



Electrochemical Methodology of Metallurgy

Reduction of metal is done in solution or molten state of salt

Electrochemical equation reveals the principle

$$\Delta G^\circ = -nE^\circ F$$

n is no. electrons ; E° is the electrode potential of the **redox couple** formed in the system.

More reactive metals \rightarrow large $-E^\circ \rightarrow$ reduction is difficult.

Difference of two E° values corresponds $\rightarrow +E^\circ \rightarrow -\Delta G^\circ$

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Less reactive metal will come out of the solution

More reactive metal will go to the solution



In electrolysis, the M^{n+} ions are discharged at negative electrode (cathode) and deposited there.

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Aluminium

Purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2

Lowers the melting point of alumina and brings conductivity.

The fused matrix is electrolysed.

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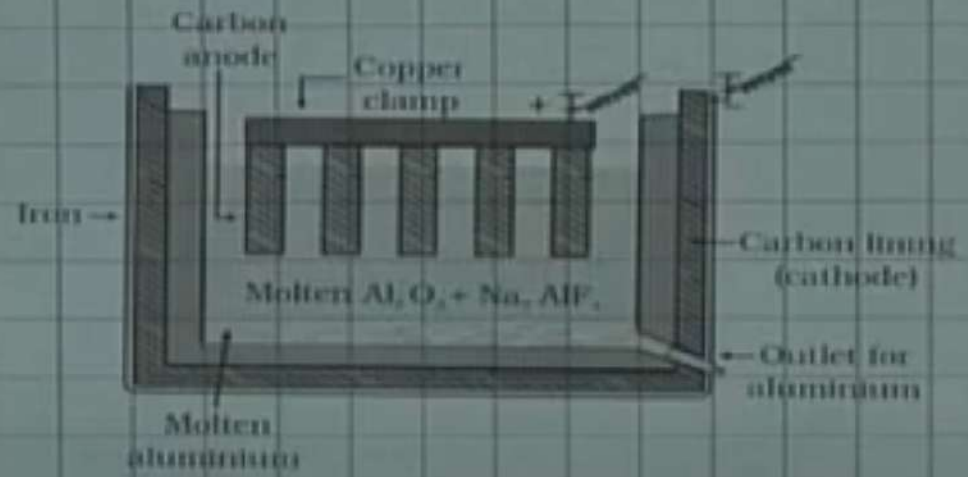


Fig. 6.6: Electrolytic cell for the extraction of aluminium

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Steel vessel with lining of carbon acts as cathode
graphite anode is used.

The overall reaction is
:
 $2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2$)

It is called Hall-Heroult process.

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The oxygen liberated at anode reacts
Carbon of anode produces CO and CO₂.
For each kg of Al about 0.5 kg of C anode is burnt.
The electrolytic reactions are:
Cathode
$$\text{Al}^{3+}(\text{melt}) + 3\text{e}^{-} \rightarrow \text{Al}(\text{l})$$

Anode
$$\text{C}(\text{s}) + \text{O}^{2-}(\text{melt}) \rightarrow \text{CO}(\text{g}) + 2\text{e}^{-}$$

$$\text{C}(\text{s}) + 2\text{O}^{2-}(\text{melt}) \rightarrow \text{CO}_2(\text{g}) + 4\text{e}^{-}$$

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Copper extraction by hydrometallurgy

Used for low grade ores. *% derived*

Ore is leached out using acid

The solution containing Cu^{2+} is treated with scrap iron or H_2

$$\text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow \text{Cu}(\text{s}) + 2\text{H}^+(\text{aq})$$
$$\text{Cu}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Fe}^{2+}(\text{aq})$$

Iron in the electrochemical series is above Cu

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Zinc or iron scraps

Zinc is above iron in the electrochemical series →
more reactive

Reduction will be faster with zinc scraps

Zinc is costlier than iron → using iron scraps is
economical

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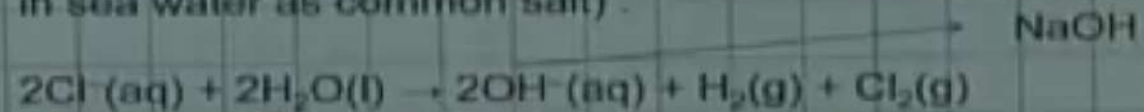


