

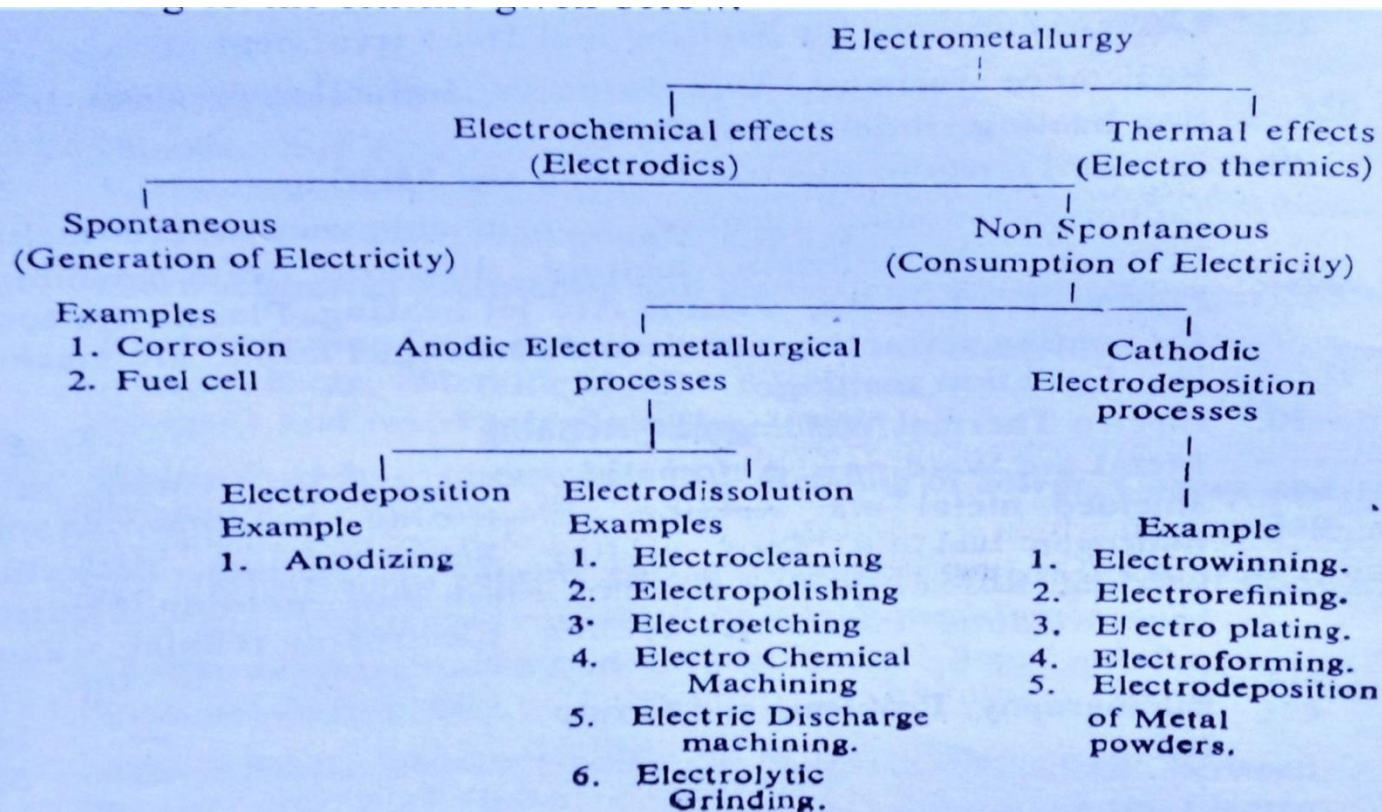
**LECTURE NOTES**  
**4<sup>th</sup> Semester B. Tech/2019-20**  
**TH-PEM**  
**BRANCH-METALLURGICAL AND MATERIALS ENGINEERING**

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**MODULE-V**

*References: An Introduction to Electrometallurgy-By: SHARAN & NARAIN  
& Extraction of Nonferrous Metals-By: H.S.RAY, R.SRIDHAR, K.P.ABRAHAM*



### Anodic Electrodeposition

Anode in an electrolytic cell is dissolved in controlled manner by adjusting operating conditions. The processes based upon electro dissolution are given below :

1. *Electrocleaning* : In order to have an adherent deposit, the articles to be electroplated are finally cleaned by electrocleaning methods. Electrocleaning is done by electrolysis of water solution of alkaline salt, making the work piece as anode. Cleaning is effected by removal of oil which is done due to scouring effect and mechanical agitations of gases liberated at the anode, dipped in electrolytic bath.

2. *Electropolishing* : Electropolishing processes consist of production of a bright reflecting surface on the metal by its controlled anodic dissolution, being carried out in a given range of voltage.

3. *Electro-Chemical Machining* : It is a machining process in which metal is removed from electrically conducting workpiece by



electrolytic action. This is also controlled anodic dissolution of anode (workpiece) in an electrolytic cell.

