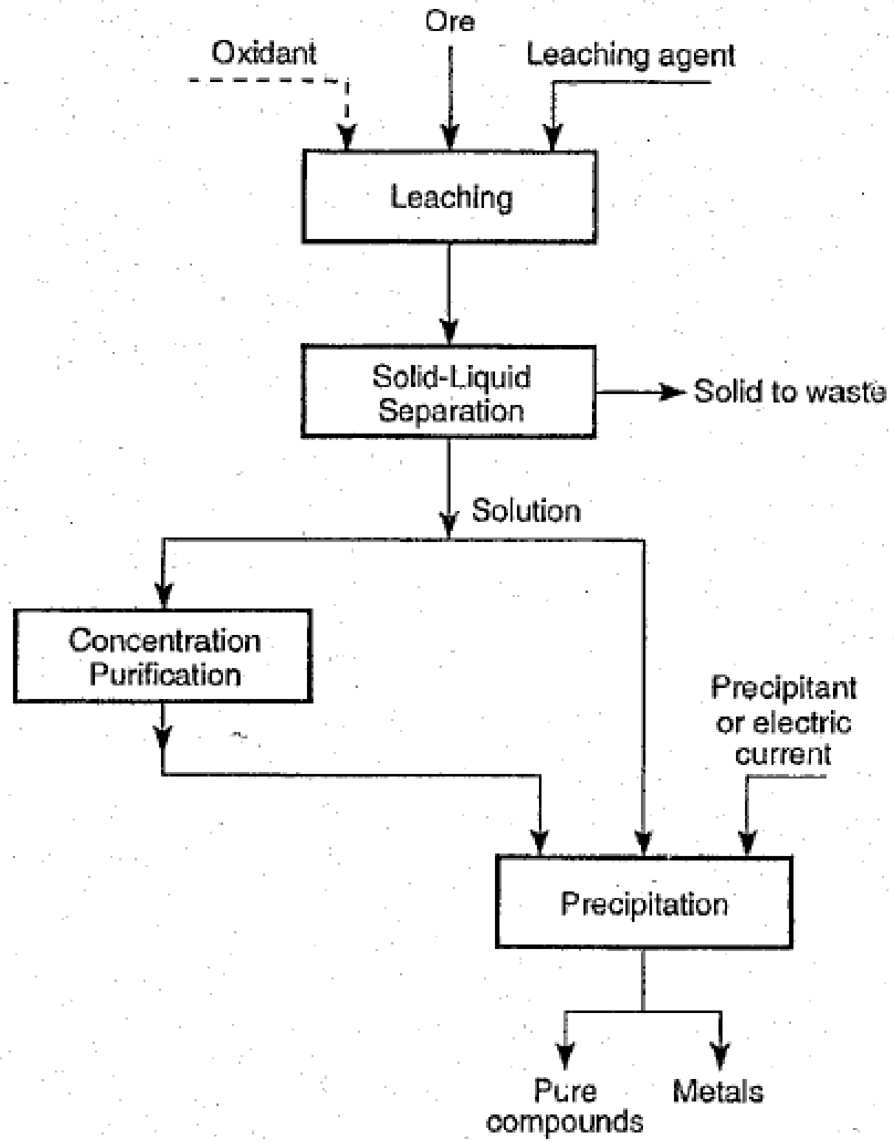
Steps of a hydrometallurgical process:

1- Leaching (dissolution of the metal values from a solid feed)

2- Purification and concentration of the solution

3- Precipitation (recovery of metal as a compound or as an element)

Steps of a hydrometallurgical process:



Hydrometallurgy versus Pyrometallurgy:

1-Sulfur dioxide generation

2-Material handling

3-Energy consumption

4-Dust formation

5- Treatment of complex ores

6-Treatment of low-grade ores

7-Waste disposal 👎

8-Economics

Leaching:

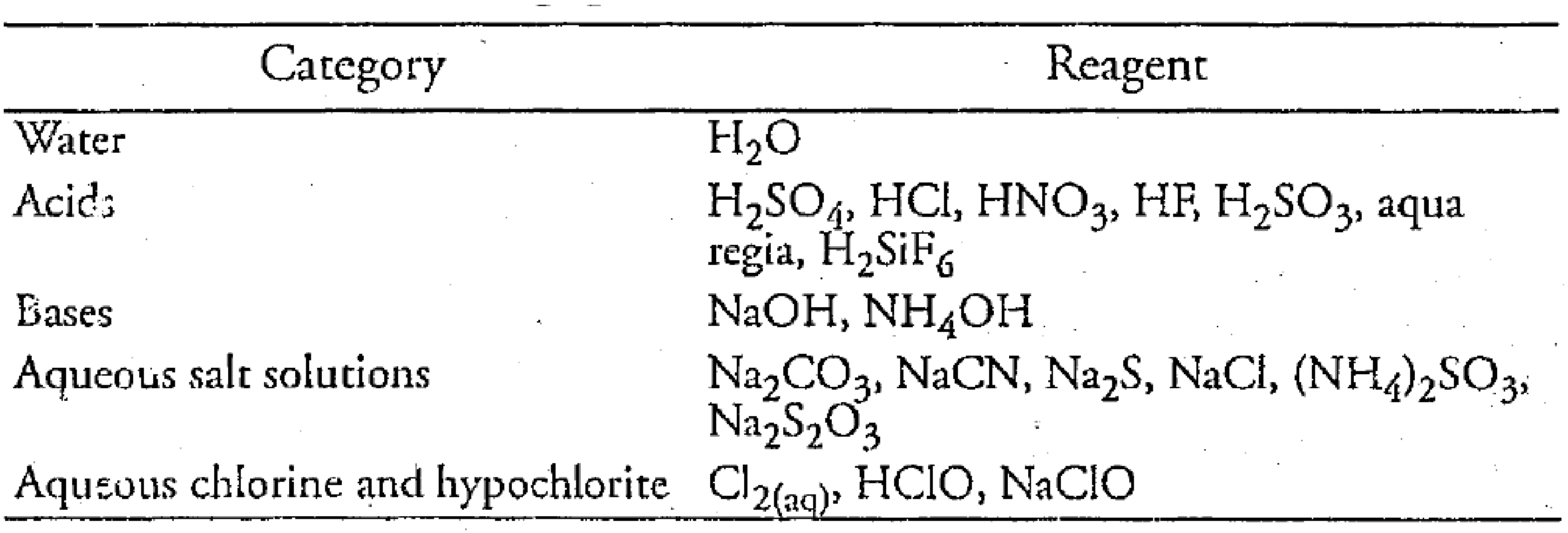
Definition: Leaching is the process of extracting a soluble constituent from a solid by means of a solvent.

Choice of a leaching agent depends on:

- Solubility
- Cost
- Materials of construction
- Selectivity
- Regeneration
- Toxicity

Leaching:

Common leaching agents:



Category	Reagent
Water	H_2O
Acids	H_2SO_4, HCl, HNO_3, HF, H_2SO_3, aqua regia, H_2SiF_6
Bases	NaOH, NH_4OH
Aqueous salt solutions	Na_2CO_3, NaCN, Na_2S, NaCl, $(NH_4)_2SO_3$, $Na_2S_2O_3$
Aqueous chlorine and hypochlorite	$Cl_{2(aq)}$, HClO, NaClO

Leaching:

Practice of leaching:

Agitation Leaching:

The leaching agent is added to the finely ground raw material such that the mixture forms a pulp that has to be agitated continuously to prevent the solids from settling and to terminate the leaching process in the shortest possible time.

Methods of agitation:

- Mechanical (using motor-driven impellers)
- Peneumatic (using air or steam)[Pachuca Tank]

Pressure and Temperature conditions of Agitation Leaching:

- Ambient pressure
  - ➢In open vessels at ambient or moderate temperature
  - ➢At a temperature near the boiling point of the solution with the reflux condenser to prevent the loss of vapors.
- Pressure leaching

Leaching:

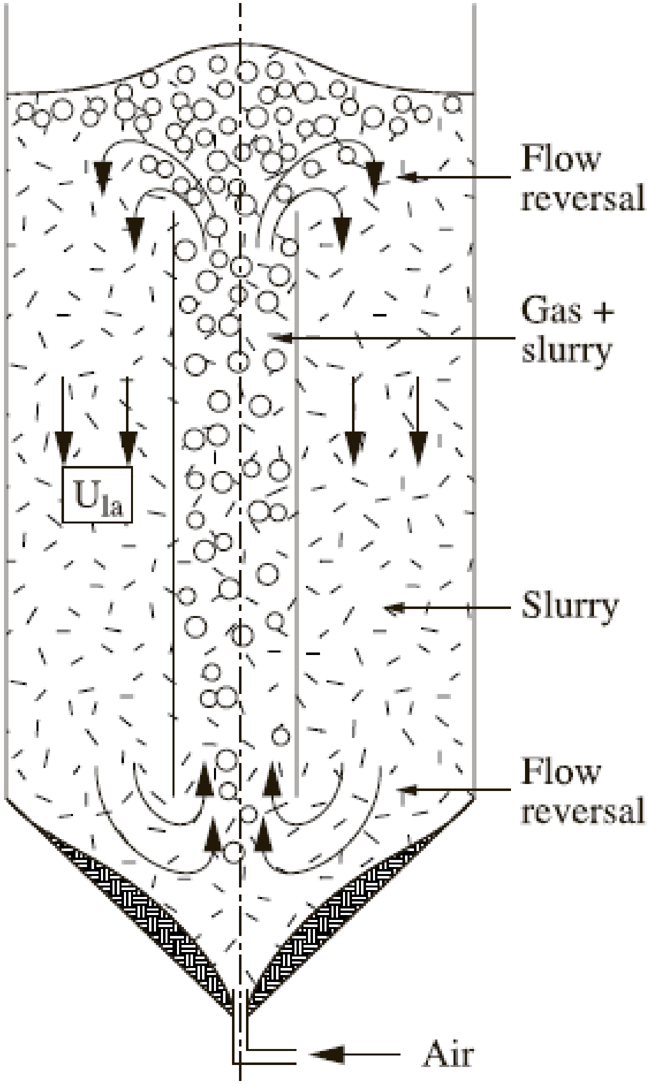
Practice of leaching:

- Mechanical agitated leaching tank

Leaching:

Practice of leaching:

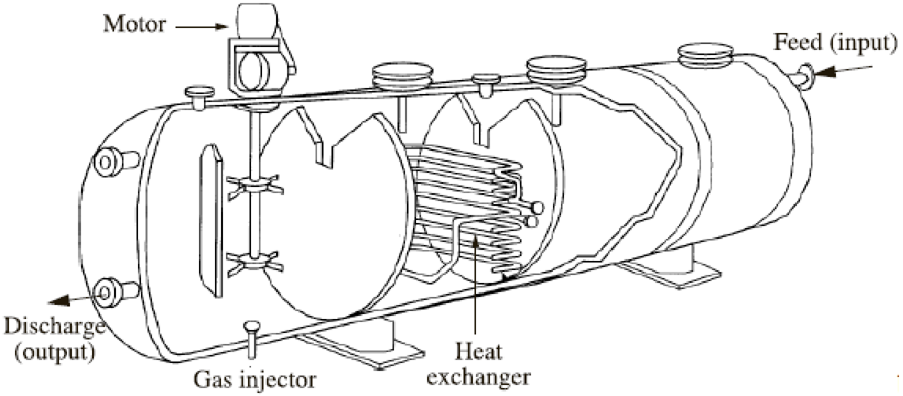
- Pachuca tank



Leaching:

Practice of leaching:

- Pressure Leaching in autoclave



Leaching:

Practice of leaching:

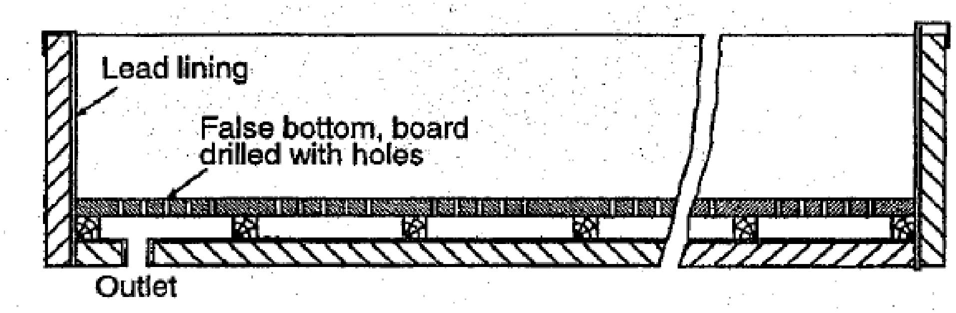
Percolation or vat Leaching:

- This method is applied to relatively low-grade ores of coarse particle size. The ore is leached in large vats or tanks which are often fitted with filter-type bottoms to facilitate solution flow through the ore bed.
- The material to be leached is placed in a tank. The leach solution is added at the top of the tank and is allowed to percolate through the material.
- Tanks having a capacity of 12000 tons of ore are in common use.
- Leaching time varies from 2 to 4 days.
- Advantages: minimum reagent consumption, the production of concentrated pregnant solution, and elimination of the use of expensive filtration processes .

