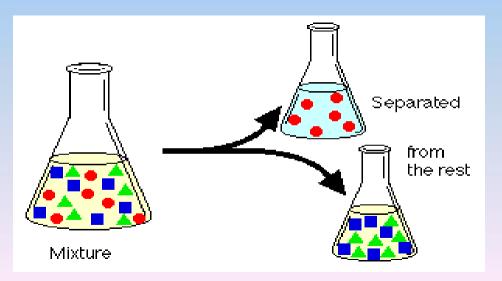
SOLVENT EXTRACTION

What is Solvent Extraction ?

Solvent Extraction, also known as liquid-liquid extraction, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent.

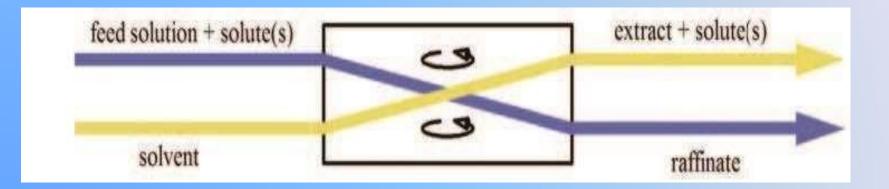


Importance of the process:

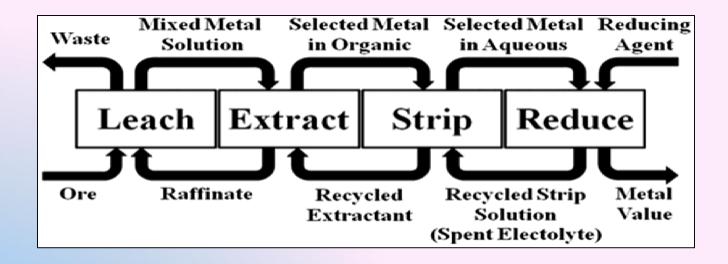
- The Solvent Extraction(S.E.) process was first developed as a tool of analytical chemistry. Every metallic element of the periodic table could be virtually separated by this process.
- Back in 1940's , S.E. was primarily used to separate nuclear and rare earthelements.
- However, availability of inexpensive and effective reagents led to the establishment of large scale S.E. processes for extraction of non-ferrous metals from hydrometallurgical leach liquors.

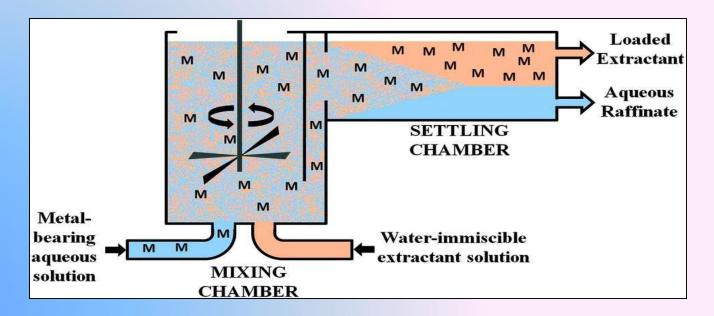
Solvent Extraction, consists of transferring one (or more) **solute**(s) contained in a **feed solution** to another immiscible liquid (**solvent**).

The solvent that is enriched in solute(s) is called **Extract** & the feed solution that is depleted of solute(s) is called **Raffinate**.



S.E. as a part of hydrometallurgy





Types of Solvent Extraction

- SOLVATING EXTRACTION
- CATIONIC EXCHANGE
- ANIONIC EXCHANGE
- CHELATING EXTRACTION

• SOLVATING EXTRACTION Solvent used:

- 1) Tri Butyl Phosphate (TBP)
- 2) Tri Octyl Phosphine Oxide(TOPO)
- 3) Methyl Iso Butyl Ketones(MIBK)

Application:

Extraction/Separation of Lead , Zinc , Uranium, Iron , Cadmium, Hafnium , Zirconium & Plutonium.