4. *Electric discharge Machining* : Electric discharge machining is based on the principle of removal of metal by spark discharge between the electrodes, making the work piece as anode.

5. *Electrolytic Grinding* : Electrolytic grinding is a combination of electrochemical machining and abrasive grinding in which metal removal mainly results from electrolytic action.

The comparative idea of anodic processes can be obtained from table 1.1.

### **Cathodic Electro-Deposition**

The cathodic processes applied to metallurgy can be mainly classified into five types.

1. *Electrowinning* : Electro-winning processes are those in which the metal is obtained by the electrolysis of the soluble salts of its mineral or more refined compounds, prepared and extracted from its ores.

2. *Electrorefining* : Electro refining processes also utilize the principle of electrolysis as in electrowinning processes except that in these processes pure metal is obtained by cathodic deposition from anodic dissolution of impure metal.

3. *Electroplating* : In the electroplating processes a continuous and coherent coating is applied to metal articles by principle of electrolysis to improve its corrosion resistance and surface properties or for decorative purposes.

4. *Electroforming* : Electroforming process are these processes in which the articles are produced or reproduced by plating on a substrate and then the substrate is removed. Electroforming is applied mainly to manufacture of articles of the complex shape.

5. *Electrodeposition of Metal Powders* : These processes also utilize the same principles as in electroplating except that the operating conditions are modified in such a way so as to obtain as less adherent as possible so that it may easily be removed from the cathode.

References: An Introduction to Electrometallurgy-By: SHARAN & NARAIN

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### **FARADAY'S LAWS OF ELECTROLYSIS**

Faraday's first law states that, during electrolysis, the chemical action produced by a current at an electrode is proportional to the quantity of electricity passed, and his second law states that

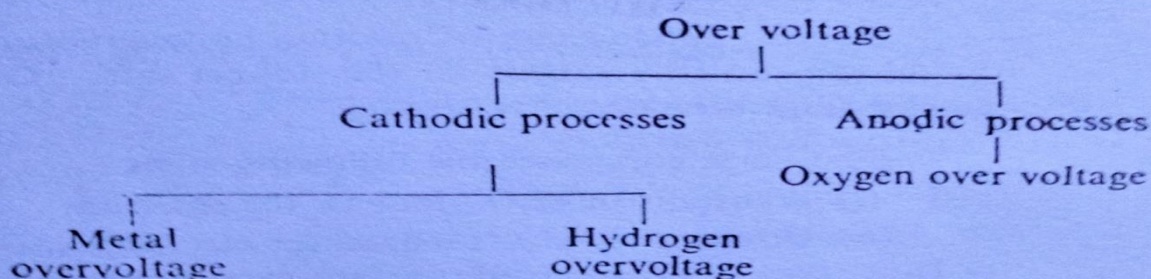


## ✓ OVER VOLTAGE

Over voltage is the voltage in excess of reversible voltage that must be impressed across a cell in order to bring about a cell reaction at an appreciable rate. Thus the difference between  $E_i$  and the equilibrium potential  $E_{rev}$  is known as the electrical over voltage which is denoted by  $\eta$

$$\eta = E_i - E_{rev} \quad (4.4)$$

The phenomena of over voltage is attributed to slow attainment of equilibrium at anode and cathode. This means higher the over voltage, slower is the reaction. Slowness occurs either in transfer of electrons or in the acceptance of electrons from ions in solution. Thus a free energy of activation is necessary for the reaction to proceed and the excess applied voltage serves to provide this.



### OVERVOLTAGE IN CATHODIC PROCESSES

1. *Metal Over Voltage* : Deposition of metal takes place relatively with small over voltage. Overvoltage is particularly low for metals such as zinc, copper, cadmium. Metals such as cobalt, nickel, iron, however, exhibit high over voltage.

It is to be noted that over voltage of metal increases with increase in current density but the increase is very small. Over voltage of metal is also increased when metal can exist as a complex ion. For example silver exhibits high over voltage in cyanide solution than in silver nitrate solution.

2. *Hydrogen Over Voltage* : Hydrogen evolution at cathode is generally considered as a very likely process. The evolution of hydrogen requires a higher value of potential than the theoretical value necessary for its liberation.



## Factors Affecting Hydrogen Over Voltage

1. *Current Density* : Hydrogen over voltage increases linearly with current density according to Tafel relationship.

$$\eta = a + b \log_{10} I$$

where  $I$  is the current density,  $a$  and  $b$  are Tafel line parameters or Tafel constants. Tafel constant  $a$  differs from metal to metal while Tafel constant  $b$  varies more or less constant to about 0.120 volt. The dependence of current density illustrated in Fig. (4.3)

