Non-ferrous Extractive Metallurgy
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Lecture No. # 08
Principles of Electrometallurgy

Today, we will start lectures from module four of this lecture series. In this module we are going to discuss two subjects, which may look unrelated; one is electrometallurgy, and the other is refining of metals.

We have previously discussed Pyrometallurgy and hydrometallurgy, and I defined a Pyrometallurgy as metallurgical operations at high temperatures using high temperature phases, and hydrometallurgy as metallurgical operations mostly in a course media sometimes using organic solvents, but almost always at pretty low temperatures.

I am discussing electrometallurgy separately for two reasons, first of all electrometallurgy came into the seen much later than pyrometallurgy or hydrometallurgy. You know it had to wait for the discovery of electricity, invention of electricity which happened only in the mid nineteenth century al so. Until Faraday had the invention of electricity, there was no question of electrometallurgy he could not possibly have produced metals by electrolysis. So, electrometallurgy is a relatively recent metallurgical activity.

But that is not the only reason why I am separating it out from pyrometallurgy and hydrometallurgy, it so happens that in electrometallurgy very often you produce metals which do not need further refining two prime examples are a zinc produced by electrolysis, aluminum produced by electrolysis, zinc from eco solutions, aluminum from few sort media. Actually we could have done with less purity, at least in the case of zinc because much of zinc goes in for galvanizing where very high purities are not required but to have electrolysis of eco solutions you need to have solutions which are very pure which do not have other impurities which will also get electrolyze at that time. So, there is a great deal of purification before the zinc (( )) is made for electrolysis, so whether we want it or not the zinc comes out as 99.9 percent pure. In the case of aluminum also, aluminum produced this very pure that is why I consider electrometallurgy to be a kind of a processing step which gives you pure metals very often.

And then of course, we will discuss a refining of metals, which are necessary for bulk metals produced by pyrometallurgy because in pyrometallurgy very often the gold is to produce lot of metal at a time and then not only purify the metal but recover from the metal many other metals which are there. In hydrometallurgy also we need refining of the (( )), lot of compound that you produce. So, in this module we will first discuss electrometallurgy, that will need about two, three lectures after that, our consider general principles of refining of metals.

You will note that, so far we have not started discussing extracting metallurgy of any metal in specifically. We have given examples, of production of this metal or that metal like, in the lecture just did yesterday we talked about precipitation of Nickel and Cobalt, by (( )) reduction of Nickel amines and Cobalt amines in eco solution. But they were to give as an illustration of a principle, we have not started talking about specifically extraction of any metal, we will we will do that after couple of lectures had finished talking about the principles of Electrometallurgy, principles of refining then we will start with metals in groups.

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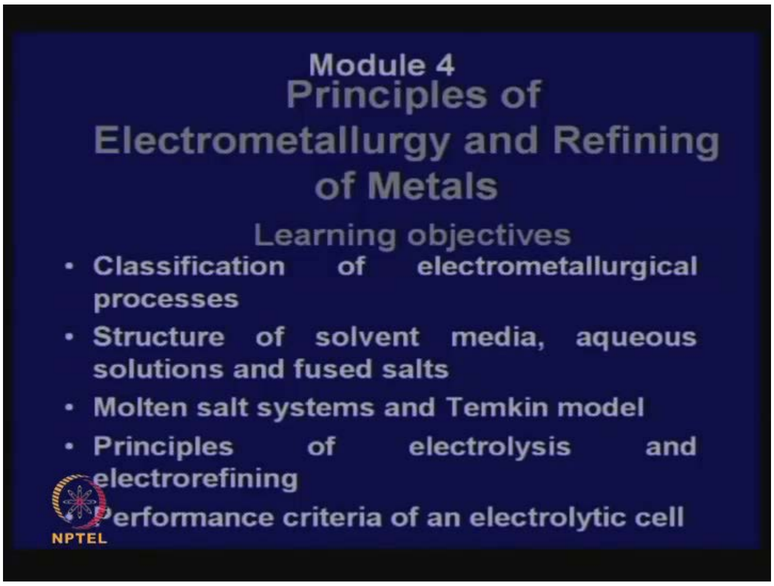