- CATIONIC EXCHANGE Solvent used:
 - 1) Di-2-ethylhexy Phosphoric Acid(D2EHPA)
 - 2) Naphthenic Acid
 - 3) Versatic Acid

Application:

Extraction/Separation of Copper, Zinc, Nickel, Cobalt, Silver

- ANIONIC EXCHANGE Solvent used:
 - 1) Primary Amines(RNH₂)
 - 2) Secondary Amines(R₂NH)
 - 3) Tertiary Amines(R₃N)

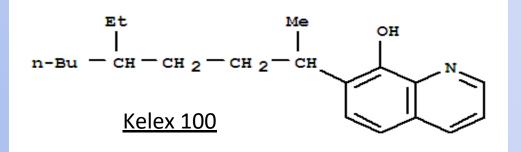
 $(R = C_{12} - C_{14})$

Application:

Extraction/Separation of Uranium, Thorium, Vanadium, Cobalt

• CHELATING EXTRACTION Solvent used:

- 1) Lix63, Lix65
- 2) Kelex 100



Application:

Extraction/Separation of Copper, Nickel, Cobalt

Two basic steps of S.E.

Extraction

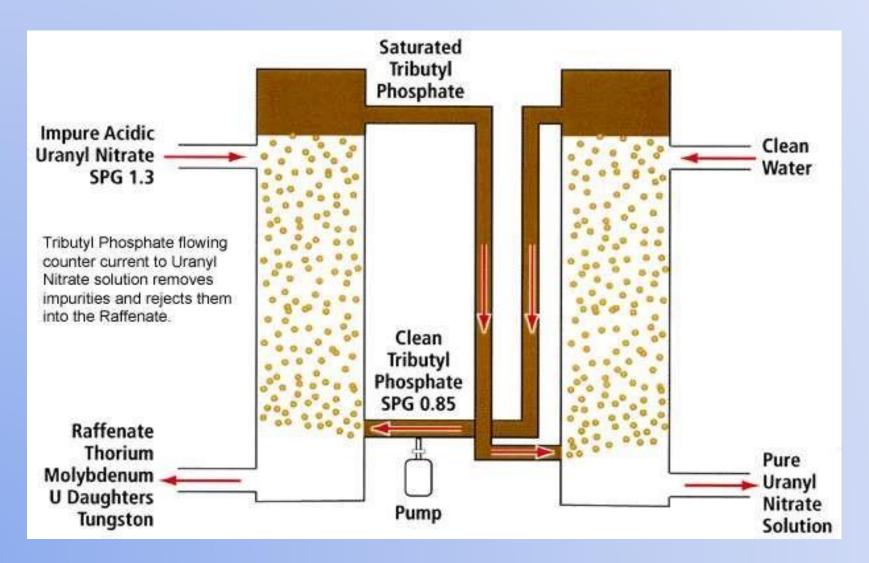
 $UO_{2}(SO_{4})^{4^{-}} + 2(R_{3}NH)_{2}SO_{4} = (R_{3}NH)_{4}UO_{2}(SO_{4})_{3} + 2(SO_{4})^{2^{-}}$

□ Stripping

 $(R_3NH)_4UO_2(SO_4)_3 + Na_2CO_3 = R_3N + Na_4UO_2(CO_3)_3^{4-} + H_2O + Na_2SO_4$

 $2Na_4UO_2(CO_3)_3^{4-} + 6NaOH = Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O$