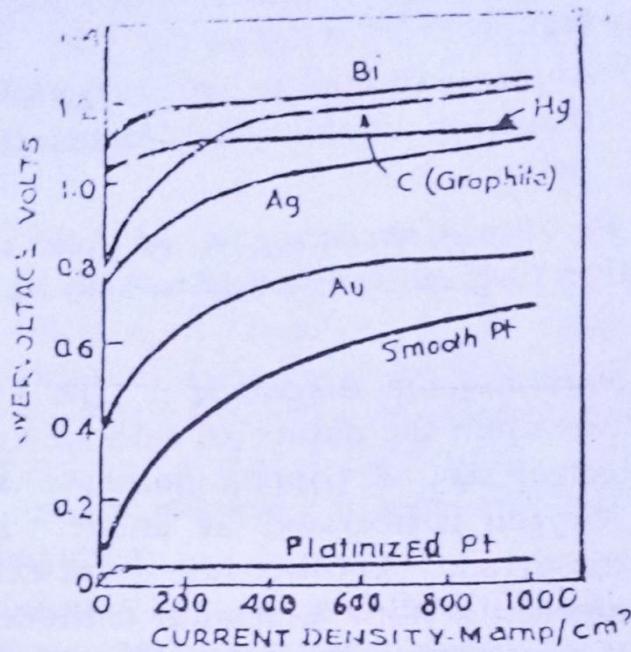


Fig. 4.3. Hydrogen over voltage of various metals

2. *Temperature* : Hydrogen overvoltage decreases with increase in temperature. In certain cases, it can reduce to zero values at higher temperature. For example hydrogen over voltage on nickel is zero at 90°C.

3. *Pressure* : At higher pressure, the values of hydrogen over voltage changes only very slightly, but at lower pressure, it rises sharply on copper, nickel and mercury cathodes.

4. *Cathode Material* : The hydrogen over voltage value varies considerably from one cathode material to another as shown in table 4.2. It is evident from the table that hydrogen over voltage can be very high at certain electrode made of lead and tin.

5. *Cathode Surface* : Hydrogen over voltage is greater on smooth shining and polished surface than on rough unpolished surfaces. Shape and curvature of the cathode also effects the hydrogen over voltage.



Total Cell Voltage:

## CELL VOLTAGE

For an electrolytic process to proceed at a given current  $I$ , the required voltage is greater than the decomposition voltage  $E_D$ . The total voltage  $E_T$  required to maintain the electrolytic process is given by,;

$$E_T = E_D + E_R + E_\eta + E_K$$

Where  $E_D$  is the minimum voltage required to effect decomposition of the electrolyte,  $E_R$  is the voltage required to overcome the ohmic resistance of the electrolyte and is equal to the product of current  $I$  flowing through the cell and resistance  $R$ ,  $E_\eta$  is the polarization over voltage associated with the deposition of a metal and/or liberation of gas and is sum of anodic ( $\eta_a$ ) and cathodic ( $\eta_c$ ) polarization over voltage, and  $E_K$  is the sum of contact potentials at each electrode and in connections between the electrodes and busbars.

Series And Parallel Electrical Circuits In Refining:

### Cell and Electrode Arrangement

Two types of arrangements are used :

1. Multiple or Monopolar System.
2. Series or Bipolar System.

#### 1. Multiple System

In this system the anodes and cathodes are arranged parallel in each tank while a large number of tanks are arranged in series. All the cathodes are connected to one common busbar and all the anodes to the other. (Fig. 22.1).

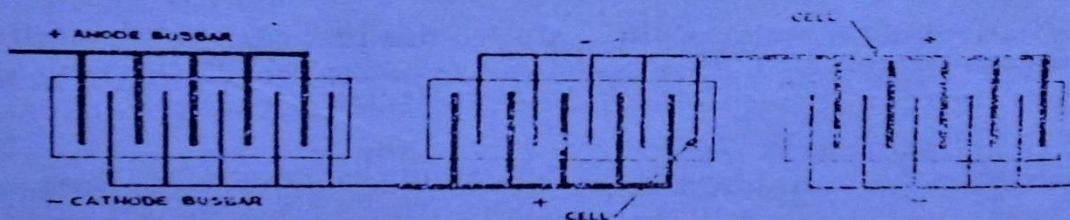


Fig. 22.1 Multiple arrangement of electrodes.

The greatest disadvantage of this simple arrangement is that



in a large tank house the above arrangement requires an enormous amount of copper. Hence the capital cost of the plant increases. To overcome this several modification are adopted.

### **Advantages and Disadvantages of the Multiple System :**

#### *Advantages*

- (i) Large distance between the anode and cathode makes it possible to utilize anodes containing a higher percentage of impurities since dissolved impurity can not reach the anode.
- (ii) Working costs are less because large anodes are prepared by simple casting.
- (iii) No stripping of the cathodes is required.
- (iv) There is less loss of precious metal.

#### *Disadvantages*

- (i) A greater current density is absorbed by each tank.
- (ii) A large number of cathode have to be prepared.
- (iii) There are large number of contacts which involve a loss of energy in the corresponding resistances.



## 2. Series System

In this system each individual cell contains suspended electrodes side by side but only the first and last electrodes act as cathode and anode.