Oxidation based extraction

Suitable for non-metals

Example

Extraction of chlorine from brine (chlorine is abundant in sea water as common salt)



The $\Delta G^\circ = + 422 \text{ kJ}$. \rightarrow using $\Delta G^\circ = - nE^\circ F$

$$E^\circ = - 2.2 \text{ V}$$

Required external e.m.f. $>$ greater than 2.2 V.

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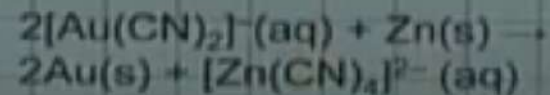
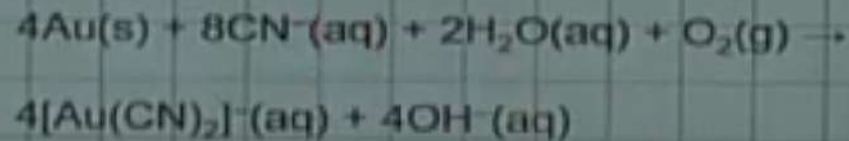




Oxidation is used for metals. For example

In extraction of gold and silver leaching with CN^- is an oxidation reaction ($\text{Ag} \rightarrow \text{Ag}^+$ or $\text{Au} \rightarrow \text{Au}^+$).

The metal is recovered by displacement method.



Zinc acts as a reducing agent

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Refining

Metal extracted by any method is usually contaminated

Preparation of metals of high purity is Refining

Some of the techniques used are

- | | |
|---------------------------|-----------------------------|
| (a) Distillation | (b) Liquation |
| (c) Electrolysis | (d) Zone refining |
| (e) Vapour phase refining | (f) Chromatographic methods |

Method depends upon properties of the metal and the impurity.

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Distillation

Very useful for low boiling metals like zinc and mercury.

The impure metal is evaporated

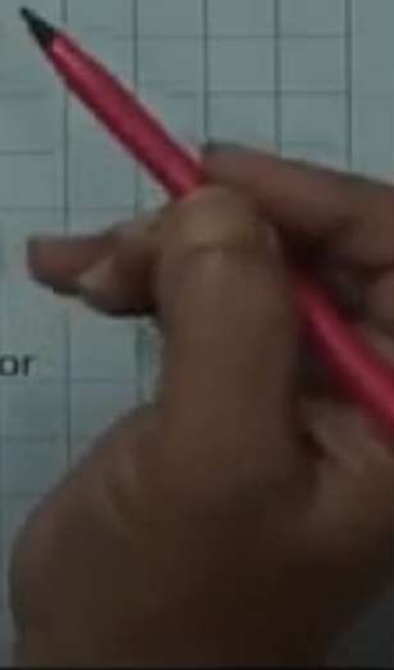
Pure metal obtained as distillate.

Liquation

Useful for low melting metal like tin

Molten metal is made to flow on a slopped floor

It separates from higher melting impurities.



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Electrolytic refining (Wider applications)

Impure metal is made anode.
A strip of the same metal in pure form is used as cathode.

They are put in a suitable electrolytic bath containing soluble salt of the same metal.

The more basic metal remains in the solution and the less basic ones go to the anode mud.

The reactions are:
Anode: $M \rightarrow M^{n+} + ne^{-}$
Cathode: $M^{n+} + ne^{-} \rightarrow M$

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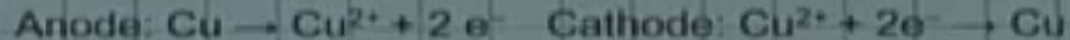




Refining of Copper by an electrolytic method.