Solvent Extraction of Uranium

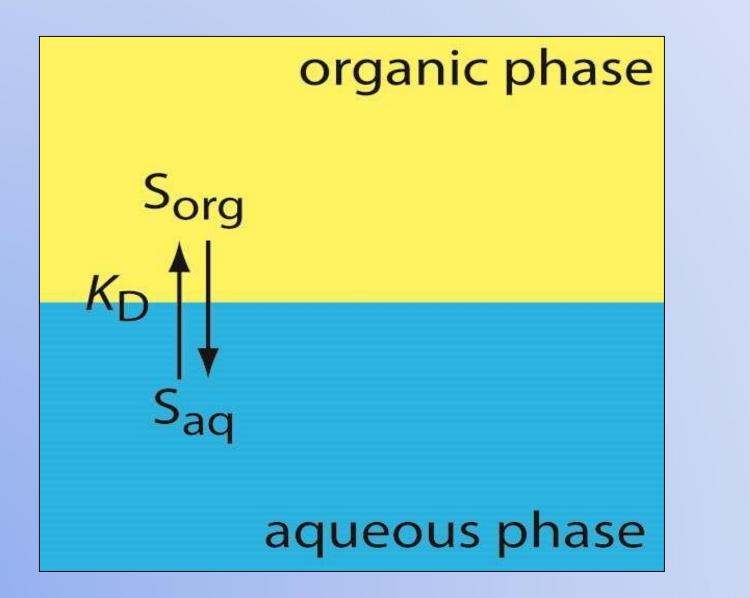


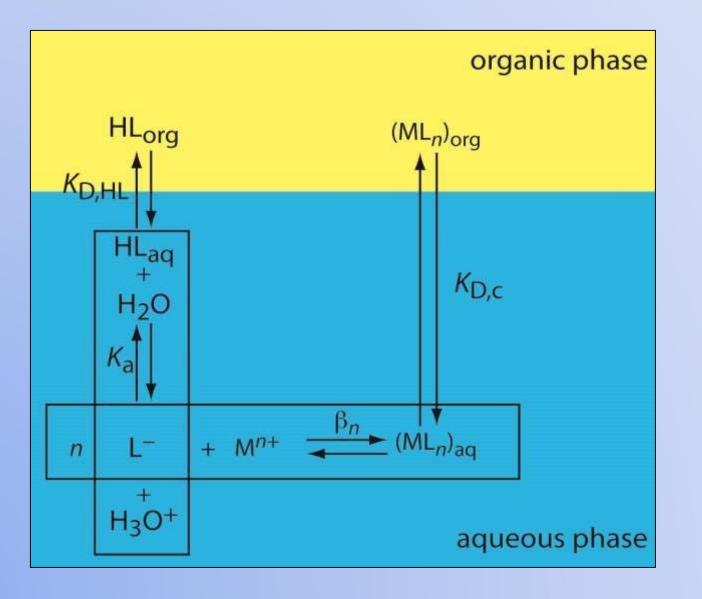
Distribution Coefficient

At a certain temperature, the ratio of concentrations of a solute in each of the solvents is always constant.

This ratio is known as the **Distribution Coefficient**(K_D)

 $D = \frac{\text{Conc. of metal ion in Organic Phase}}{\text{Conc. of metal ion in Aqueous Phase}}$





Extraction Equilibria

For a chelating reagent, HR, the extraction reaction for a metal ion Mⁿ⁺ can be represented as:

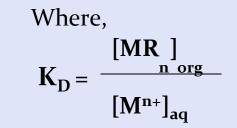
$$M_{aq}^{n+} + n HR_{org} \iff MR_{n org} + H_{aq}^{+}$$

The Extraction Constant(K_{ex}) is given by:

$$\mathbf{K}_{ex} = \frac{[\mathbf{MR}_n]_{org} [\mathbf{H}^+]^n_{aq}}{[\mathbf{M}^{n+}]_{aq} [\mathbf{HR}]^n_{org}}$$

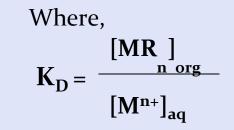
The extraction constant can also be expressed as:

$$K_{ex} = \frac{K_D \cdot [H^+]^n_{aq}}{[HR]^n_{org}}$$



The extraction constant can also be expressed as:

$$\mathbf{K}_{ex} = \frac{\mathbf{K}_{D} \cdot [\mathbf{H}^{+}]^{n}{}_{aq}}{[\mathbf{H}\mathbf{R}]^{n}{}_{org}}$$



$\log K_{D} = \log K_{ex} + n pH + n \log [HR]_{org}$

Extraction Coefficient

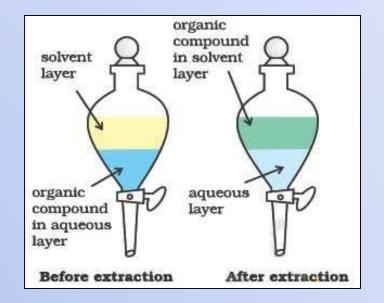
It indicates how much of the metal will move from the aqueous phase to the organic phase in a single contact.