Leaching:

Practice of leaching:

Percolation or vat Leaching:



Leaching:

Practice of leaching:

Heap and dump Leaching:

- Heap and dump leaching are similar in operation but differ in the type and amount of material being leached.
- In heap leaching, mined low-grade ores are broken and piled into relatively small heaps (up to 100,000 tones) on impervious ground, or on a concreted or asphalted or rubber surface with slight inclination and drainage channels and pipes to carry away the pregnant solution to a collecting pond.
- Dumps attain a greater scale and usually consist of mine wastes that may still contain sufficient value minerals for treatment to be profitable.

Leaching:

Practice of leaching:

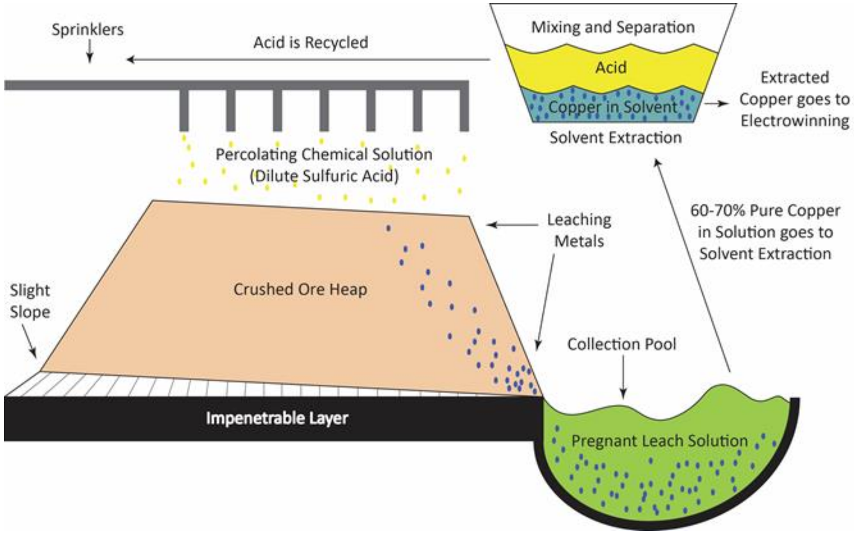
Heap and dump Leaching:

- Leach solution is fed periodically by sprays over the heaps or dumps or through perforated pipes let into the material or via lagoons formed on the heaps.
- Leaching periods may extend for months in the case of heaps, whereas the coarse dump material may require several years.
- Dump and heap leaching have been applied extensively for low grade copper ores and recently for gold and uranium ores.

Leaching:

Practice of leaching:

Heap and dump Leaching:

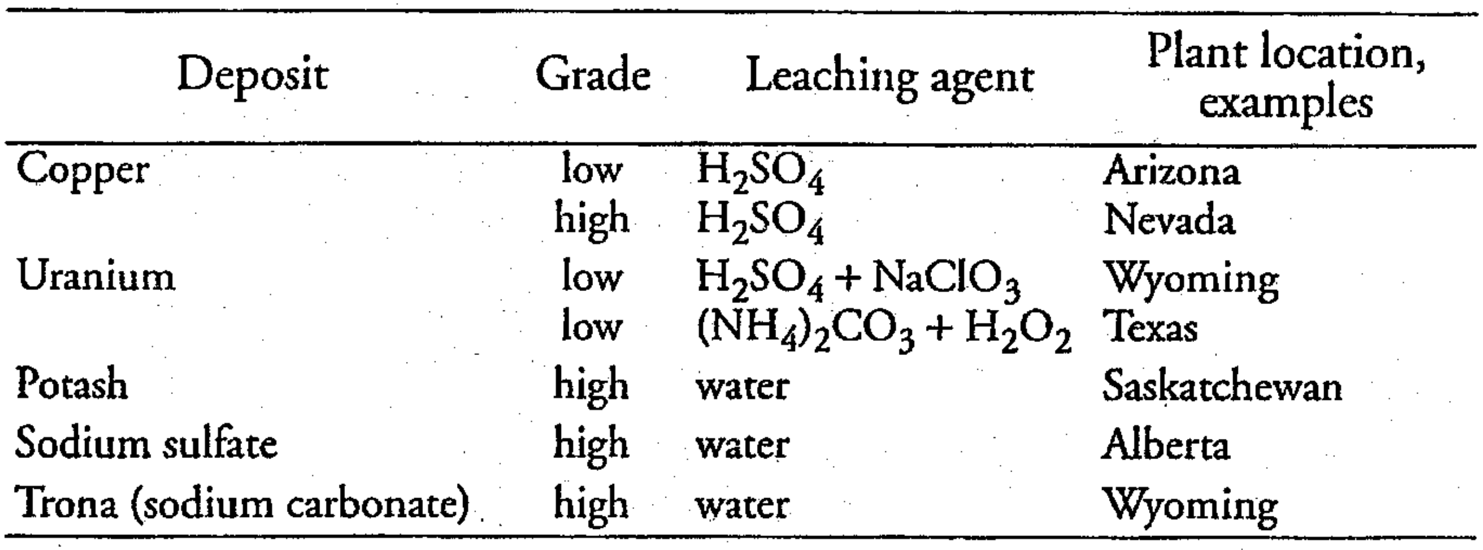


Leaching:

Practice of leaching:

In-situ Leaching (Solution mining):

- It involves dissolving selectively the mineral values by spraying or injecting the leaching agent in the deposit, then collecting the pregnant solution.
- It is applied for extracting soluble salt deposits from the underground as well as uranium and copper ores.



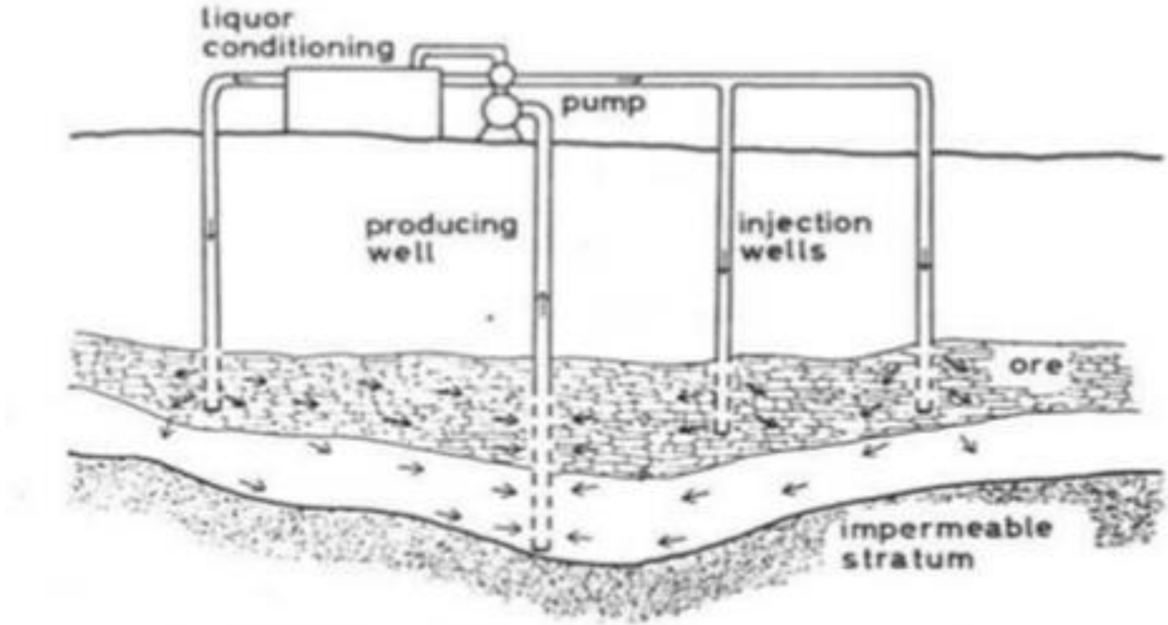
Deposit	Grade	Leaching agent	Plant location, examples
Copper	low	H_2SO_4	Arizona
	high	H_2SO_4	Nevada
Uranium	low	$H_2SO_4 + NaClO_3$	Wyoming
	low	$(NH_4)_2CO_3 + H_2O_2$	Texas
Potash	high	water	Saskatchewan
Sodium sulfate	high	water	Alberta
Trona (sodium carbonate)	high	water	Wyoming

Leaching:

Practice of leaching:
In-situ Leaching (Solution mining):

The basic criteria required for an underground deposit to be considered suitable for in-situ leaching:

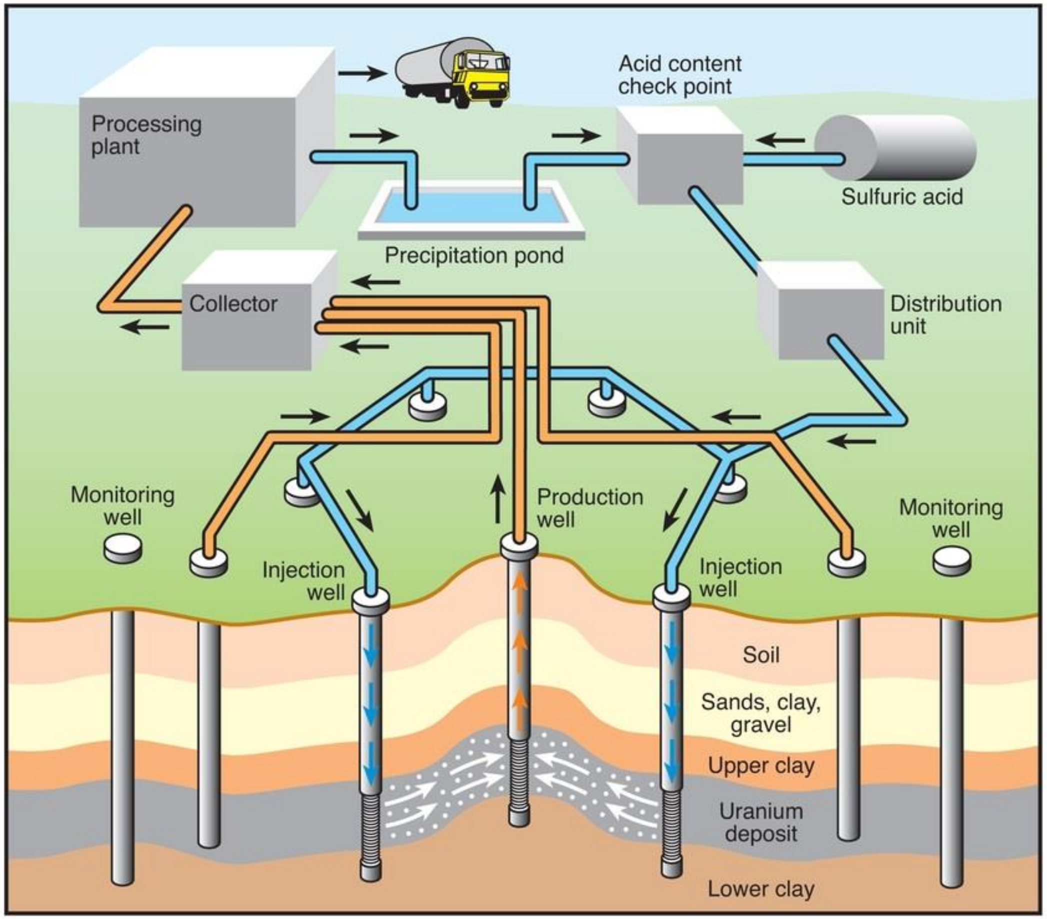
- The ore body must be enclosed between impermeable strata that will prevent the loss of solution
- It must be permeable to the leaching solution.