Module 4
Principles of Electrometallurgy and Refining of Metals

Learning objectives

- Classification of electrometallurgical processes
- Structure of solvent media, aqueous solutions and fused salts
- Molten salt systems and Temkin model
- Principles of electrolysis and electrorefining
- Performance criteria of an electrolytic cell

Now, the principles of Hydrometallurgy, Electrometallurgy lectures, we have the in this the following learning objectives, as we have listed. We will start with classification of Electrometallurgical processes.

Generally, we think that electrometallurgy means only electrolysis of aqueous media and fused salts, but that is not a case actually the definition of electrometallurgy is, metallurgical processes which make use of electricity or electrical effects, use of electricity and electrical effects and under that many things come, we will come to that after I have gone through this list of learning objectives. We will go through a classification of electrometallurgical processes, we will discuss something about the structure of solvent media eco solutions as well as fused salts, we will talk about molten salts systems and a model called Timken model for molten salt systems. Then you come to principles of electrolysis and electrorefining.

Because in electrometallurgy, we are going to discuss electrolysis and electrorefining only, I will not discuss a many other things which come under electro metallurgy finally, we will also talk about performance criteria for an electrolytic cell, when do we say an electrolytic cell is operating well?

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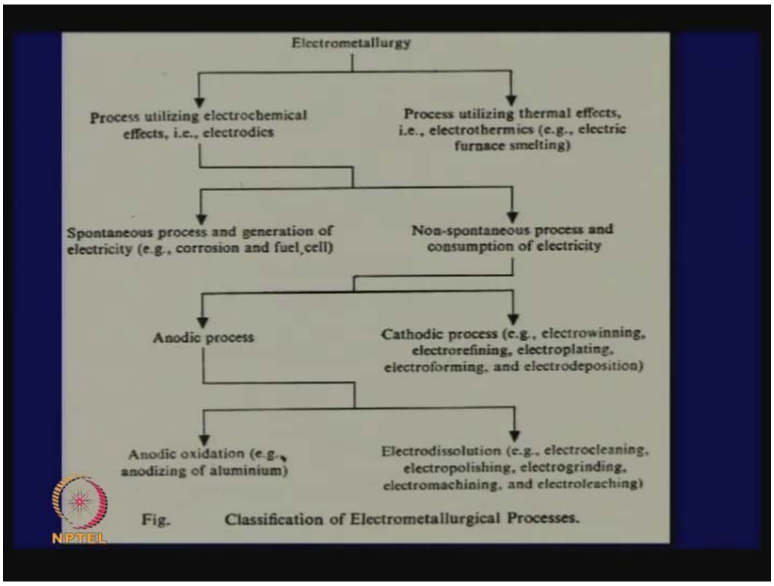

Electrometallurgy

Process utilizing electrochemical effects, i.e., electrodics

Process utilizing thermal effects, i.e., electrothermics (e.g., electric furnace smelting)

Spontaneous process and generation of electricity (e.g., corrosion and fuel cell)

Non-spontaneous process and consumption of electricity

Anodic process

Cathodic process (e.g., electrowinning, electrorefining, electroplating, electroforming, and electrodeposition)

Anodic oxidation (e.g., anodizing of aluminium)

Electrodissolution (e.g., electrocleaning, electropolishing, electrogrinding, electromachining, and electroleaching)

Fig. Classification of Electrometallurgical Processes.

Let us look at the way Electrometallurgy is classified. Electrometallurgy can mean processes using electrochemical effects that necessarily make use of electrodes and that also has two classifications, like we can have spontaneous process and generation of electricity, like we have in corrosion and fuel cell these also come under electrometallurgy, non-spontaneous processes and consumption of electricity, under this will come Anodic processes and Cathodic processes. Cathodic processes refer to electro winning electrorefining, electroplating, electroforming electrodeposition, in all these cases metal ions deposit at the Cathode.