Anodes are of impure copper and
Pure copper strips are taken as cathode.
Electrolyte is acidified solution of copper sulphate

Electrolysis results in the transfer of copper
in pure form from the anode to the cathode:



Impurities [Sb, Se, Te, Ag, Au and Pt] from the blister Cu
deposit as anode mud

Recovery of these elements may meet the cost of refining.

Zinc may also be refined this way

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Zone refining
Its principle is that the impurities are more soluble in the melt than in the solid state of the metal.

Fig. 6.7: Zone refining process.

A circular mobile heater is fixed at one end of a rod impure metal (Fig. 6.7).

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Fig. 6.3. Zone refining process

Molten zone moves along with the heater moved forward.
As the heater moves forward, the pure metal crystallises

From melt and the impurities pass on into adjacent molten zone

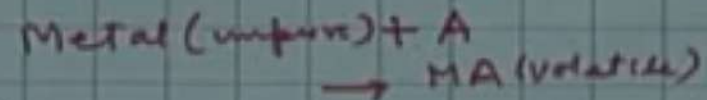
Process is repeated several times moving heater
in the same direction.

At one end, impurities get concentrated. This end is cut off.

Method is very useful for producing semiconductor and
other metals of very high purity, e.g., Ge, Si, B, Ga, In

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Vapour phase refining

Metal is converted into its volatile compound and collected

It is then decomposed to give pure metal.

Two requirements are:

- (i) the metal should form a volatile compound with an available reagent,
- (ii) the volatile compound should be easily decomposable, so that the recovery is easy.

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Mond Process for Refining Nickel:

Nickel is heated in a stream of carbon monoxide

Result a volatile complex, nickel tetracarbonyl:

$$\text{Ni} + 4\text{CO} \rightarrow \text{Ni}(\text{CO})_4 \text{ (330 - 350 K)}$$

Ni carbonyl on heating to 450 – 470 K
Decompose giving the pure metal:

$$\text{Ni}(\text{CO})_4 \rightarrow \text{Ni} + 4\text{CO}$$

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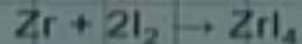


van Arkel Method for Refining Zirconium or Titanium:

It is very useful for removing all the oxygen and nitrogen present in the form of impurity in metals like Zr and Ti.

The crude metal is heated in an evacuated vessel with I_2 .

The metal iodide being more covalent, volatilizes:



The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K.

The pure metal is deposited on the filament



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Chromatographic Separation Compound

Principle: different components of a mixture are differently adsorbed on an adsorbent (filled in a column)

The mixture is taken in liquid or gaseous medium and moved through the adsorbent

Different components are adsorbed at different levels on the column

Adsorbed components are removed (eluted) by using suitable solvents (eluant).