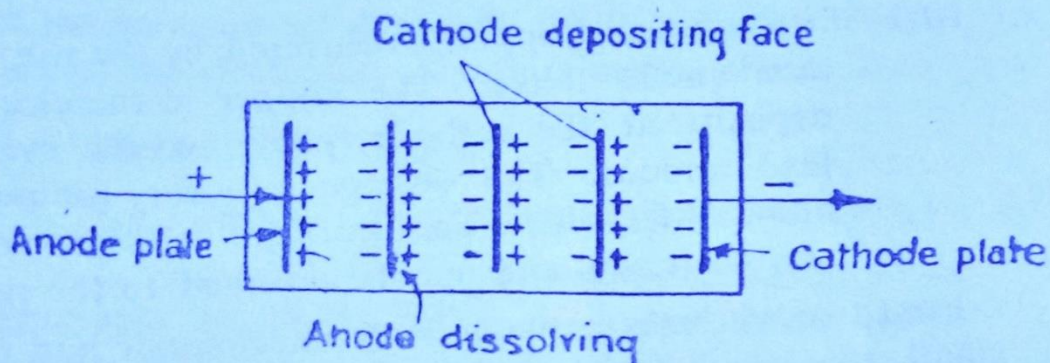


Fig 22.4. Series System of Electrodes

Rest of the electrodes act as bipolar, one side as cathode and the other as anode. When current passes through the electrolyte, the intermediate electrode anode side gets dissolved and pure copper is deposited on the other side. To prevent adherence, the side receiving copper is coated with graphite. The intermediate electrodes are suspended by copper links from iron bars, but these bars make no electrical contact.

### Advantages, Disadvantages of Series System :

#### Advantages

- (i) Less power is consumed in each tank for an equal number of electrodes so that there is smaller loss of electrical energy through joule effect and smaller amount of copper is required for current distribution net work.
- (ii) Most of the tank and electrical connections are reduced or eliminated.
- (iii) The series system requires less tank room space for a given out put because the tanks may be placed closer together and there are more electrode in each tank.
- (iv) Smaller distance between the electrodes offers the following advantages.

- (a) Decrease in ohmic resistance of the electrolyte.
- (b) Decrease in the quantity of electricity.



## ELECTROLYSIS OF AQUEOUS SOLUTIONS

The fact that water can dissolve relatively high concentrations of salt renders it suitable for electrolysis. It may be noted that aqueous solutions have a high conductivity at ambient temperatures, especially when acidic.

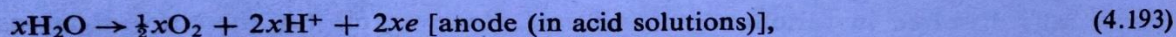
The stages involved in the overall extraction process leading to the electrowinning of metals from aqueous solutions are:

- (1) Leaching of a roasted ore (e.g., an oxide) to a form soluble in an acid



- (2) Purification and concentration of the leaching liquor.

- (3) Anode and cathode reactions during electrolysis



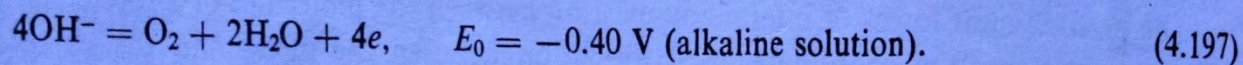
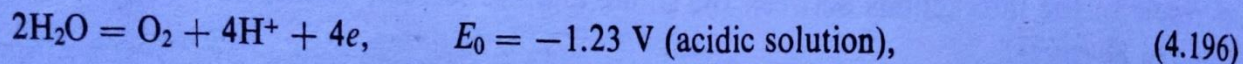
- (4) Recirculation of the acid liberated at the anode for leaching purposes.

The overall reaction for the conversion of the oxide roast to the metal is written simply as



Reaction (4.195) indicates that there should be no overall consumption of water or acid when the anode product is oxygen. Sulphuric acid favours the evolution of oxygen, while in a hydrochloric acid solution, chlorine would probably be evolved.

During electrolysis, the reactions take place at two distinct regions, namely, at the cathode and at the anode. At the cathode, the metal ion is discharged and the metal deposited. At the anode, the reactions depend on the nature of the electrolyte. For example, the reactions in acidic and alkaline aqueous solutions, respectively, are



As just stated, the anode reaction favours the evolution of oxygen.

The decomposition potential is the difference between the reversible potentials for the anode and cathode reactions. The operating voltage of a cell should be greater than this difference because it must also include additional terms such as activation and concentration overpotentials at the electrodes, the voltage loss due to the resistance offered by the electrolyte and due to resistance to the circuit and contacts. Generally, the operating voltage varies between 2 and 5 volts and the current efficiency between 80 and 90 per cent. In a cell, when the anode is unstable, the cathode is either a Pb-Sb-Ag alloy or graphite. The metal is deposited on a variety of cathode surfaces. The purity of the metal is usually higher than 99.95 per cent.