Whereas, the Anodic processes have two classification, Anodic oxidation for example, anodizing of aluminum or electrodissolution, that instead of depositing a metal you may actually dissolve it by passing electricity and example is electrocleaning, electropolishing, electrogrinding, electromachining and electroleaching. It can take out the metal from the surface using electricity and it is a non-spontaneous process, it does not happen on its own you have to apply voltage across electrodes, you have to pass an electricity, where are the in the spontaneous processes it happens without you are trying to apply a voltage or we are trying to pass a current.

Then, we have processes utilizing thermal effects like, electrothermics. This arc furnaces that use for smelting electricity, they also come under electrometallurgy but here in this course we will restrict ourselves to only these two electrowinning and electrorefining. Because these are directly related to metal production, the other things are important also but I am afraid there is no time for discussing those things here. Now, for electrolysis or electrorefining we necessarily need a proper electrolyte, in which through which we will pass current, there are some requirements for a proper electrolyte and I have listed these here.

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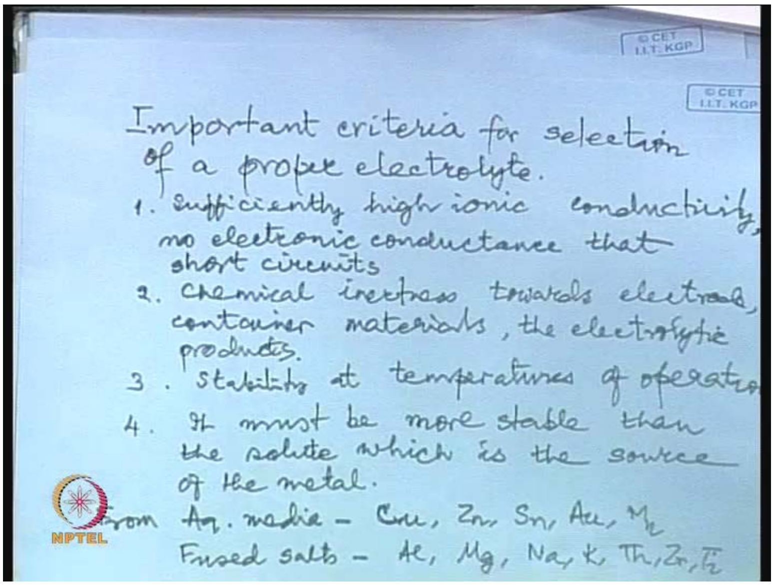

Important criteria for selection of a proper electrolyte.

1. sufficiently high ionic conductivity, no electronic conductance that short circuits
2. Chemical inertness towards electrode, container materials, the electrolytic products.
3. Stability at temperatures of operatio
4. It must be more stable than the solute which is the source of the metal.

From Aq. media – Cu, Zn, Sn, Au, Mn

Fused salts – Al, Mg, Na, K, Th, Zr, Ti

An electrolyte for application in electrolysis or electrorefining must have sufficiently high ionic conductivity, means entire electronic conduction must be through migration of ions. Now, not all electrolytes have, even though they may be ionic not all electrolytes are equally good electrolytes, we need electrolytes where the conductivity is high, where the ions move fast where there lots of ions. We want know electronic conductance, electronic conductance like, we have in metallic substances with short circuit electrodes, means current will pass through that body without creating or achieving any ionic dissociation, it will pass through only to heat the body we do not want that.

Secondly, the electrolyte to be used must be inert towards the electrode, the container materials and the electrolysis products. It is obvious, if the electrolysis products start reacting with the electrolyte as that can happen sometimes, then it is not a good electrolyte, it becomes a reactant, it has to be a medium where the metal from which the metal will come out and we will not redissolve.