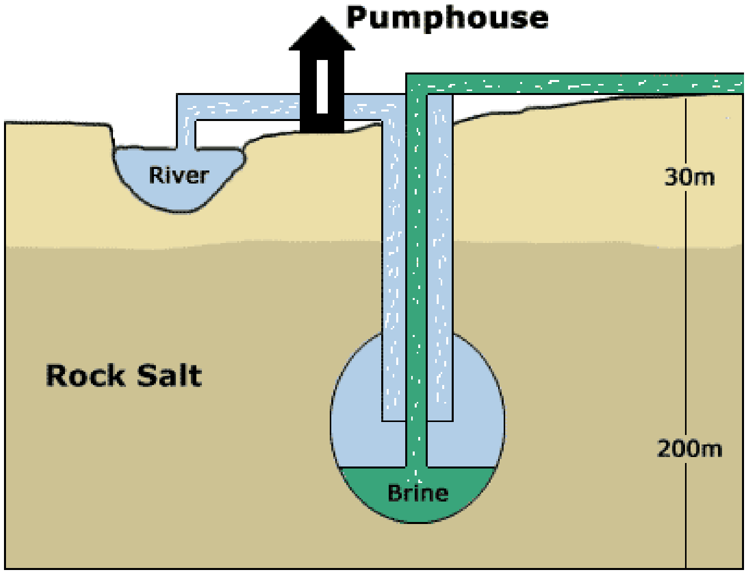


Leaching:

Practice of leaching:

In-situ Leaching (Solution mining):





Leaching:

Types of leaching reactions:

Dissolution reaction types:

A- physical

The solvent is water and applies mainly for ionic solids. There is no chemical transformation

$$Na^+Cl^-_{(s)} + (n + m)H_2O \rightarrow Na(H_2O)^+_{n(aq)} + Cl(H_2O)^-_{m(aq)}$$

Physical processes are strongly influenced by the speed of agitation but less influenced by temperature.

B- Chemical:

Dissolution of ionic or covalent solids with the strong lattice bonds may not done by water alone. These solids may be solubilized in the presence of a certain reagent in solution. Electron transfer does not occur for the element being leached.

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$$

$$PbSO_4 + 4Cl^- \rightarrow [PbCl_4]^{2-} + SO_4^{2-}$$

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$$

Leaching:

Types of leaching reactions:

Dissolution reaction types:

C- Electrochemical

There is a transfer of electrons, i.e. the process involved an oxidation-reduction couple. The oxidation and the reduction reactions proceed simultaneously.

- Reductive leaching

The metal converts to a soluble ion as a result of a cathodic reaction or reduction.

+4

$$UO_{2(s)} + e + 4H^{+} = U^{3+}_{(aq)} + 2H_2O$$

+3

- Oxidative leaching

The metal converts to a soluble ion as a result of a anodic reaction or oxidation.

+4

$$UO_{2(s)} = UO^{2+}_{2(aq)} + 2e$$

+6

Leaching:

Reductive leaching processes:
Reductive leaching of pyrolusite with H_2SO_3 (SO_2 injection into dilute sulfuric acid)

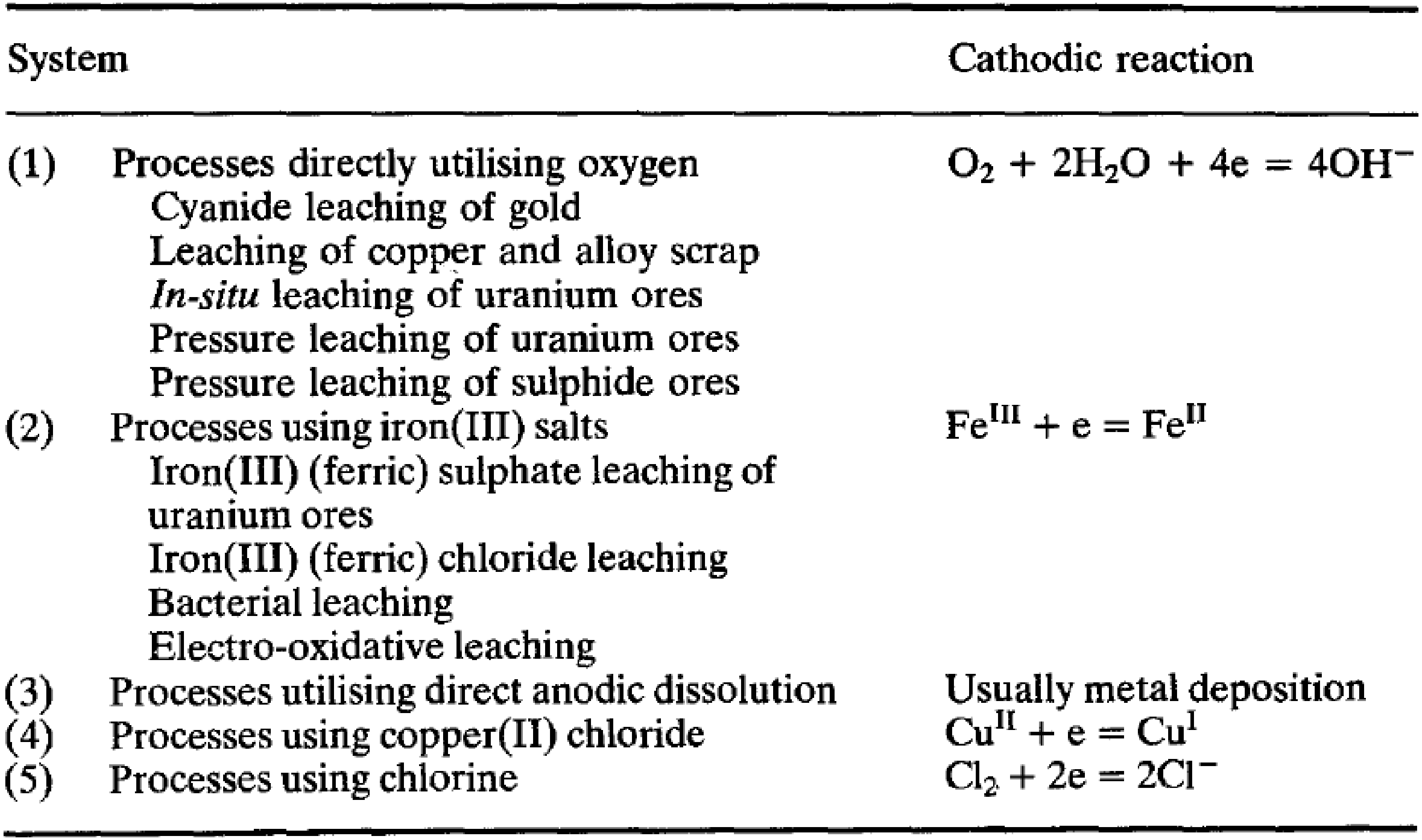
$$\begin{array}{ll} \text{cathodic process} & MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O \\ \text{anodic process} & H_2SO_3 + H_2O = SO_4^{2-} + 4H^+ + 2e \\ \cline{2-2} \text{overall process} & MnO_2 + H_2SO_3 = Mn^{2+} + H_2O + SO_4^{2-} \\ \cline{2-2} \end{array}$$

Reductive leaching of pyrolusite with Fe^{2+} ($FeSO_4$ from Waste sulfuric acid pickling liquors):

$$\begin{array}{ll} \text{cathodic process} & MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O \\ \text{anodic process} & 2Fe^{2+} = 2Fe^{3+} + 2e \\ \cline{2-2} \text{overall process} & MnO_2 + 2Fe^{2+} + 4H^+ = Mn^{2+} + 2Fe^{3+} + 2H_2O \\ \cline{2-2} \end{array}$$

Leaching:

Oxidative leaching processes:



System		Cathodic reaction
(1)	Processes directly utilising oxygen	$O_2 + 2H_2O + 4e = 4OH^-$
	Cyanide leaching of gold	
	Leaching of copper and alloy scrap	
	In-situ leaching of uranium ores	
	Pressure leaching of uranium ores	
	Pressure leaching of sulphide ores	
(2)	Processes using iron(III) salts	$Fe^{III} + e = Fe^{II}$
	Iron(III) (ferric) sulphate leaching of uranium ores	
	Iron(III) (ferric) chloride leaching	
	Bacterial leaching	
	Electro-oxidative leaching	
(3)	Processes utilising direct anodic dissolution	Usually metal deposition
(4)	Processes using copper(II) chloride	$Cu^{II} + e = Cu^{I}$
(5)	Processes using chlorine	$Cl_2 + 2e = 2Cl^-$

Leaching:

Oxidative leaching processes:

Cyanide leaching of gold

One of the earliest devised leaching processes in which oxygen participates via the atmosphere involves the dissolution of gold by alkaline cyanide solutions

$$4Au + 8CN^- = 4Au(CN)_2^- + 4e$$

$$O_2 + 2H_2O + 4e = 4OH^-$$

$$4Au + 8CN^- + O_2 + 2H_2O = 4Au(CN)_2^- + 4OH^-$$

At the Vaal Reef mine of the Anglo-American Corporation of South Africa the ore, after grinding to -200 mesh (-75 µm), is leached in a series of Pachuca tanks with dilute sodium cyanide using air agitation. The residence time of the pulp in the tanks is 12-14 hours.

A recent development in the extraction of gold and silver have been the heap leaching of low-grade ores.

Leaching:

Oxidative leaching processes:

Pressure leaching of sulfide ores

Sphalerite, ZnS is leached at 150°C and 7 atm oxygen pressure using dilute sulfuric acid. This process which is now used in Canada solves the problem of SO_2 emission and production of excess sulfuric acid. Elemental sulfur is liquid at these temperatures. Special surfactant are needed to prevent the adhesion of liquid sulfur on the surface of ZnS particles.

$$ZnS \rightarrow Zn^{2+} + S + 2e^-$$
$$^1/_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

$$ZnS + 2H^+ + {}^1/2O_2 \rightarrow Zn^{2+} + S + H_2O$$

Leaching:

Oxidative leaching processes:

Ferric sulfate leaching of uranium ores

An acidic iron (III) sulfate leaching process is extensively used for uranium(IV) ores. Manganese dioxide or sodium chlorate is used to regenerate the iron(III).

Anodic reaction $UO_2 = UO_2^{2+} + 2e$

Cathodic reaction $FeSO_4^{+} + e = Fe^{2+} + SO_4^{2-}$

iron(III) regeneration

$$2Fe^{2+} + MnO_2 + 2H_2SO_4 = Mn^{2+} + 2FeSO_4^{+} + 2H_2O$$

Milled ores are usually treated by vat or agitation leaching with the dilute sulfuric acid typically using Pachuca tanks.

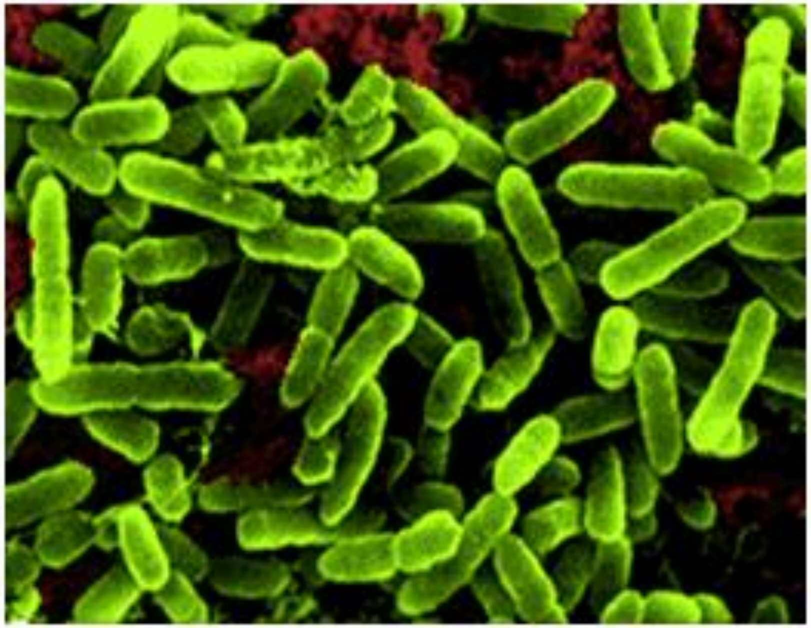
There is generally sufficient iron in the ore to provide an adequate concentration of iron(III) in solution and up to ~4.5 kg of manganese dioxide per ton of ore may be used.

Leaching:

Oxidative leaching processes:

Bacterial leaching(Bioleaching)

A significant amount of geological weathering is due to microbiological degradation processes and the most important of is the mineral oxidative dissolution brought about by the acidophilic bacteria, Thiobacillus ferro-oxidans and Thiobacillus thio-oxidans.