Effective extraction coefficient (E_F) can be expressed as:

$$E_{F} = \frac{[M^{n+}]_{org} (Vol.)_{org}}{[M^{n+}]_{ac}} (Vol.)_{aq}$$

Single Stage vs. Multistage

- Single Stage S.E.
 - Single stage process is commonly followed in laboratory scale.



 Contacting is carried out by taking two phases together in a separating funnel followed by vigorous agitation so that the phases may disperse in each other as fine droplets. Ceasing the agitation lead to the separation of phases in two distinct layers.

Single Stage S.E.

From mass balance it can be shown that:

$$\frac{X_{0}}{X_{1}} = 1 + \frac{[M^{n+}]_{org} (Vol.)_{org}}{[M^{n+}]_{aq} (Vol.)_{aq}}$$

where,

X₀ = Conc. of metal ions in the feed solution i.e. the aqueous phase before any contact.

X₁ = Conc. of metal ions in the aq. raffinate i.e. the aqueous phase after a single contact.



Single Stage S.E. From mass balance it can be shown that:

$$\frac{X_0}{X_1} = \mathbf{1} + E_F$$

where,

X₀ = Conc. of metal ions in the feed solution i.e. the aqueous phase before any contact.

X₁ = Conc. of metal ions in the aq. raffinate i.e. the aqueous phase after a single contact.



Multi Stage Counter Current S.E.

- For extraction of metalson Industrial scale, multi stage counter current solvent extraction process is followed.
- The aqueous raffinate from one extraction unit is fed to the next unit as the aqueous feed, while the organic solvent flows in the opposite direction, thereby picking up more metal ions in successive contacts.
- Dividing the organic phase into small parts & making multiple contacts is the most efficient way of extracting.

$$\frac{\mathbf{X_0}}{\mathbf{X_1}} = \mathbf{1} + \mathbf{E_F}$$

$$\frac{\mathbf{X_0}}{\mathbf{X_1}} = \mathbf{1} + \mathbf{E_I}$$

For multistage contact (assuming **n** contacts):

$$\frac{\mathbf{X}_{0}}{\mathbf{X}_{n}} = (\mathbf{1} + \mathbf{E}_{F}/\mathbf{n})^{n}$$

$$\frac{\mathbf{X_0}}{\mathbf{X_1}} = \mathbf{1} + \mathbf{E_1}$$

For multistage contact (assuming **n** contacts):