The electrolyte must be stable at temperatures of operation, there is no problem in the case of aqueous media but when we talk about fused salt fused salt electrolysis, we need to have salts which are stable, which will not vaporize or which will not dissociate. A very important criterion, which should be obvious but it needs mentioning is that, if we have a salt dissolved in a media, then the media must be more stable than the salt under the voltage were applying for electrolysis. We do not want the media to get electrolyzed we want only the solute to be electrolyzed.

And what I have said applies both in the case of aqueous media, as well as in the case of fused salts. From aqueous media, we industrially produce Copper, Zinc, Tin, Gold, Manganese and some other things. In fused salt media, industrially from fused salt media we get Aluminum, Magnesium, Sodium, Potassium, Thorium, Zirconium and Titanium. In theory, almost all metals can be obtained through fused salt electrolysis, in theory but then these are the once which find maximum application.

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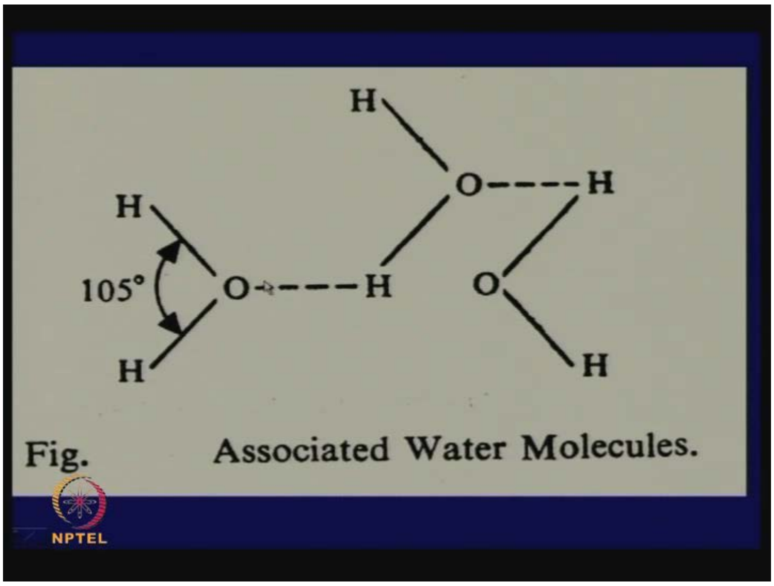

Fig. Associated Water Molecules.

Now, before I proceed let me say few words about the structure of electrolytes. Normally, we do not pause to think what structure of water is like, we think water is made up of H 2 o molecules, it is not exactly that. The molecule of H 2 O is written like this, it is called a, what we call a pooler molecule means, we do not have the hydrogen on opposite sides of oxygen, so as to be straight in one line. For some reason the hydrogen atoms are attach to oxygen in an angle of hundred and five degrees.

Now, this implies that it is not completely neutral charge wise because in this space and this side there is a negative charge, on this side there is some residual positive charge, so it is slightly negatively charge, this is slightly positively charge because of this angularity and because of this, they slightly positively charge oxygen is attracted to a slightly positively charge hydrogen atom and there is these get attach to each other in the in the water medium.

So, the result of such association is a liquid, which has a very high dielectric constant. Because it is not one simple single molecule, another single molecule they have all got associated, they are call associated molecules. And because of this association, we have a medium with why a very high dielectric constant, which helps in the breakdown of crystal lattice of ionic compounds. When ionic compounds like sodium chloride or some other things have put there, it is this high dielectric constant water which helps to break them and dissociate them.