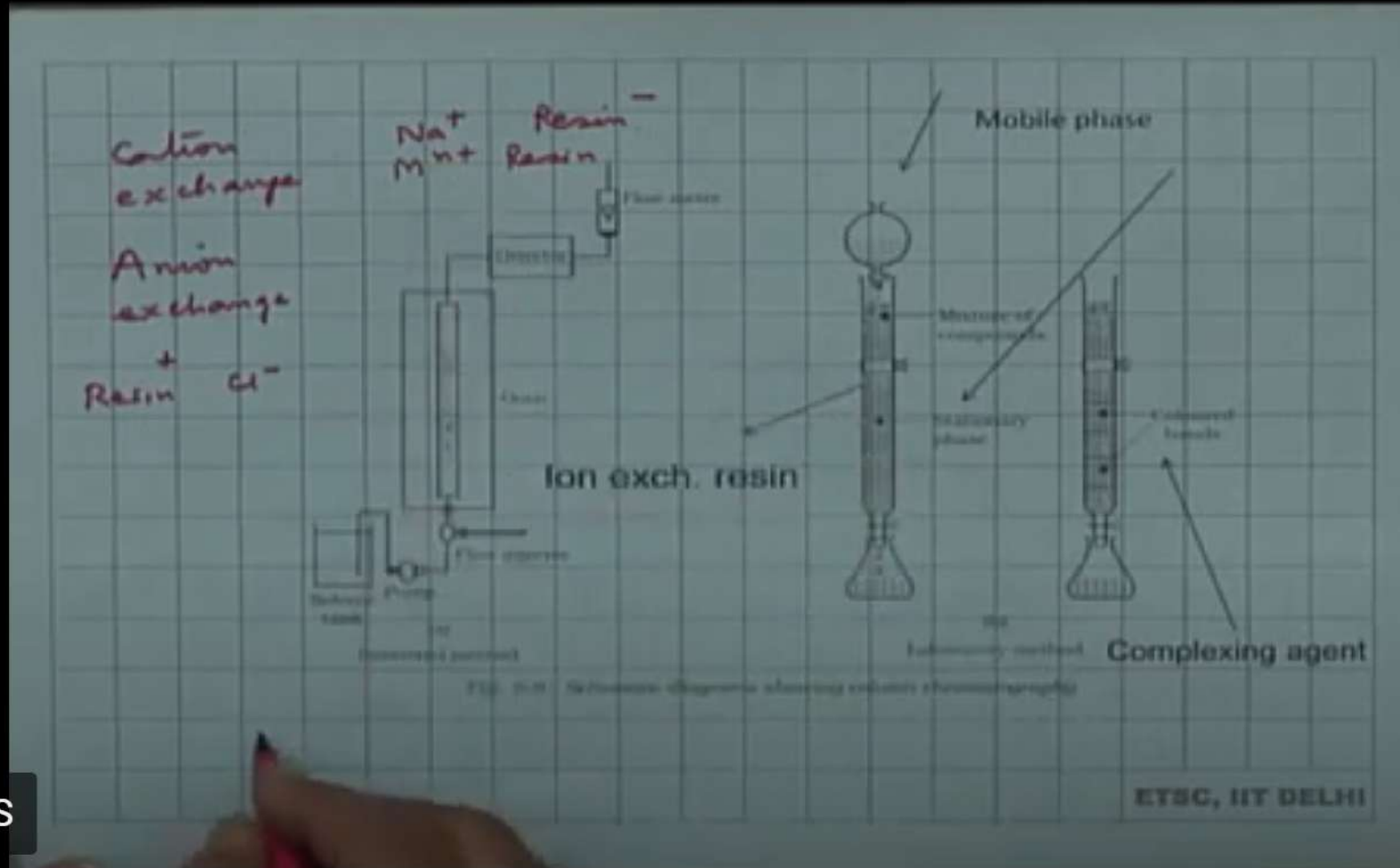


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Method is called Column Chromatography
Metal has to ^{be} brought in solution *(Small amt can be purified)*

Useful for purification of the elements present in minute quantities with impurities not very different in chemical Properties from the element to be purified.

Eluents: Complexing Agents

Chloride, EDTA

They work as different metal ions form complexes of varying solubility

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Anion-exchange separation of iron, cobalt and nickel

From 90% acetone-10% 6 M hydrochloric acid medium, Co and Ni are strongly adsorbed on the anion-exchange resin Dowex I-X8;

Iron is not adsorbed and can be separated from cobalt and nickel.

Cobalt and nickel are then separated by elution with 70% acetone-30% 2 M hydrochloric acid

Nickel is eluted before cobalt.

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Ion exchange chromatography

Complexing agents

Separation of lanthanoids

The lanthanoids, are separated on columns of cation-exchange resin.

Solutions of citrates, lactates, or other salts whose anions form negatively charged complexes with lanthanoid are used to wash the ions from the column.

The metal ions themselves are held by the resin; the complexes are not.

Ions that form more stable complexes do not adhere to the resin and move off the column quickly.

Ions that complex only weakly come out later in order of stability.

3+
size

cut Resin

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Cation exchange in general is not a selective process,
Above process, termed differential complex formation,
renders it more so.

✓ In lanthanoid separations the exchanger is like an
undiscriminating sponge that simply holds the metal ions,

Real separation of the lanthanoid is accomplished by
weakness or strength of the complexes formed

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