$$\frac{X_0}{X_n} = (1 + E_F/n)^n$$
As $\lim n \to \infty$

$$\frac{X_n}{X_0} = \frac{1}{\exp(E_F)} = \exp(-E_F)$$

$$\frac{\mathbf{X_0}}{\mathbf{X_1}} = \mathbf{1} + \mathbf{E_1}$$

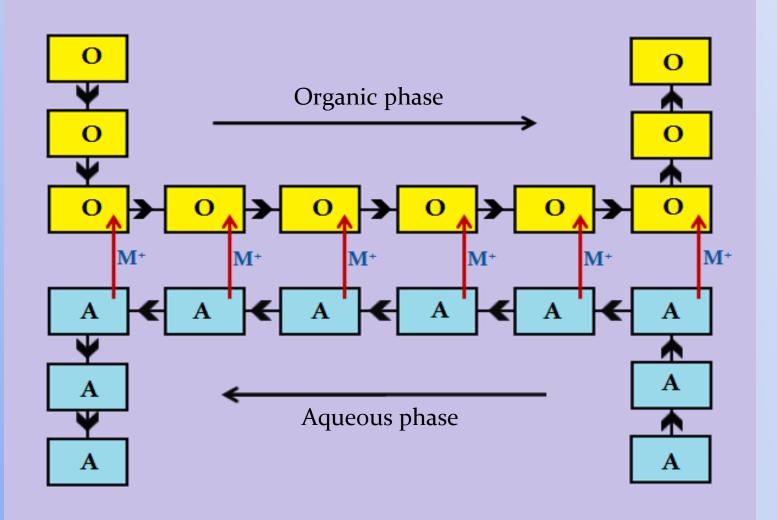
For multistage contact (assuming n contacts):

$$\frac{X_0}{X_n} = (1 + E_F/n)^n$$
As $\lim n \to \infty$

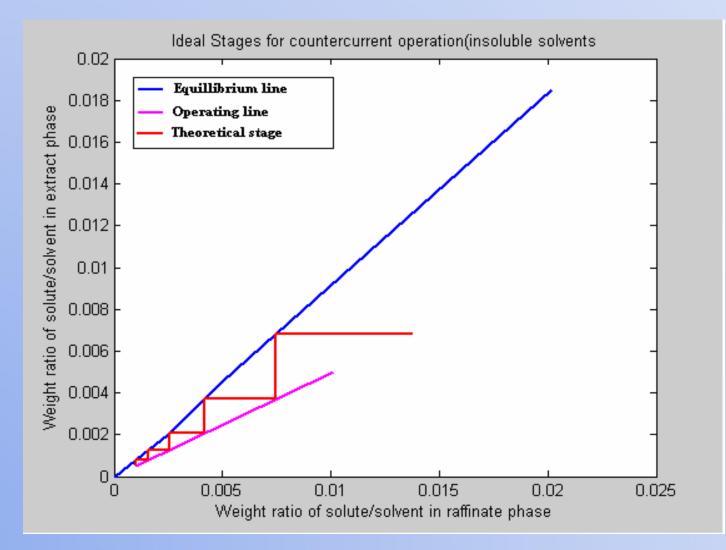
$$\frac{X_n}{X_0} = \frac{1}{\exp(E_F)} = \exp(-E_F)$$

So, Multistage contacting is Best

Multistage Counter-current S.E.



McCabe diagram



Selection of Organic Solvent

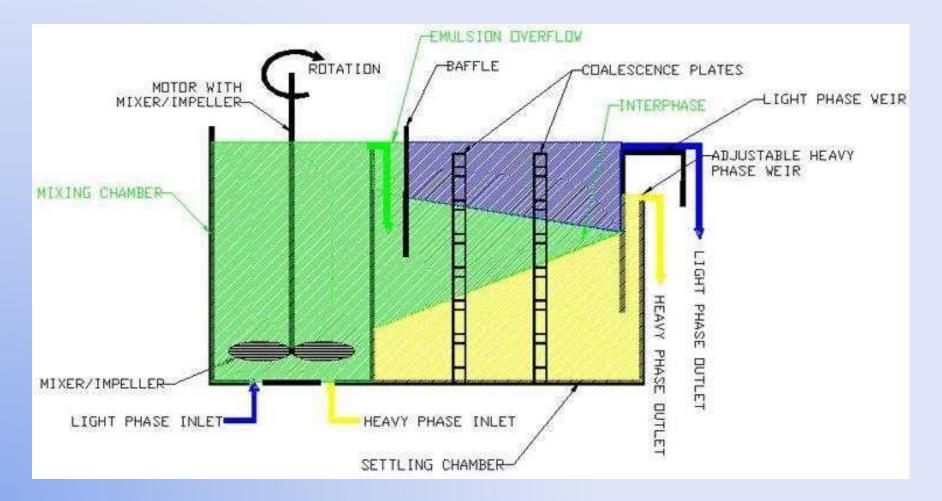
- High extraction capacity
- Selectivity
- Easily Stripped
- > Immiscible in aqueous phase
- Sufficient density difference with the aq. phase
- Low Viscosity
- Non toxic
- Non explosive
- Cheap