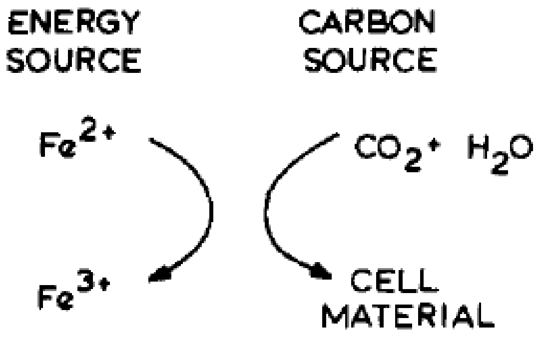
Leaching:

Oxidative leaching processes:

Bacterial leaching(Bioleaching)
Atmospheric natural leaching reactions like these are very slow:

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ = 2Fe^{3+} + H_2O$$

Thiobacillus ferro-oxidans is capable of promoting the reaction at a significantly greater rate. This reaction is a source of energy for the bacteria and they are capable of utilizing CO_2 for cell building in a process analogous to photosynthesis.



Leaching:

Oxidative leaching processes:

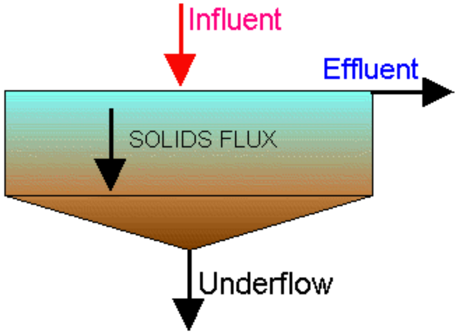
Bacterial leaching(Bioleaching)
The Thiobacillus thio-oxidans derives energy from the oxidation of elemental sulphur and $S_20_3^{2-}$, and hence converts the sulfur released in leaching reactions like $\mathrm{CuS = Cu^{2+} + S^{\circ} + 2e}$ to sulfuric acid.

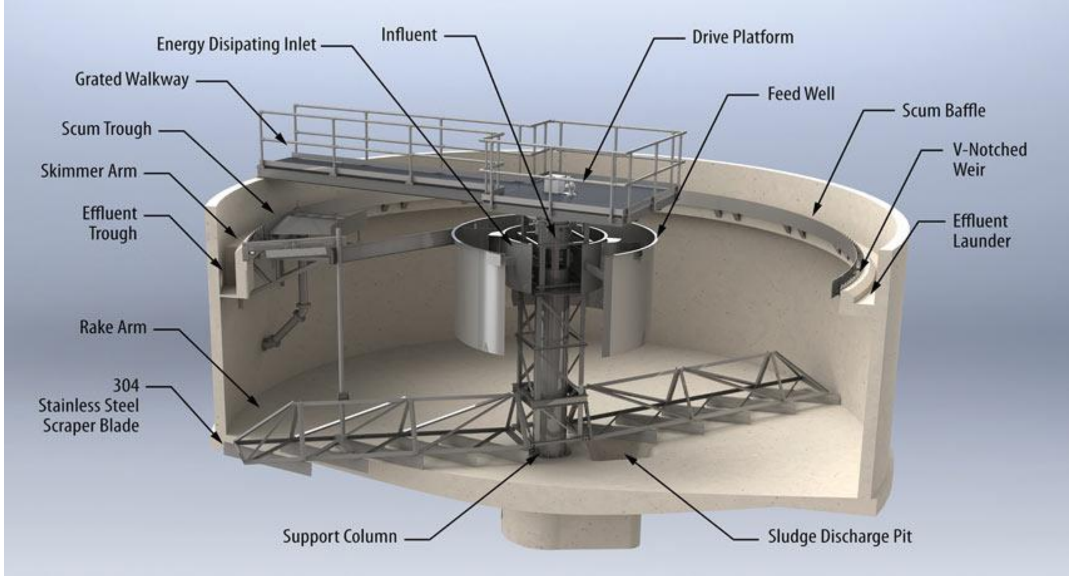
By the act of bacteria: $\mathrm{2S + 3O_2 + 2H_2O = 2H_2SO_4}$

The thiobacilli can tolerate high concentrations of metal ions by adaptation and are only active in acidic conditions of pH 1-3.5. Above pH 6.0 the bacteria become dormant, and in conditions exceeding pH 9 they are destroyed.

Leaching:

Solid-Liquid separation:
A: Thickening (sedimentation)
Separation of suspended solid particles from a liquid stream by gravity settling.





Leaching:

Solid-Liquid separation:

B: Filtration

Filtration is a process of separating solids from a liquid by means of a porous medium which holds back the solids and permits the liquid to clear.

Depending on the nature of the slurry, the driving force required for separation may be grouped into four categories, namely, gravity, vacuum, pressure, and centrifugal.

Conventional filtering machines in hydrometallurgical plants are:

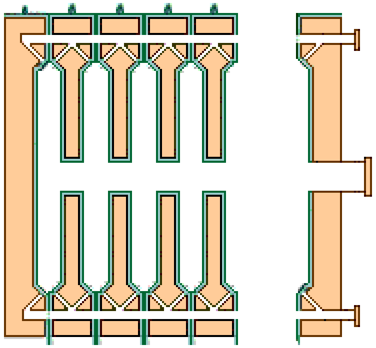
- Filter press
- Vacuum filter

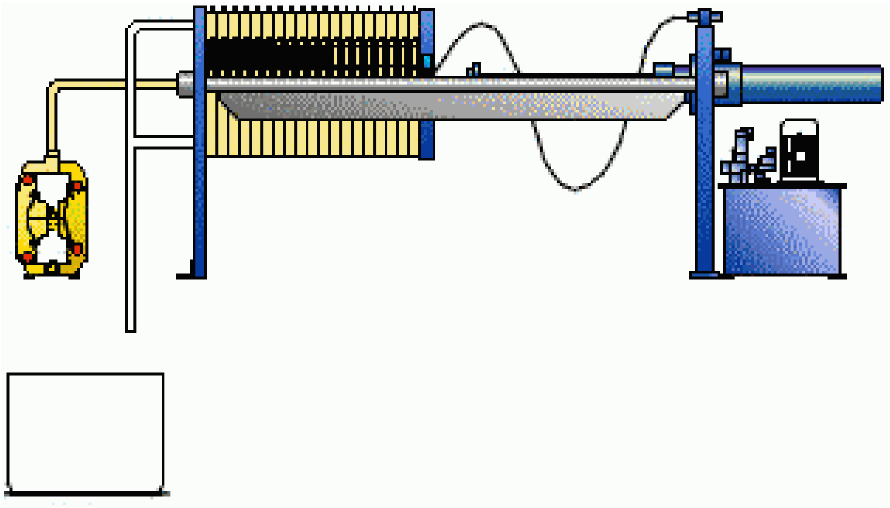
Leaching:

Solid-Liquid separation:

B: Filtration

- Filter press





Leaching:

Solid-Liquid separation:

B: Filtration

- Vacuum filter

Purification and Concentration:

Classification of methods:

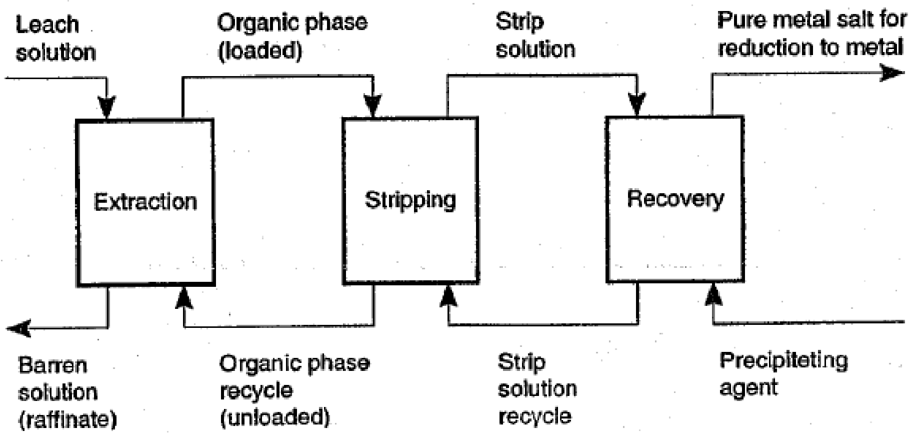
- Ion exchange
- Adsorption on activated charcoal
- Solvent Extraction or SX or liquid-liquid separation

Adsorption on activated charcoal and ion exchange processes are conducted in columns filled with charcoal or ion exchange resins. The circuit involves two steps: loading or **sorption** of the desired metal and unloading **or elution**.

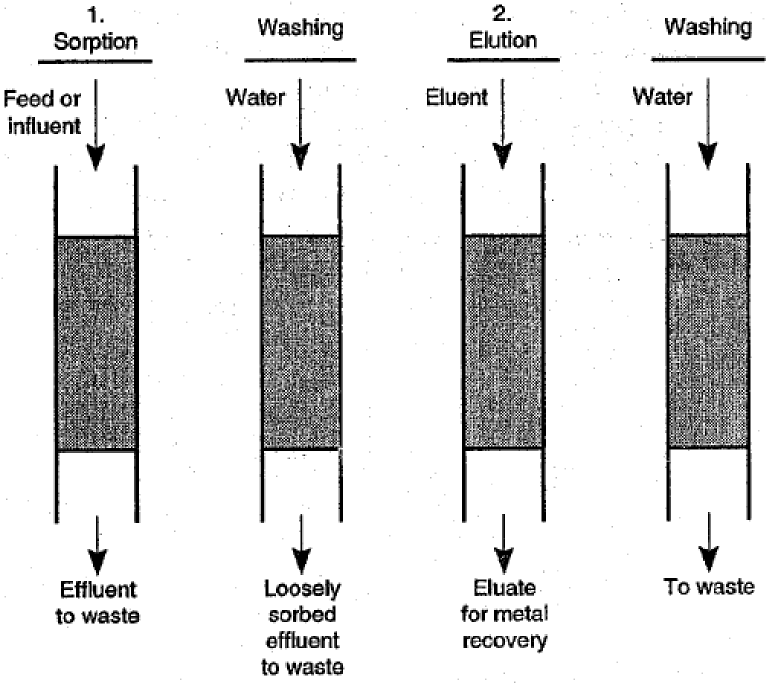
In solvent extraction the leach solution is mixed with **an immiscible organic solvent** so that the desired metal ion in the aqueous phase is transferred to the organic phase(**Extraction**). The two phases are then allowed to separate. The process is then repeated by contacting the loaded organic phase with an aqueous solution now capable of transferring the desired metal ion back to the aqueous phase (**stripping**).

Purification and Concentration:

Classification of methods:



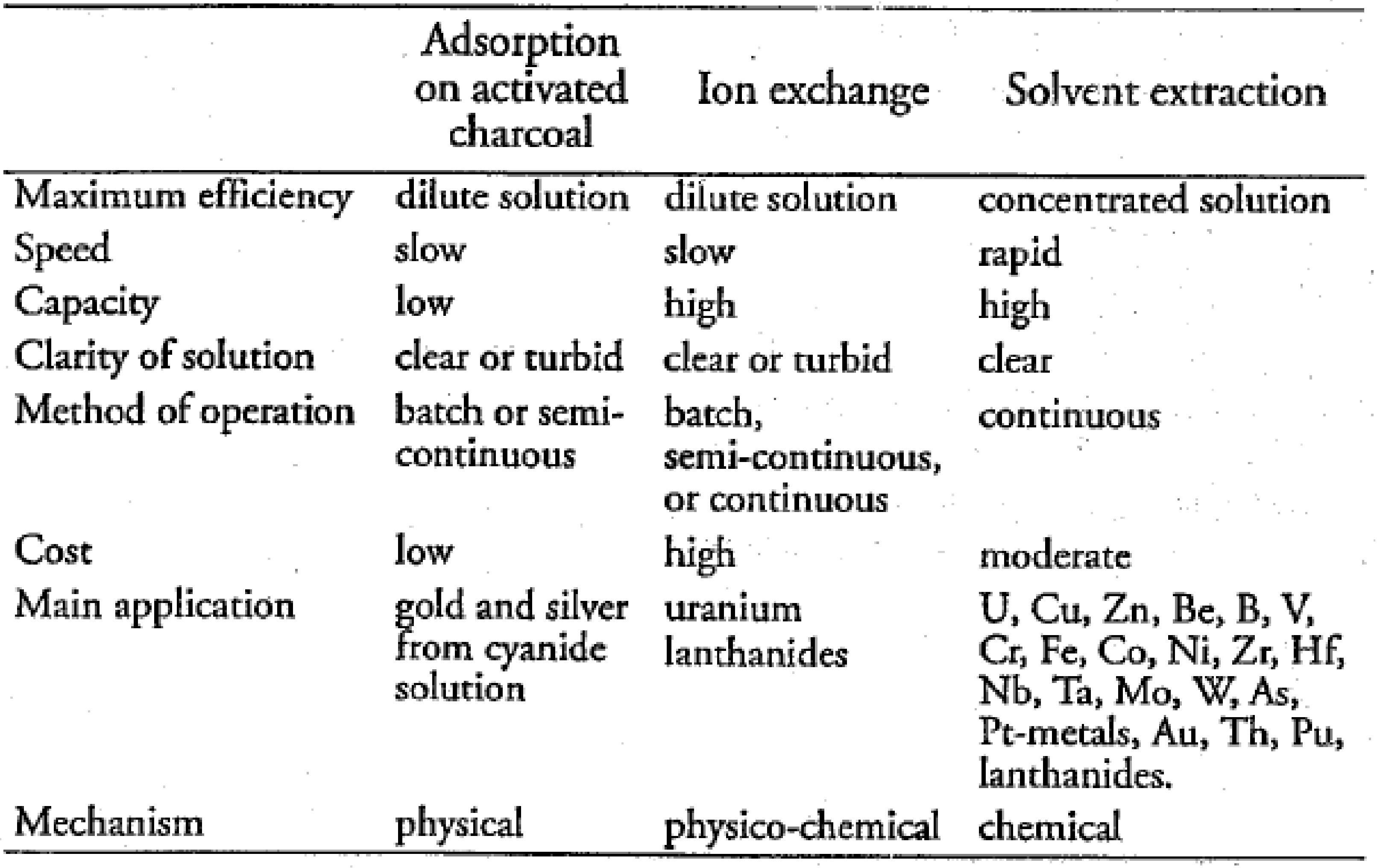
General scheme in solvent extraction.