During electrorefining, an impure anode is corroded and the purified metal is deposited at the cathode. The theoretical voltage for a reversible condition is, of course, zero. Under normal



operating conditions, only a small voltage is required, mainly to overcome the resistance of the electrolyte. Consequently, the power consumption is low. The energy required for electrorefining is usually about one-fifth of that required for electrowinning.

In Chapter 2, it has been shown that during the actual electrolytic process, the potential at an electrode deviates from equilibrium due to the effect of the activation overpotential and the concentration overpotential. In fact, in practice, no deposition or solution process can proceed at the reversible electrode potential of the system. Hydrogen evolution on a platinized platinum electrode, however, comes close to equilibrium conditions.

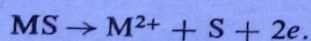
The electrolytic behaviour of metals is mainly of two types. Normal metals, when immersed in their salt solutions, rapidly establish a reversible potential. Since the activation overpotential is low, the displacement behaviour exhibits a good correlation with the electrochemical series of standard electrode potentials. Examples of this type are, Cu, Zn, Ga, Cd, Sn, Au, and Bi. These metals are deposited with a high current efficiency. Some other metals, for example, the transition metals, are deposited with a high activation overpotential and a low current efficiency.

The hydrogen overvoltage decreases as the temperature and the current density increase. The practical effect of hydrogen overvoltage, as already pointed out, is to make possible the electrowinning of metals such as zinc which, because of the hydrogen overpotential, do not displace hydrogen from an acid solution as long as the current flow is maintained.

Some typical operational data for the electrowinning and electrorefining of a few metals in aqueous solutions are given in Tables 4.4 and 4.5.

#### ANODIC DISSOLUTION OF METAL SULPHIDES

The anodic dissolution of metal sulphides in an aqueous medium has received considerable attention recently. The reaction at a sulphide anode in an aqueous electrolyte is



Sulphide electrodes can be made from mattes. Commercial plants based on the anodic dissolution of nickel sulphide are presently being operated successfully.

#### ELECTROLYSIS OF FUSED SALTS

The emf series—in which the electrode potentials are arranged with respect to the potential of the standard hydrogen electrode—indicates that the metals placed above hydrogen should not normally be amenable to electrolytic deposition. Nevertheless, due to polarization phenomena, some metals, although placed above hydrogen, become stable in aqueous solutions during the passage of a current. However, the polarization phenomena can be exploited only in the case of metals up to manganese. Metals placed above manganese are too reactive to be produced from aqueous solutions, and are produced by electrolyzing water-free fused salt mixtures.

Theoretically, any metal can be obtained by the direct electrolysis of one of its salts, for example, a pure halide. In practice, however, it is often advantageous to dissolve a compound such as a halide in a mixture of more stable halides such as sodium chloride and potassium chloride. This procedure improves the conductivity of the melt, lowers the melting point of the medium, and reduces the possibility of dissolution of the metal in the salt.

Operations in high-temperature media such as molten salts have some distinct advantages, for example, a reactive metal may be readily obtained in the absence of hydrogen ions. The conditions are favourable for attaining a more complete heterogeneous equilibrium because all



the reactions are accelerated. The metal produced, if molten, may be easily removed. Overvoltages on molten metals are often small enough to allow high current densities and, therefore, greater throughput. Further, at high temperatures, diffusion rates are high and, therefore, during some electrorefining processes, impurities can be transferred from the anode to the cathode so as to purify the metal. In such processes, only very small amounts of metal impurities need to be transferred electrochemically. ✓

The use of high temperatures, however, has some disadvantages too. The efficiency is lowered due to the increased possibility of side reactions taking place, for example, between the products of electrolysis and the electrodes. In most molten salt electrolytic processes, the anode material is graphite, which leads to formation of CO and CO<sub>2</sub>, unless inert gases are used. Sometimes, CO may diffuse through the melt or the gas phase to reach the metal and seriously contaminate it, affecting its mechanical properties.

In most fused salt electrolytic processes, several side reactions may take place apart from the desired decomposition reaction. These reactions and other diverse factors are responsible for an apparent deviation from Faraday's laws. Consequently, the current efficiency is far below the optimum value of 100 per cent. Theoretically calculated current consumption values hold good only in very simple systems, such as in silver halide electrolysis using inert electrodes. In some cases, for example, during the electrolysis of CdCl<sub>2</sub> or BiCl<sub>3</sub>, the initial cathode current efficiency may even be zero; which means that, in the initial stages, no metal is deposited on the cathode. Further, the magnitude of current lost is very high in some systems, for example, in a Pb-PbCl<sub>2</sub> system. We now summarize the factors that lead to a lower current efficiency and state how these can be avoided.

(1) Mechanical losses (handling losses) of the substances formed at the electrodes. These losses can be minimized by using improved operational techniques.

(2) The evaporation of the metal from the cathode. This may take place during the electrolytic liberation of sodium from fused sodium chloride because the operating temperature would be close to the boiling point of the metal. The problem can be solved by dissolving the sodium chloride in a suitable medium to form a low melting mixture, thus lowering the operating temperature.