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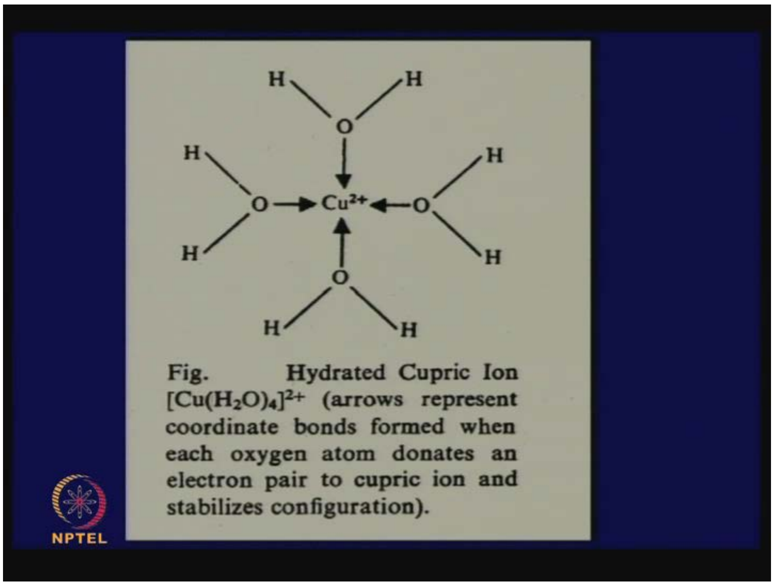

Fig. Hydrated Cupric Ion $[Cu(H_2O)_4]^{2+}$ (arrows represent coordinate bonds formed when each oxygen atom donates an electron pair to cupric ion and stabilizes configuration).

And after they are dissociated, they form complexes like this with the metallic ions, where is a hydrated cupric ion written as c u H 2 O 4 2 plus as shown here, the arrows represent coordinate bonds formed when each oxygen atom donates an electron pair to cupric ion and stabilizes the configuration.

As I said, it is slightly negatively charge, (( )) slightly positively charge this side, so because it slightly negatively charge it gets attach to c u 2 plus ion and this happens from four sides we get a complex like this. Now, this kind of complex is can be formed with ammonia NH 3, chlorine ions, c n minus ions, o h ions, p 2 of seven form minus ions. So, all these kind of thing complex can form in ionic media and we have I have refer to this

Nickel amine and Cobalt amines earlier. In general, I can say that most ecosolutions of metal compounds contain, complexed metal ions, not metal ion free as such and this complex side may be formed as I said by NH3 c l minus, c n minus, o h minus, p 2 seven etcetera.

In ammoniacal solution Nickel and sponge a series of amines, which we can write as n I n h 3 2 plus sub x, where x varies from 1to 6. If h c l is added to an ecosolution of copper sulfate, they solvate it cupric ion progressively losses water molecules to finally, form a complex containing only chlorine ion but before that there is series of complex ions.

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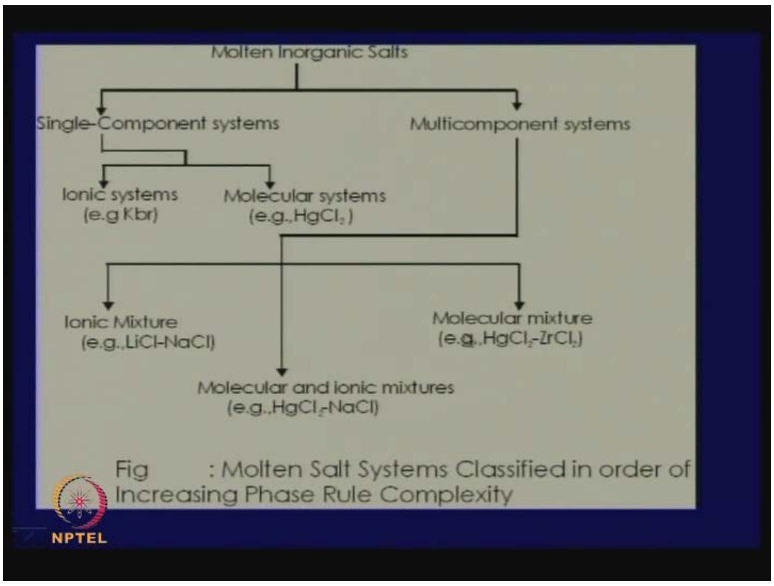