Sequence of operations in adsorption and ion exchange processes.

Purification and Concentration:

Classification of methods:



	Adsorption on activated charcoal	Ion exchange	Solvent extraction
Maximum efficiency	dilute solution	dilute solution	concentrated solution
Speed	slow	slow	rapid
Capacity	low	high	high
Clarity of solution	clear or turbid	clear or turbid	clear
Method of operation	batch or semi-continuous	batch, semi-continuous, or continuous	continuous
Cost	low	high	moderate
Main application	gold and silver from cyanide solution	uranium lanthanides	U, Cu, Zn, Be, B, V, Cr, Fe, Co, Ni, Zr, Hf, Nb, Ta, Mo, W, As, Pt-metals, Au, Th, Pu, lanthanides.
Mechanism	physical	physico-chemical	chemical

Purification and Concentration:

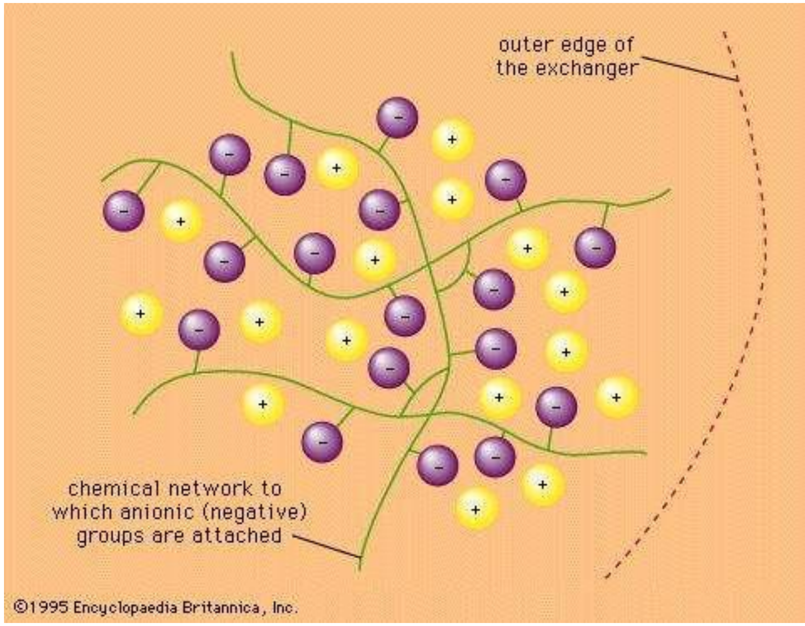
Ion Exchange:

An ion exchanger is a framework which carries a positive or a negative charge (fixed). This is compensated by ions of opposite sign(exchangeable with ions of the same sign).

When the exchangeable ion is positive, the exchanger is a **cation exchanger**, since it can exchange anions. When the exchangeable ion is negative, the exchanger is an **anion exchanger**.

Anionic: $R^+X^- + A^- \rightarrow R^+A^- + X^-$

Cationic: $R^-Y^+ + B^+ \rightarrow R^-B^+ + Y^+$



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Purification and Concentration:

Ion Exchange:

Ion exchange materials:

- Inorganic
  - Natural Alominosilicate minerals known as zeolites. The zeolite lattice consists of SiO_4^{4-} and AlO_4^{4-} tetrahedral. Scince aluminum is trivalent, the lattice carries a negative electric charge. This is balanced by alkali or alkaline earth cations which do not occupy fixed positions, but are free to move in the lattice framework. Therefore, zeolites have the capacity to exchange cations.
  - Synthetic. Materials similar to zeolite have also been synthesized.
- Organic

Organic exchangers, consist of an elastic 3d network of hydrocarbon chains which carry fixed ionic groups. The charge of the groups is balanced by mobile exchangeable ions.

Purification and Concentration:

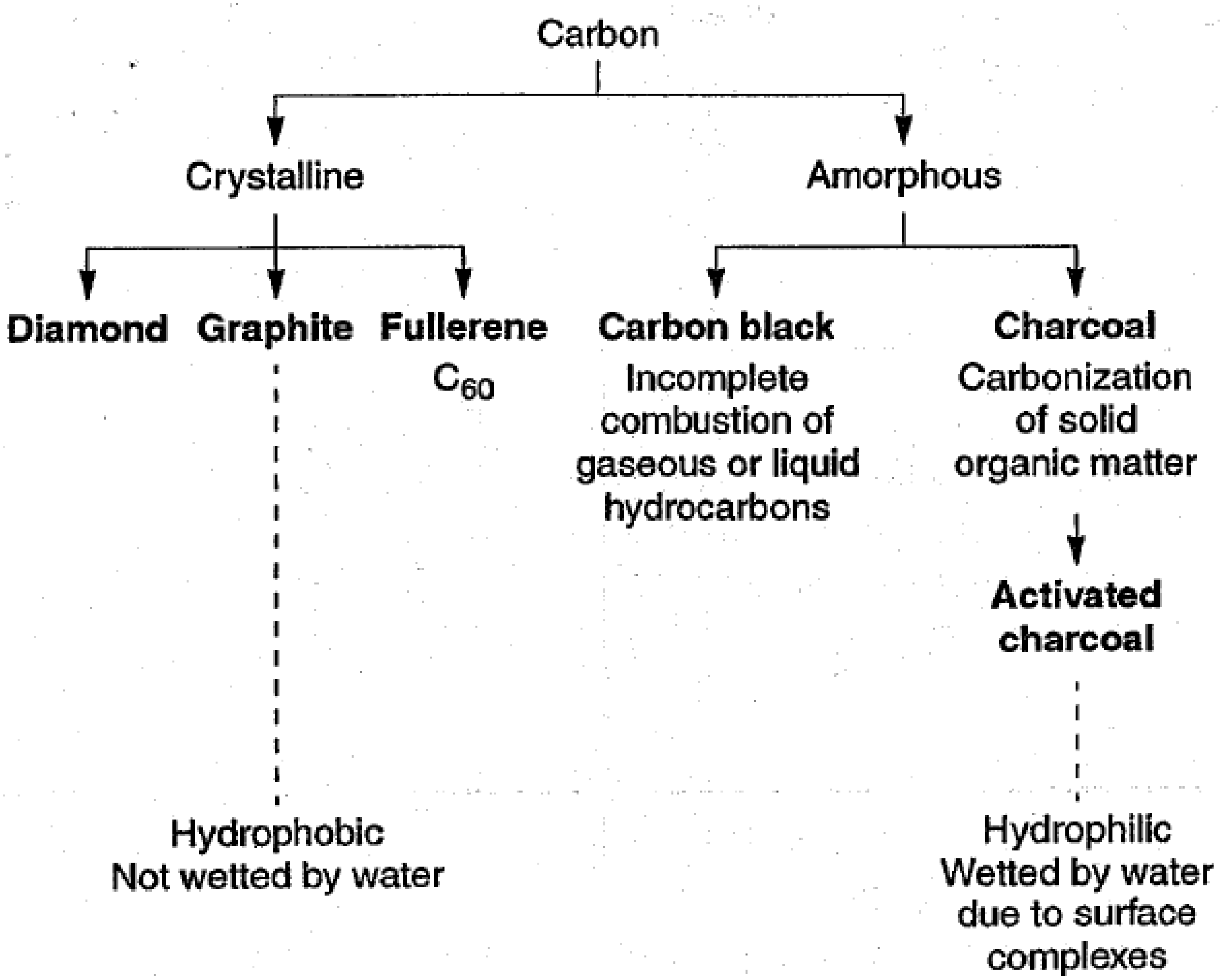
Adsorption on activated charcoal:
Activated charcoal:
The adsorption of metal ion by activated charcoal is slight as compared to ion exchange resins and is usually favorable only to anions and not to cations. However, activated charcoal is a much cheaper material.

Preparation:
Charcoals are prepared by heating of solid carbonaceous material such as coal, wood, nut shells, sugar and coconut shells and synthetic resins at about 600°C in the absence of air-a process known as *carbonization*.
Such charcoals have low porosity, but when heated at 400-800°C for a limited time with air, chlorine or steam, a highly porous material is produced known as activated charcoal and is used as an adsorbent in the chemical and metallurgical industry, usually in the form of pellets about 2 mm in diameter.

Purification and Concentration:

Adsorption on activated charcoal:

Activated charcoal:

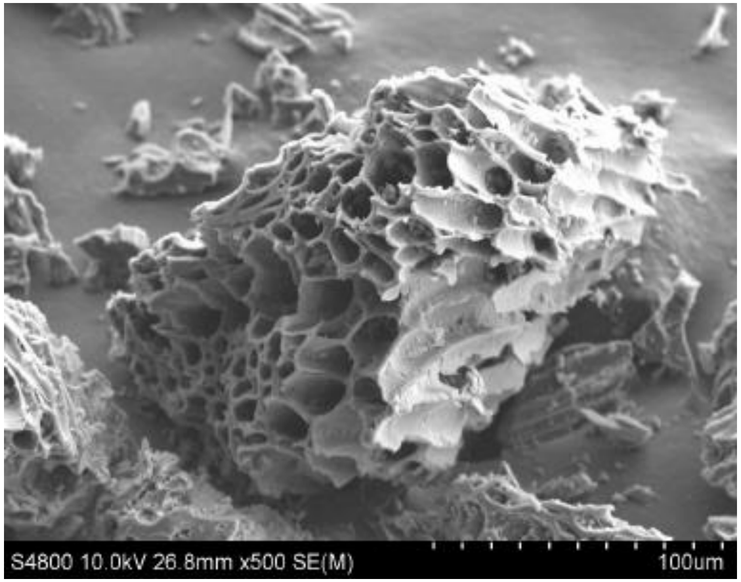


Purification and Concentration:

Adsorption on activated charcoal:

Activated charcoal:

Surface area of activated charcoal made from coconut shells is hard and abrasion-resistant but possesses a large surface area of about 1200 m^2/g and a high porosity, the pore volume within particles being 0.7-0.8 cm^3/g.



Purification and Concentration:

Adsorption on activated charcoal:
Mechanism of adsorption:
One early theory by *Frumkin* suggested that oxygen in aqueous solution is reduced by the charcoal:

$$O_2 + 2H_2O + 2e = H_2O_2 + 2OH^-$$

The loss of electrons by the carbon leaves positively charged sites which are then favorable to the adsorption of gold and silver anionic complexes.

The reaction represented by above reaction may also account for the greater adsorptive capacity for gold observed in solutions of lower pH.

Purification and Concentration:

Adsorption on activated charcoal:
Mechanism of adsorption:

Adsorption of gold and silver on activated charcoal from cyanide solutions has been shown to conform with the **Freundlich** equation:

$$Q = kc^n$$

Q = equilibrium quantity of adsorbed metal cyanide complex on the charcoal ([µmol/g of C)
c = equilibrium concentration of metal cyanide complex in the solution (µmol/L)
and k and n are constants.

k was found to decrease with increasing temperature.
These varied in the case of silver from 245 at 25°C to 71 at 73.5°C.