(3) Chemical side reactions. The unwanted side reactions can be controlled by choosing the proper electrolyte and using a lower operating temperature.

(4) The formation of lower valency compounds at the cathode. For example, in the electrolysis of SnCl<sub>4</sub>, in the initial stages, tin reacts with the electrolyte to form SnCl<sub>2</sub>, and the cathode current efficiency is zero. In most instances, the melt is soon saturated with the lower valency compounds, and after a while, the metal starts depositing on the cathode.

(5) The formation of higher valency compounds at the anode. This reduces to zero the anode current efficiency in the initial stages of electrolysis. For example, during the electrolysis of SnCl<sub>2</sub> in the initial stages, the chlorine liberated at the anode reacts to produce SnCl<sub>4</sub>. However, after some time, the melt becomes saturated with SnCl<sub>4</sub>, and further reaction would cease.

(6) The dissolution of the metal in the fused salt. This drawback can be eliminated to a great extent by dissolving the metal salt in a more stable salt to form a relatively dilute solution.

(7) The recombination of the electrolysis products with the original salt. (This problem assumes serious proportions in the production of reactive metals such as magnesium. During the



electrolysis of  $\text{MgCl}_2$ , the liberated metal and gas should never be allowed to come in contact.) Recombination can be eliminated by the immediate and complete isolation of the electrolysis products by employing an electrolytic cell with a special design.

(8) Current losses due to the presence of moisture. This problem is not serious in the case of fluorides because they can be prepared and stored in a dry state without much difficulty. Most chlorides, however, are extremely hygroscopic, and precautions have to be taken to completely eliminate the moisture. To do so, chlorides are produced *in situ* in the electrolytic cell, by feeding the metal oxide slowly into the cell. The hot gases formed in the cell are used to eliminate all traces of moisture, and the chlorine evolved is used to chlorinate the oxide inside the cell.

## ELECTRO REFINING OF COPPER

Almost all copper produced today is electrolytically refined. The electrolytic refining process serves two purposes.

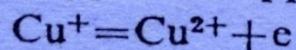
1. To produce highly purified ( $>99.95$ ) copper for electrical industries.

2. To recover precious metals (Ag, Au, Pt). Fire refining methods can not serve these purposes. In such cases electrorefining is the only available economic method.

Copper anodes are placed in a tanks with a solution of copper sulphate to which is added sulphuric acid. The cathodes are pure copper sheets which are suspended between the anodes. Under current action, copper dissolves at the anode and deposits at the cathode. Dissolution and deposition reactions are given as below :

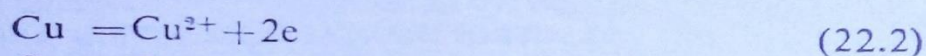
### Anode Dissolution Reaction

On passage of the current, the anode (crude copper) dissolves and gives rise to two types of copper ions mono and divalent.



(22.1)





Divalent ions are in a large concentration due to lower electric tension of reaction (22.1) and (22.2). However, equilibrium is set up between  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  in the presence of metallic copper, according to the reaction (22.4).

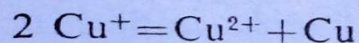


At the start of electrolysis,  $\text{Cu}^{2+}$  ions are present in a very large quantity while  $\text{Cu}^+$  ions are present in very small quantity. The increase in the concentration of  $\text{Cu}^{2+}$  has two effects :—

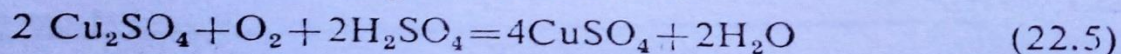
1. Shifting the equilibrium of the reaction in direction of formation of  $\text{Cu}^+$  ions.

2. Shifting the electric potential of reaction (22.3) in more noble direction and therefore formation of  $\text{Cu}^+$  ions is facilitated.

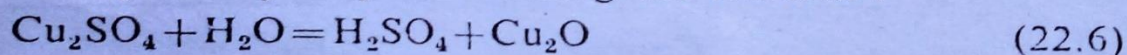
$\text{Cu}^+$  ions, thus formed are disposed in two ways : Part of  $\text{Cu}^+$ , gets deposited on the bottom until equilibrium is obtained according to the reaction.



Another part of  $\text{Cu}^+$  is oxidized by atmospheric oxygen in the presence of free acid according to the reaction.



However, if the solution does not contain free sulphuric acid, the cuprous sulphate hydrolysis according to the reaction :



### Copper Deposition Reactions

At cathode, reduction of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  occurs according to the reactions :



The principal cathode reaction is always discharge of  $\text{Cu}^{2+}$  ions. The reduction of  $\text{Cu}^{2+}$  can also occur to re-establish the equilibrium of reaction (22.4).