Molten Inorganic Salts

Single-Component systems

Multicomponent systems

Ionic systems (e.g Kbr)

Molecular systems (e.g., $HgCl_2$)

Ionic Mixture (e.g., LiCl-NaCl)

Molecular mixture (e.g., $HgCl_2$-$ZrCl_2$)

Molecular and ionic mixtures (e.g., $HgCl_2$-NaCl)

Fig : Molten Salt Systems Classified in order of Increasing Phase Rule Complexity

Now, this is the way we look at ions in a aqueous medium. How do we write the electrolysis that takes place in an aqueous medium?

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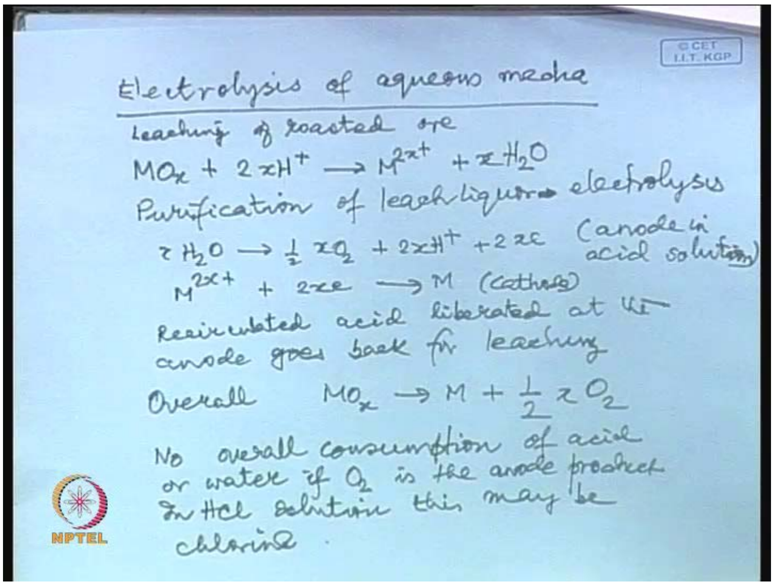

Electrolysis of aqueous media

Leaching of roasted ore

$MO_x + 2xH^+ \longrightarrow M^{2x+} + xH_2O$

Purification of leach liquor → electrolysis

$xH_2O \longrightarrow \frac{1}{2}xO_2 + 2xH^+ + 2xe$ (anode in acid solution)

$M^{2x+} + 2xe \longrightarrow M$ (cathode)

Recirculated acid liberated at the anode goes back for leaching

Overall $MO_x \rightarrow M + \frac{1}{2}xO_2$

No overall consumption of acid or water if O_2 is the anode product In HCl solution this may be chlorine.

If you consider what happens normally that we have a leached or roasted ore, say we had an ore m o x, we will we have obtained by roasting from a say sulfide, if it is dissolved in an acid we from metal ions, these metal ions as I said may maybe complexed. But let us look at the way we will produce metal by aqueous electrolysis. After purification of the leach liquor we proceed for electrolysis, where there is the anode and cathode reaction like this, we can write like this x H 2 O giving you the anode hydrogen ions and oxygen and metal ions giving metal at the cathode.

On the whole the recirculated acid that a liberated at the anode goes back for leaching, at the anode we are liberating acid which can be consumed for a leaching and the overall reaction is m o x giving opening up to metal and oxygen. So, if things are done properly in acid media if we electrolyze a the metal oxide, that we have got from a sulfide and that we have dissolved in the acid, there would be no overall consumption of acid or water. On the whole everything can be recirculated, because acid is being regenerated and you are not consuming on the whole any oxygen, in h c l solution this may be chlorine. However, this is in theory this may not happen in practice, because of a variety of reasons. Now coming to electrolysis of fused salts, we should first know what we mean by molten salts. Molten salts are ionic media and they come under the category of melts, by melts we mean molten media which are ionic or which may not be ionic but no water.