Purification and Concentration:

Adsorption on activated charcoal:
Desorption and reactivation:

Loaded activated charcoal has been burned and smelted directly to recover the gold and silver in some plants.

A more economic procedure is to strip the metals from the carbon and follow this by a reactivation treatment, regenerating the charcoal for reuse.

From previous considerations it may be expected that the desorption or stripping of gold and silver from loaded charcoal will be enhanced when hot solutions of relatively high pH value and high cyanide concentration are allowed to contact the charcoal.

Purification and Concentration:

Adsorption on activated charcoal:
Desorption and reactivation:

The basic stripping solution has been one containing 10 g/L sodium hydroxide and 2 g/L sodium cyanide. An operating temperature of at least 90°C is crucial and even at this temperature the stripping process may take up to 48 hours or even longer.

An alternative way of decreasing the desorption period is by the addition of approximately **10% alcohol** to the basic alkaline cyanide solution. Under these conditions highly effective stripping is achieved even with temperatures as low as 60-80 °C.

Following stripping and water washing, reactivation of the charcoal is brought about by heat-treatment at 600-900°C. By treating the charcoal with limiting air access, steam activation occurs and oxidation is avoided. This is usually followed by screening to remove undersize.

Purification and Concentration:

Adsorption on activated charcoal:
Practice:
<u>Column process:</u> Adsorption columns charged with granular activated charcoal are used when the ore can be filtered easily and clear solutions can be obtained.

<u>Carbon-in-Pulp process:</u> this process is used to treat <u>slimy</u> ores which are difficult to filter. In this process, the cyanide leaching pulp is agitated in tanks with the charcoal pellets. When adsorption is complete, the pulp is <u>screened</u> to separate the gold-laden pellets.

<u>Carbon-in-Leach process:</u> this process is used to treat ores containing <u>organic matter</u>. Since organic matter may act as adsorbents, their presence renders the gold cyanide complex susceptible of being lost in the residue. Hence, granular activated carbon is added in the leaching tanks so that it can adsorb the gold cyanide complex as soon as it is formed and more effectively than organic matter.

Purification and Concentration:

Solvent Extraction(SX):
Partition between immiscible liquids:

If a solute is dissolved in two immiscible solvents, A and B, which are in contact, the free energy of the solute in liquid A and B may be expressed by:

$$G_A = G_A^\circ + RT \ln a_A \qquad G_B = G_B^\circ + RT \ln a_B$$

When equilibrium is established $G_B = G_A$ and therefore:

$$G_B^\circ + RT \ln a_B = G_A^\circ + RT \ln a_A$$

$$\ln \frac{a_B}{a_A} = \frac{G_A^\circ - G_B^\circ}{RT} \qquad \ln \frac{a_B}{a_A} = \text{constant} \qquad a_B/a_A = P^\circ$$

P° is the partition constant

Purification and Concentration:

Solvent Extraction(SX):
Partition between immiscible liquids:
Partition law: A solute will distribute itself between two immiscible solvents until the ratio of the activities of the solute in the two liquids is constant at any given T, irrespective of the absolute value of the activities.

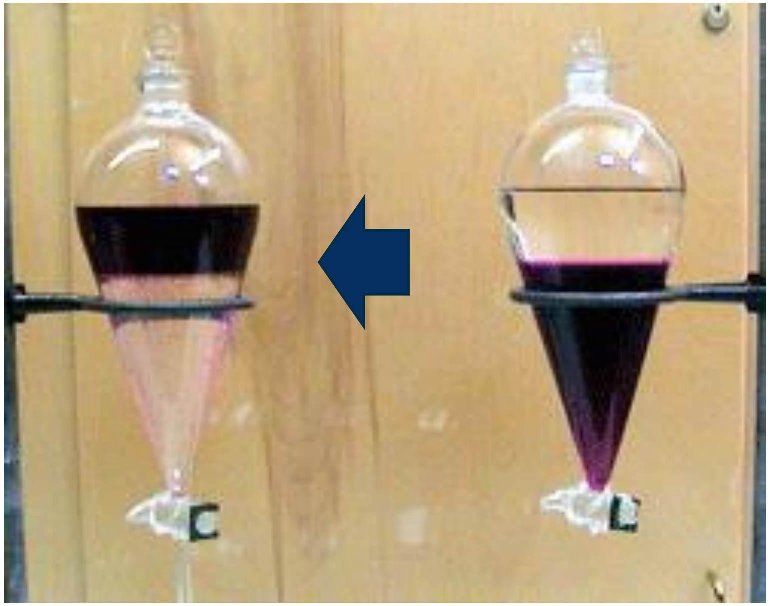
The value of the partition constant depends on the nature of the solute and the solvents involved, and also the temperature.

The partition law refers only to the one particular solute species that is common to both solvents.
A more meaningful expression is the distribution ratio, D which for a given metal is the ratio of the total of the metal concentration in the organic solvent phase to the total of the metal concentration in the aqueous phase.

$$D = \frac{\sum[\mathrm{M}]_{o}}{\sum[\mathrm{M}]_{aq}}$$

Purification and Concentration:

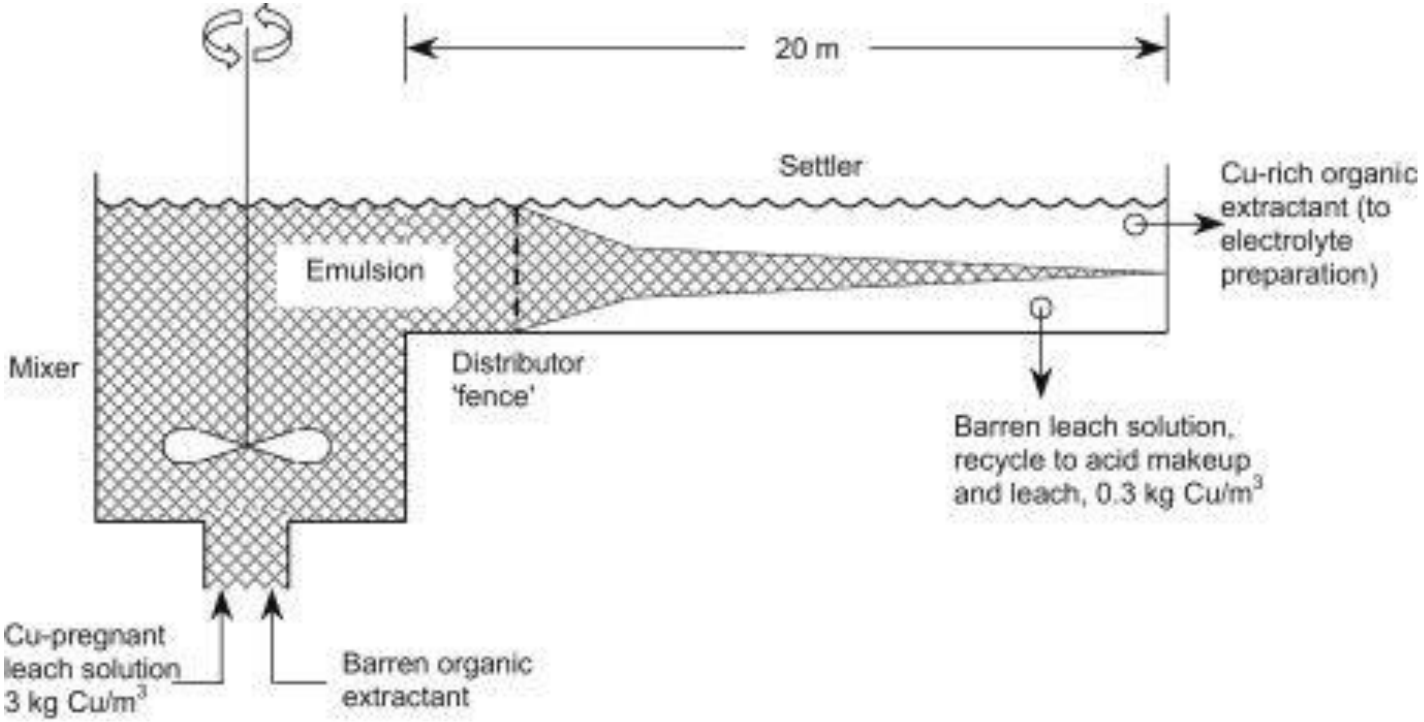
Solvent Extraction(SX):
Partition between immiscible liquids:
When a volume V_O of organic solvent is equilibrated with a volume V_{aq} of the metal-rich aqueous phase, the fraction of the metal extracted into the organic phase(or Recovery factor) is given by:



$$\text{fraction extracted} = \frac{D}{D + (V_{aq}/V_o)}$$

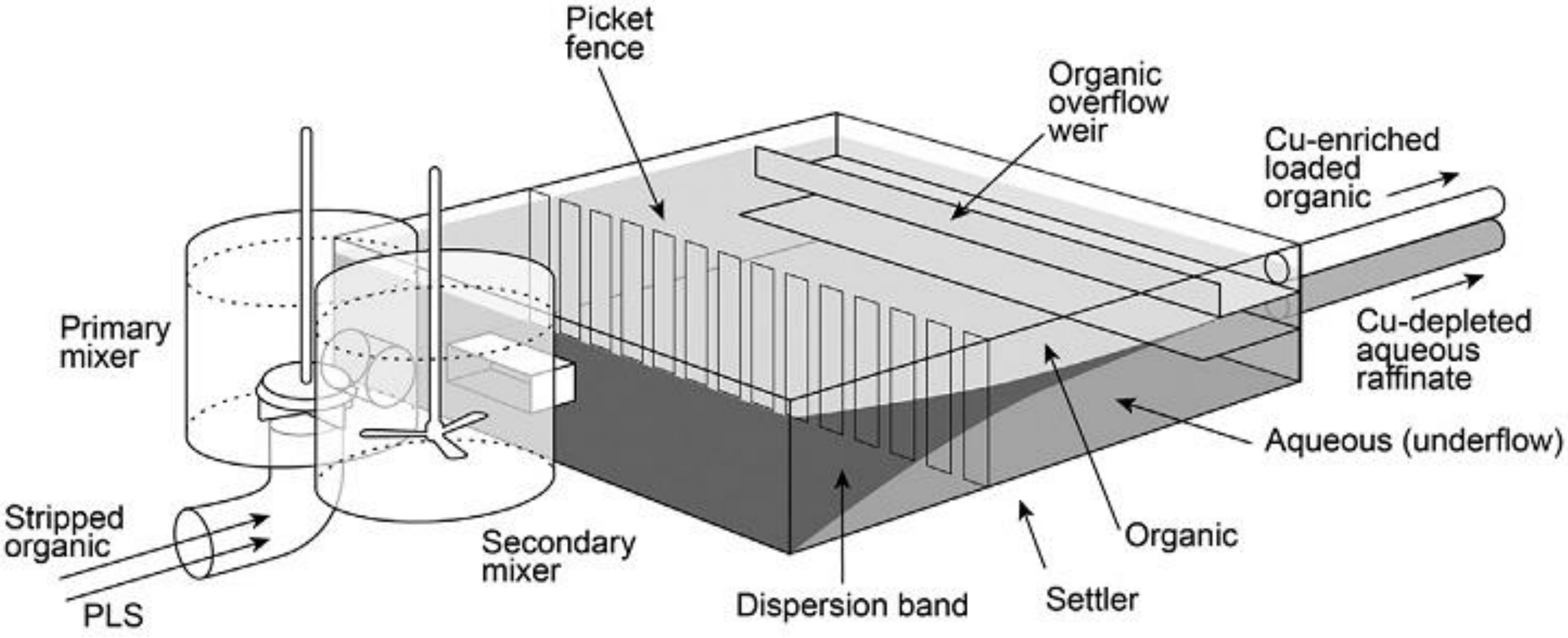
Purification and Concentration:

Solvent Extraction(SX):
Engineering aspects:
Mixer-Settler
Mixer-Settlers are composed of a mixing chamber where the aqueous and organic phases are mixed together by a rotating impeller, and a settling chamber where the mixed phases are given enough time to separate. Each such unit composes a **stage**.