## Operation Conditions

1. *Applied Voltage* : In electrorefining, energy absorbed in liberating the copper at the cathode is counter balanced by the energy generated in dissolving copper at the anode, i.e. equilibrium potentials of the anode and cathode are practically same ( $E_a - E_c \approx 0$ ). The voltage necessary for the electrorefining is the sum of the voltage to overcome the resistance of electrolyte, resistance of electrodes, slimes clinging to the anode and contact resistances.

2. *Current Density* : Current density should be fairly high but not too high due to the following reasons :

- (i) To avoid simultaneous discharge of  $H^+$  ions which causes deposit to be spongy, solution near cathode to be alkaline and facilitate the hydrolysis of the cuprous sulphate.
- (ii) To avoid the reduction reaction  $Cu^{2+} + e \rightarrow Cu^+$  which lowers the current efficiency.

3. *Temperature* : The following are effects of increase in temperature.

- (i) It increases the conductance of the bath.
- (ii) It diminishes the electrode polarization of electrodes.
- (iii) It increases the rate of chemical corrosion of anode. This increases the copper content in electrolyte.
- (iv) It also increases the chemical dissolution (upto 20%) of the deposited metal at cathode.

Temperature is fixed as a compromise because some of effects of temperature are desirable, while some are undesirable. Temperature of the electrolyte is maintained at about 50 to 60°C.

## Electrolysis Products

- 1. *Copper* : The copper deposited at cathode is 99.98%.
- 2. *Anode Sludge* : The anodic sludge or black slimes which represents about 0.8-1.2 % of copper used consists of mainly of copper and silver. It also contains all the gold originally present in the anode and other insoluble impurities.



3. *Exhausted Electrolyte* : As the electrolysis proceeds, the electrolyte gets contaminated by various anodic impurities such as copper, nickel, arsenic, antimony etc. Removal of these impurities from the tank is essential because these impurities increases the resistance of the electrolyte.

## Electro Refining Of Au:

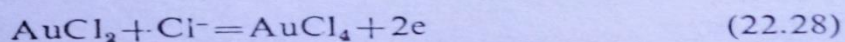
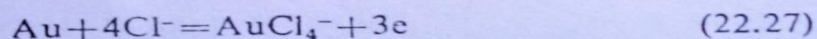
### ELECTRO REFINING OF GOLD

All classes of the bullions that come for refining, including bars, rich gravity concentrate, cyanide precipitate, slimes from the electrolytic recovery of copper and nickel, amalgamated metals and also industrial and domestic scraps are usually associated with number of impurities particularly base metals, silver and platinum group metals. Electrolytic refining offers the method to produce gold from the impurities mentioned above. Common process of electrolytic refining of gold is Wohlwill process which makes the use of impure gold anode and  $\text{AuCl}_3$  with free hydrochloric acid as electrolyte.

Under current action gold dissolves from the anode and deposits at the cathode. The reactions are given below.

#### Anode Dissolution Reactions

Gold from anode does not dissolve in  $\text{AuCl}_3$  solution due to its passivation. However, in the presence of  $\text{Cl}^-$  ions gold dissolves into solution as monovalent and trivalent ions according to the reactions given below :



Excess of  $\text{Cl}^-$  ions can be provided by the addition of small amount of  $\text{HCl}$  or  $\text{NaCl}$  in  $\text{AuCl}_3$ . Equilibrium is established between mono and trivalent ions at the anode according to the reaction.



This reaction causes precipitation of some gold at the bottom of the cell.

#### Gold Deposition Reactions

The gold deposits on the cathode as a dense and hard layer. The mechanism of the cathodic reaction is not clear because mono and trivalent gold cations are present near the cathode, only in low concentration. Cathodic deposition might be possible due to secondary reactions between the gold containing anions and the product of more likely primary reactions.



If the anodes contain less than 80% of gold, the purity may be increased by treatments with nitric acid (Quartation) or boiling with concentrated sulphuric acid (Affination).

The Wohlwill process is carried out in a glazed porcelain or acid proof stone ware cell. The anodes are suspended on gold hooks, the hooks themselves are not immersed in the electrolyte. Anode are enclosed in cloth bags in order to prevent the insoluble from the fouling the electrolyte. The cathode consist of thin sheets of gold foil. Anodes and cathodes are connected in multiple system as in copper refining.

### Modification

Anode containing 10-20% impurities which must however, be mainly silver can still be refined electrolytically by superimposing an alternating current on direct current. The alternating current must have low frequency and intensity about 10% greater than of direct current so as to obtain periodic and asymmetric inversion of the current. The amount of power consumption is equal to the sum of both currents but the amount of gold deposited is a function of direct current only.

This imposition of A.C. current has the following advantages.

1. It makes the anodic film of AgCl loose and poorly adherent so that it can easily be removed.
2. It acts as depolarizer and therefore lowers the anodic polarization and hinders the passivation, making it possible to use high current density.
3. It also diminishes the form of  $Au^+$  and thus lowers the loss of gold in the form of powder into the anodic sludge.
4. It heats the bath therefore electrolysis may be concluded at lower temperature.
5. It reduces the e.m.f. of the cell.
6. It prevents the liberation of chlorine at the anode.