Diluents

- Diluent is required for dissolving or diluting the organic extractant so that its physical properties like viscosity and density become more favorable for better mixing of the two phases and their separation.
- Aliphatic or Aromatic hydrocarbons or a combination of both, are used as diluent.
- Diluent affects the extraction, scrubbing, stripping and phase separation process quite significantly.
- Examples of some common diluents:
 - Kerosene
 - Benzene
 - Chloroform
 - Xylene
 - Naptha
 - Toluene

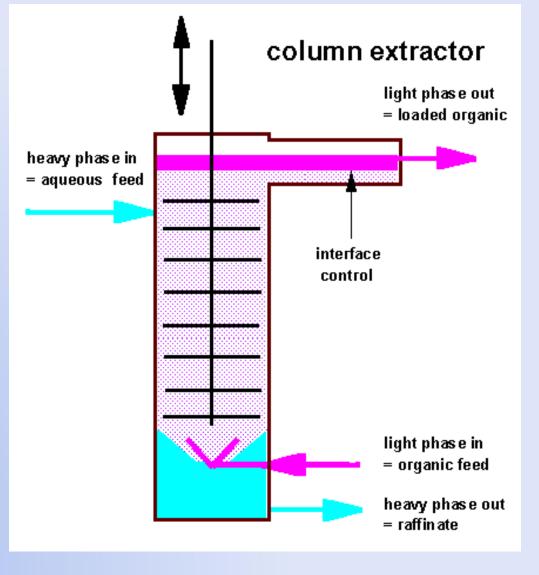
Equipments for Solvent Extraction

• Mixer-Settlers



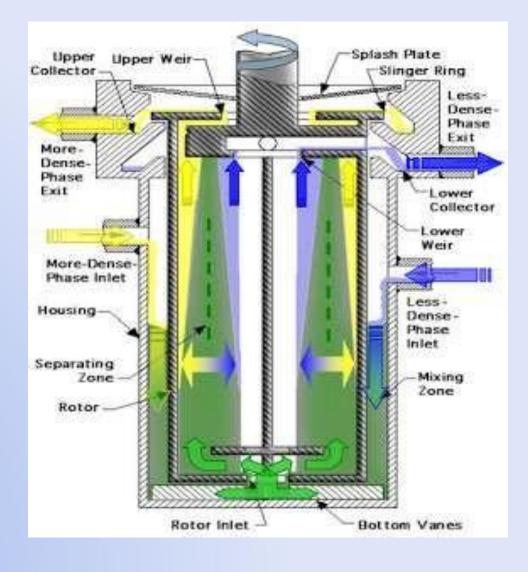
Equipments for Solvent Extraction

• Column Contactor



Equipments for Solvent Extraction

• Centrifugal Contactor



Application

Today the process of Solvent Extraction is widely applied in miscellaneous fields of Science and Technology

- Analytical Chemistry
- Extraction of Rare-earths & PGM
- Waste water treatment
- Mineral oil treatment & dewaxing
- Food industry(essential oil extraction)
- Perfume industry(fragrance extraction)
- Pharmaceutical industry



In spite of having the advantage of a rapid extraction kinetics with a feasibility of recycling the solvent, there are some drawbacks of this process.

- Use of toxic and flammable organic diluents
- Sometimes the cost of solvent system becomes too expensive
- In several cases there is loss of organic solvent in the process
- Solvent Extraction may not pollute the air as much as other pyrometallurgical processes, but a lot of toxic chemicals find their way into the waterbodies, polluting them.

The extensive application of S.E. has become a field(& industry!) of its own. With proper modeling of the process, invention of new equipments, use of more effective extractants and a better understanding of the science behind it may lead it to be one of the most important extraction processes in metallurgy.

Thank You