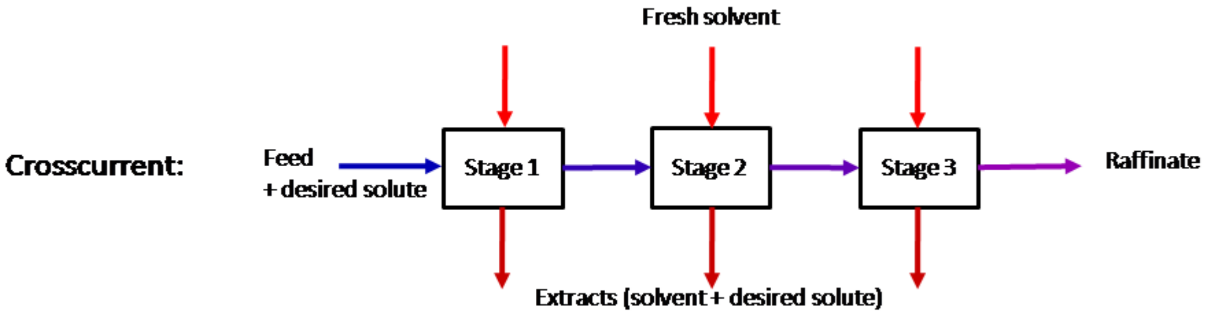
Purification and Concentration:

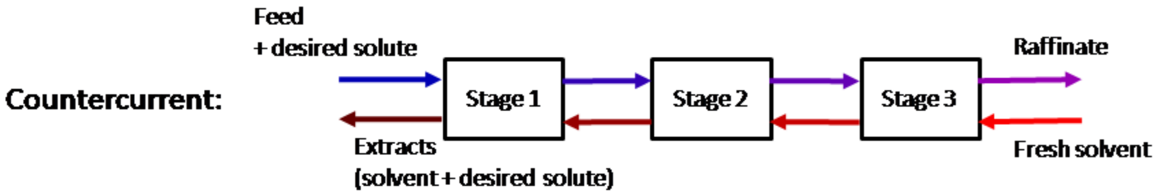
Solvent Extraction(SX):
Mixer-Settler:



Purification and Concentration:

Solvent Extraction(SX):
Engineering aspects:
Usually many stages are used (3 to 5) and are operated in counter-current or cross-current in the extraction as well as in the stripping steps.





Precipitation (recovery):

- Physical precipitation(Crystallization)
- Chemical precipitation
- Reduction
  - Electrowinning
  - Cementation
  - Reduction using reducing agents

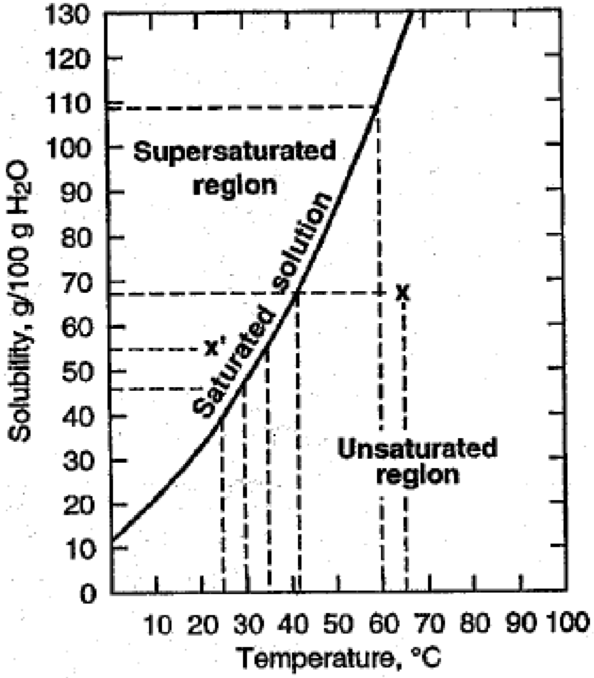
Precipitation (recovery):

Physical precipitation(Crystallisation)

It is a physical process in which no reagents are added but the concentration and temperature of the solution are so adjusted to lead to the formation of an ionic solid crystalline phase which may contain water of crystallization. $yM^{x+} + xA^{y-} + nH_2O \rightarrow M_yA_x \cdot nH_2O_{(s)}$

In contrast to chemical precipitation, the process is usually slow.

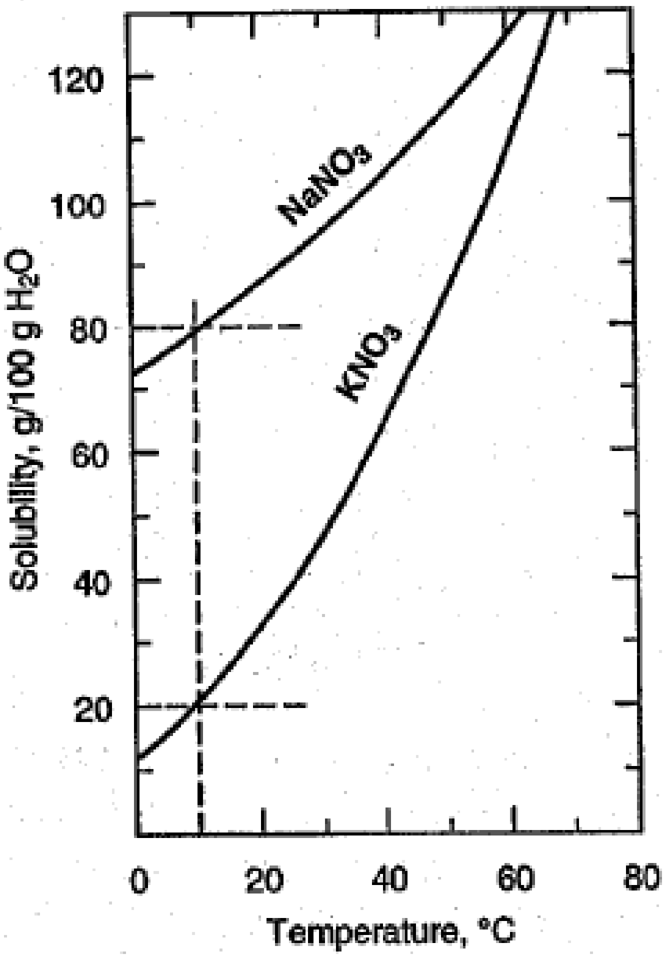
Solubility diagrams:



Precipitation (recovery):

Physical precipitation(Crystallization):

- When there is a large increase in solubility with temperature, crystallization can be affected by cooling a hot solution(like KNO_3).
- When there is a small increase in solubility with temperature, crystallization can best be effected by evaporation(like NaCl).
- Difference in solubilties may be used for separating salts.



Precipitation (recovery):

Chemical precipitation

Chemical precipitation is based on the fact that when a reagent is added to a solution containing metal ions, a compound is formed whose solubility is very low under these conditions that precipitation takes place immediately. For example:

$$Cu^{2+} + S^{2-} \rightarrow CuS$$

$$AsO_4^{3-} + Fe^{3+} \rightarrow FeAsO_4$$

The most important chemical precipitation in hydrometallurgy are the precipitation as hydroxides, sulfides and carbonates.

A precipitation process can be used to separate a metal or group of metals from others, either for the purpose of removing impurities or minor metallic constituents, or for the recovery from solution of the major metal.

Precipitation may also be used as a wastewater treatment process in the recovery of metals present in solution in low concentrations prior to such solutions going to waste.

Precipitation (recovery):

Chemical precipitation

An important practical aspect of precipitation is the subsequent necessity to separate the precipitate from the solution.

This may be achieved by thickening and/or filtration.

Separation and washing can be most effectively carried out if the precipitate is dense and crystalline in character, and such precipitates are much less subject to contamination.

This may be achieved by inducing precipitation from a hot, dilute solution.

Precipitation (recovery):

Chemical reagents

Hydroxide precipitation:
NaOH,CaO,MgO,…

Sulfide precipitation:
H_2S as gas, Na_2S,NaHS,NH_4S as liquid, CaS, FeS as solid.

Carbonate precipitation:
Na_2CO_3

Precipitation (recovery):

Cementation

Cementation involves the reductive precipitation of one metal by another.

For solutions in which the metal is present as simple aquo-cations inspection of a table of standard electrode will indicate the general feasibility of reduction.

The reduction of copper by iron may be taken as a typical example:

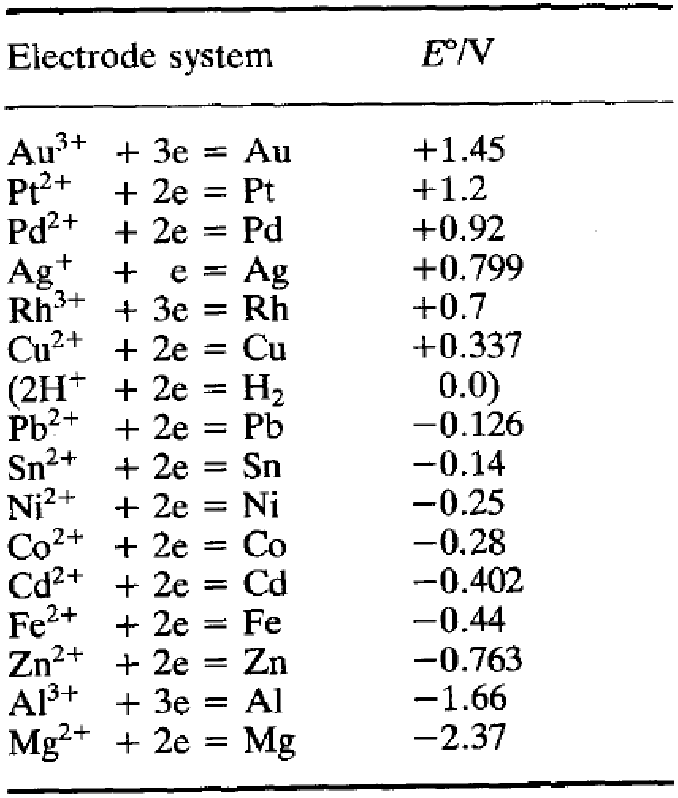
Anodic reaction $\mathrm{Fe} = \mathrm{Fe}^{2+} + 2e$

Cathodic reaction $\mathrm{Cu}^{2+} + 2e = \mathrm{Cu}$

Overall cell reaction $\mathrm{Fe} + \mathrm{Cu}^{2+} = \mathrm{Fe}^{2+} + \mathrm{Cu}$

$$E^\circ_{\mathrm{cell}} = 0.337 - (-0.440) = 0.777\ \mathrm{V}$$

$$\Delta G^\circ = -zFE^\circ_{\mathrm{cell}} = -149.9\ \mathrm{kJ.mol}$$



Electrode system	E°/V
$\mathrm{Au}^{3+} + 3e = \mathrm{Au}$	+1.45
$\mathrm{Pt}^{2+} + 2e = \mathrm{Pt}$	+1.2
$\mathrm{Pd}^{2+} + 2e = \mathrm{Pd}$	+0.92
$\mathrm{Ag}^{+} + e = \mathrm{Ag}$	+0.799
$\mathrm{Rh}^{3+} + 3e = \mathrm{Rh}$	+0.7
$\mathrm{Cu}^{2+} + 2e = \mathrm{Cu}$	+0.337
$(2\mathrm{H}^{+} + 2e = \mathrm{H}_2$	0.0)
$\mathrm{Pb}^{2+} + 2e = \mathrm{Pb}$	−0.126
$\mathrm{Sn}^{2+} + 2e = \mathrm{Sn}$	−0.14
$\mathrm{Ni}^{2+} + 2e = \mathrm{Ni}$	−0.25
$\mathrm{Co}^{2+} + 2e = \mathrm{Co}$	−0.28
$\mathrm{Cd}^{2+} + 2e = \mathrm{Cd}$	−0.402
$\mathrm{Fe}^{2+} + 2e = \mathrm{Fe}$	−0.44
$\mathrm{Zn}^{2+} + 2e = \mathrm{Zn}$	−0.763
$\mathrm{Al}^{3+} + 3e = \mathrm{Al}$	−1.66
$\mathrm{Mg}^{2+} + 2e = \mathrm{Mg}$	−2.37

Precipitation (recovery):

Cementation

Problem:

Calculate the activity ratio of Cu^{2+} to Fe^{2+} at equilibrium in the cementation of Cu using Fe metal at 25°C.

Answer:

Anodic reaction	$Fe = Fe^{2+} + 2e$
Cathodic reaction	$Cu^{2+} + 2e = Cu$
Overall cell reaction	$Fe + Cu^{2+} = Fe^{2+} + Cu$

$$E^\circ_{cell} = 0.337 - (-0.440) = 0.777\ V$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\left(\frac{a_{Cu} \times a_{Fe2+}}{a_{Fe} \times a_{Cu2+}}\right)$$

at equilibrium: $E_{cell}=0$

$$0 = 0.777 - \frac{8.314 \times 298}{2 \times 96500}\ln\left(\frac{a_{Fe2+}}{a_{Cu2+}}\right) \qquad \frac{a_{Cu2+}}{a_{Fe2+}} = 5.2 \times 10^{-27}$$

This very low value indicates that the copper ion concentration remaining in solution is likely to be extremely small.