The pulsating current is produced by connecting a.d.c. dynamo in series with a a-c generator, the voltage of A.C. being slightly higher than the other.

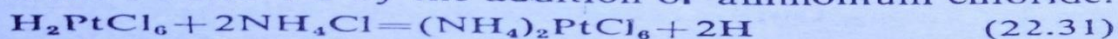
### Electrolysis Products

1. *Gold* : The gold cathodes produced are about 999.80 fine, or very nearly 24 carat.
2. *Exhausted Electrolyte* : The electrolyte is changed at regular intervals to prevent the excessive accumulation of impurities. Typical composition is given in table

Element	Concentration
Au	30-60 g/l
Pt	40-8 g/l
Pd	5-20 g/l
Other metals	Small quantities to traces



Gold is recovered from the exhausted electrolyte by treatment with  $\text{SO}_2$ , and the Pt and Pd by the addition of ammonium chloride.



The washed precipitate of platinum ammonium chloride is calcined to produce Pt sponge. Palladium, if present, is removed with sodium hydroxide, after evaporation to dryness, the copper is removed with iron scrap.

3. *Anode Sludge* : The typical composition of anodic sludge is given in table

	With A.C.	Without A.C.
Au	1%	80%
AgCl	95%	20%
Metals of the Pt group	5%	5%

If the sludge contains much gold it is melted and allowed to solidify. The still liquid silver chloride is removed from the crucible and the underlying gold is remelted and formed into anodes. If however, the silver chloride is most abundant, it is treated with zinc and HCl to reduce the silver chloride and then used for silver refining.

## ELECTROREFINING OF ALUMINIUM

The aluminium obtained from the Hall and Heroult electrolytic cell is not very pure, maximum purity being only 99.95%. It contains metallic and nonmetallic impurities. The chief metallic impurities are iron, silicon, titanium, vanadium, sodium and potassium. Under normal conditions of operation, about 60% of the iron and 40% of the silicon of raw material enters the metal whereas titanium and vanadium enters quantitatively in the metal. Non metallic impurities include alumina, aluminium carbide, electrolyte and gases such as hydrogen. These impurities may come either from the bath or from the receiver during and after the metal is run off. All of these impurities have detrimental effect on mechanical properties, electrical conductivity and corrosion resistance of the metal. To obtain a metal of purity higher than 99.99%, a refining process has to be employed. Super purity aluminium is soft, highly reflective and corrosion resistant and is used only for specialized uses. Typical applications are given below.

(i) Copacitor foil manufacture.

(i) Formation of high aluminium oxide to be used as catalyst for certain petroleum refining processes.



(iii) High finish alloys for jewellery and automotive applications.

Owing to its high boiling point ( $2270^{\circ}\text{C}$ ) and high reactivity, its refining can not be done by the methods normally employed for the refining of other metals such as controlled oxidation, distillation etc. Electrorefining is therefore, most common method.

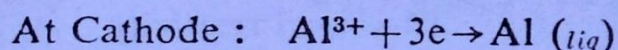
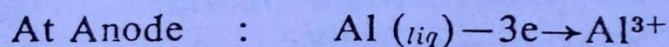
The Refining of crude aluminium is done by fused salt electrolysis with soluble anodes similar to the electrolytic refining of metals in aqueous electrolyte. It is carried out in a cell with three horizontal layers.

1. *Bottom layer or Anode Layer* : The specific gravity of this layer is maximum and consists of impure aluminium alloyed with copper to make the density greater than that of electrolyte. This layer serves as anode and therefore also called as anode layer.

2. *Middle layer or Electrolyte layer* : This consists of an electrolyte consisting of anhydrous fluorides and chlorides. The composition is so adjusted that the specific density lies between that of anode layer and pure aluminium.

3. *Top layer or Cathode Layer* : Floating on the top is a layer of aluminium which serves as cathode.

When current is passed, aluminium ions travel to the cathode through the electrolyte where they deposit as metallic aluminium. The reactions may be expressed as follows.



Theoretically the voltage required to transfer aluminium from anode to cathode is of the order of only a few milli volts. However, polarization at anode and cathode of cell and poor conductivity of the electrolyte makes it necessary to maintain the cell voltage of about 5 to 7 volts across the cell.

The purity of depositing Al exceeds 99.99%. More electro-positive impurities cannot leave the anode as long as the anode contains enough aluminium. The more electronegative impurities, however, enter into the electrolyte from the anode but cannot deposit as long as the concentration of aluminium in the electrolyte and even at cathode is high, because their deposition potential is higher than that of aluminium.

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The purity of metal depends upon the differences in the densities and their fall or rise during temperature changes and



*References:An Introduction to Electrometallurgy-By:SHARAN & NARAIN  
& Extraction of Nonferrous Metals-By: H.S.RAY,R.SRIDHAR,K.P.ABRAHAM*