Precipitation (recovery):

Cementation

Applications:

- Recovery of a metal from a leach solution, e.g., copper from sulfuric acid leach solution and gold from cyanide solution.
- Purification of a leach solution with the simultaneous recovery of the impurity, e.g. removal of cadmium and thallium from a zinc sulfate solution. In this case, it is very convenient to use metallic zinc as a cementing metal.

Purity of the product:

The metal precipitated usually contains appreciable amounts of the precipitating metal.

Due to powdery nature of the product, it is usually highly oxidized.

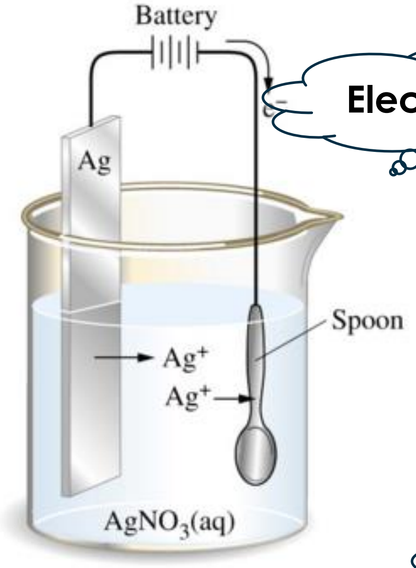
The purity of the cement copper obtained by cementation with Iron scrap varies between 85% and 90% copper.

Precipitation (recovery):

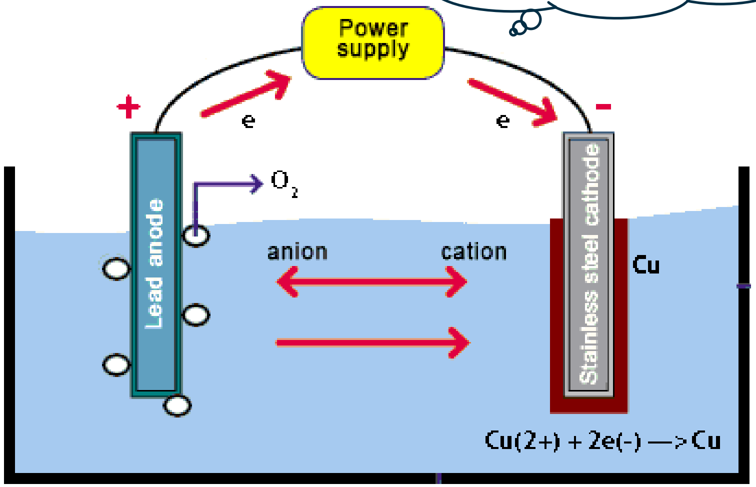
Electrowinning

Electrolysis based Industrial Processes:

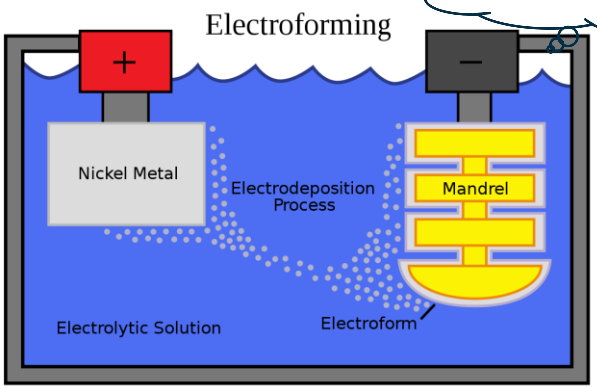
Electroplating



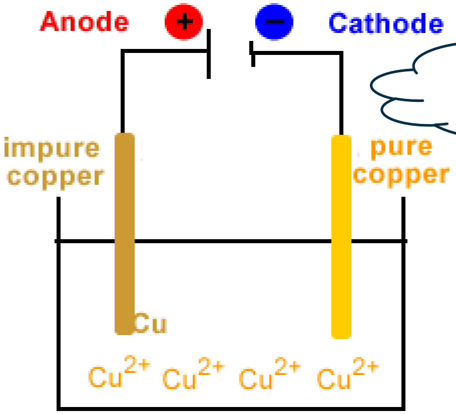
Electrowinning



Electroforming

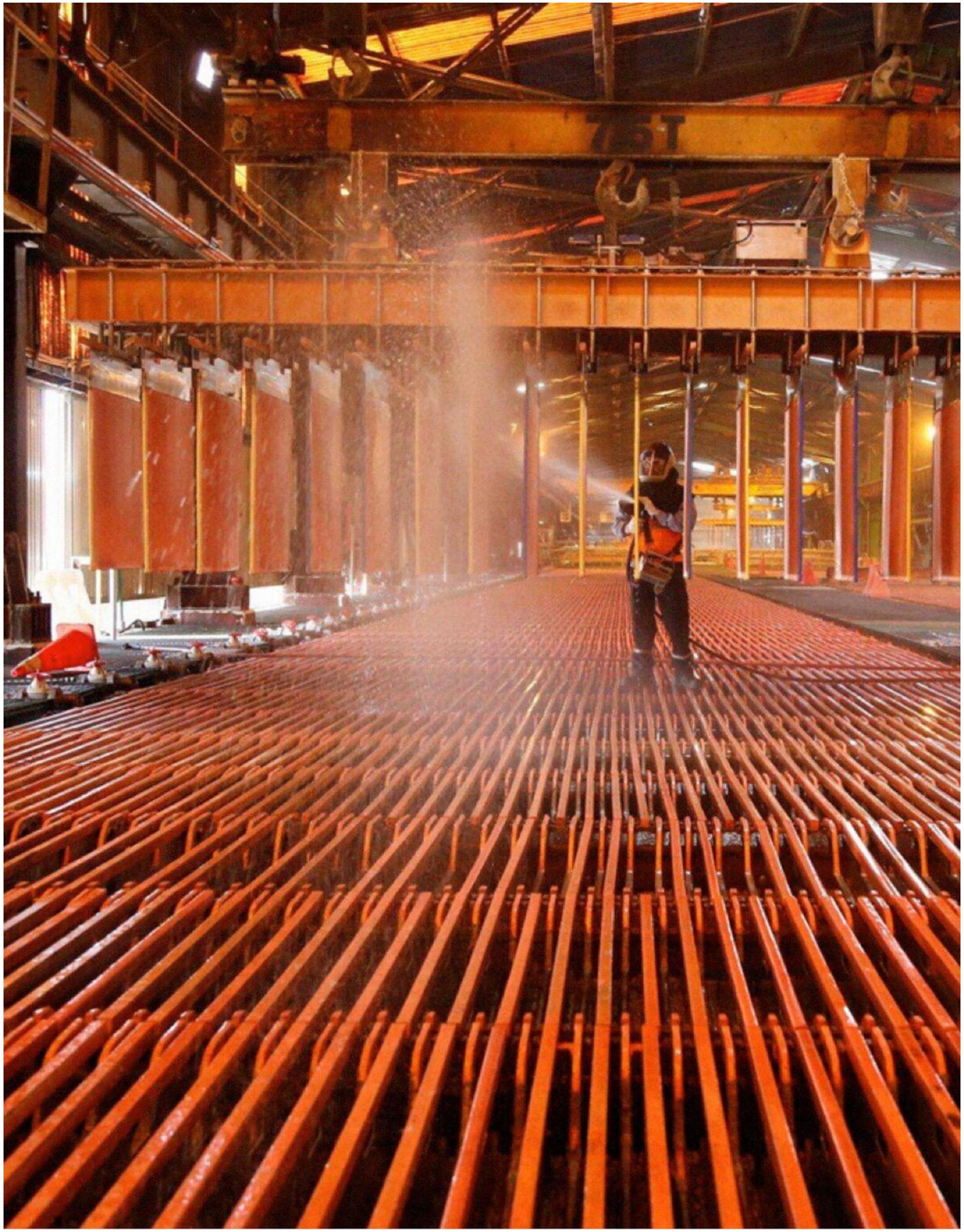


Electrorefining



Precipitation (recovery):

Electrowinning



Precipitation (recovery):

Electrowinning
In electrowinning inert or non-consumable anodes are immersed in the solution(electrolyte) and a direct current (DC) is passes through and a metal is deposited on the cathode.

Main cathodic reaction: $M^{n+} + ne^{-} \rightarrow M$

Main anodic reaction: $H_2O \rightarrow {}^{1}/_{2}O_2 + 2H^{+} + 2e^{-}$

Electrowinning of copper from the sulfate solution:
Cathodic reaction: $Cu^{2+} + 2e = Cu$
Anodic reaction: $H_2O = \frac{1}{2}O_2 + 2H^{+} + 2e$

Overall reaction: $Cu^{2+} + H_2O \rightarrow Cu + {}^{1}/_{2}O_2 + 2H^{+}$

Or $CuSO_4 + H_2O \rightarrow Cu + {}^{1}/_{2}O_2 + H_2SO_4$

Sulfuric acid regenerated at the anode, is used in leaching and copper deposited on the cathodes is melted and casted.

Precipitation (recovery):

Electrowinning
Cell Voltage:
The nominal potential difference between anode and cathode that must be exceeded for an overall cell reaction to occur is the difference between the reversible potentials of the anodic and cathodic reactions, E_a and E_c respectively, <u>the reversible cell potential</u>.

To produce a significant current through the cell, additional increments of potential are required. These include the activation overpotentials at each electrode and the potentials required to overcome the resistance of the electrolyte and the various electrical contacts.

The required shift in potential from the equilibrium value to bring about deposition or dissolution is termed the **activation overpotential**.

Precipitation (recovery):

Electrowinning

Applied potential (V_I) is the potential that must be applied to an electrolytic cell to produce a current, I, through the cell.

$$V_I = (E_A - E_C) + \eta_A + \eta_C + (IR)_{\text{electrolyte}} + (IR)_{\text{contacts}}$$

The potential increments are all taken to be positive.

Example: Estimate the applied cell potential for the electrowinning of copper if the anodic and cathodic overpotentials estimated to be respectively 0.5 and 0.05 V and the ohmic drop of potentials in the electrolyte and contacts are 0.5 and 0.1 V.

Answer:

V_I = (1.23-0.34)+0.5+0.05+0.5+0.1=2.04 V

Note: for the electrorefining of copper:

V_I = (0.34-0.34)+0.03+0.075+0.1+0.07=0.275 V

Precipitation (recovery):

Electrowinning

Faraday law:

$$m = \frac{M}{n.F}.I.t$$

m: mass of deposited metal or corroded metal(g)
M: atomic weight of the metal(g/mol)
n: number of transferred electrons
F: Faraday number 96500 A.s
I: Cell current (A)
t: Electrowinning duration (s)

Precipitation (recovery):

Electrowinning
Faraday law:
Example: Calculate the weight of nickel deposited from a $NiCl_2$ solution when a current of 0.4 A flows for 2.5 h.
Answer:
M=58.7 , n=2 , F=96500 , I=0.4 t= 2.5×60×60 s

$$m = \frac{M}{n.F}.I.t = \frac{58.7}{2 \times 96500} \times 0.4 \times 2.5 \times 60 \times 60 = 1.09\ g$$

Precipitation (recovery):

Electrowinning

Current efficiency:

Current efficiency is the ratio between the quantity of substance obtained by electrolysis and the quantity theoretically obtainable according to Faraday's law. It is determined for either cathodic or anodic reactions.

Example:

4g Ni was deposited after 10 h of electrowinning at current of 0.4 A. Calculate the cathodic current efficiency.

Answer: 91.74%

Apparent deviations can occur for the several reasons such as:

Simultaneous reactions like:

$$2H^+ + 2e^- \rightarrow H_2$$

Precipitation (recovery):

Electrowinning

Energy consumption:

The energy consumption per unit mass of metal produced is an important factor in assessing and comparing the economics of electrolytic processes. It may be expressed in units of kWh/kg of metal deposited.

$$Energy\ consumption = \frac{(V_I \times I \times t)}{m}$$

Precipitation (recovery):

Electrowinning

Cathodic current density:

The efficiency, quality of the cathode product (morphology and purity), energy consumption and productivity are strongly depend on the cathodic current density and always there is an optimum value for it:

$$C.D = \frac{I}{A}$$

Where I is the applied current and A is the total wetted area of cathodes within a cell.