So, metals are melts inorganic salts, when they are molten are melts, slag's are melts, even glasses are melts. In molten inorganic salts, there can be single component systems like say ionic systems potassium bromide this should be capital b. There can be molecular systems like mercury chloride, it is not an ionic halite, we can have multicomponent systems, which can be molecular or ionic mixtures like h g c l 2 n a c l, it can be a molecular mixture like h g c l z r c l 2 it can be an ionic mixture.

Obviously, molten salts which are not ionic but molecular in nature they cannot serve as media for electrolysis, not even when there is partly ionic and partly molecular nature, we need for electrolysis medium which is fully ionic, highly conducting and very often they are the halides, fluorides or chlorides mostly. And in halite and chlorides only halides and chlorides dissolve, very easily there very few examples, where an oxide mineral will dissolve in halide and therefore, you will find most electrolysis processes or fused salt electrolysis processes, would imply dissolution of a halide in another halide media of course, that media is more stable and the halide which is to be discomposed is less them.

The electrolysis of aluminum is a very real exception, there an oxide a l 2 o 3 is dissolved in sodium in cryolite, which is written as 3 c a f 3n a f 3, I am forgetting what is cryolite, any how I will tell you later it is a fluoride. So, if there is a case of an oxide dissolving in a fluoride but normally oxides do not dissolve in halides.

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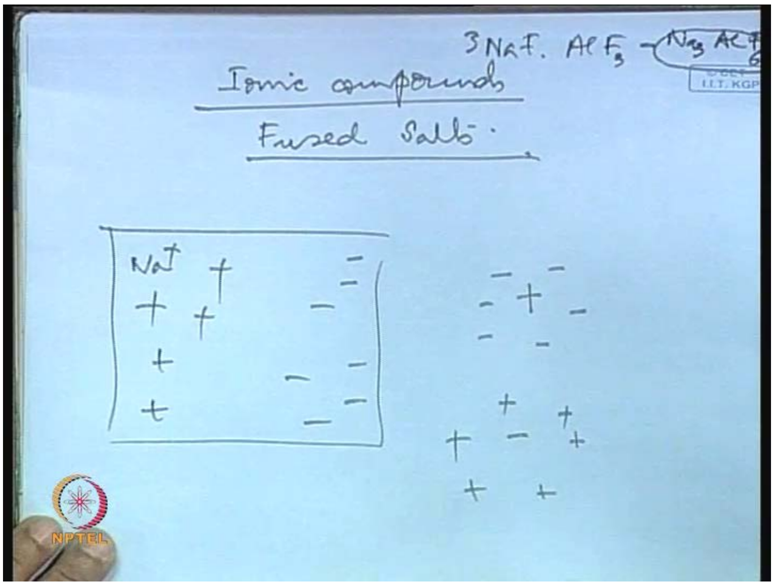

What is the nature of these ionic compounds, such as fused salts. Yes, I just remembered that cryolite is written as 3 n a f a l f 3 or n a 3 a l f 6, which is a naturally occurring mineral but it can also be artificially prepared. We will discuss that when we come to discuss earlier electrolyze of aluminum.

Now, let us discuss the structure of fused salts, now if we consider a molten salt like molten sodium chloride, obviously there are ions distributed but we cannot conceive a picture where in the liquid, the sodium ions, let me represent only by plus there are only at one side and the chlorine ions are at another corner. You cannot have segregation of plus and minus signs because if that was the case, you could think of some device where you only take out this part, so that you would have metal ions and you will have chlorine ions separated that not possible.

Because the plus signs attract the negative ions and the minus ions attract the plus ions, cations have to be always surrounded by anions and anion always has to be surrounded by cautions.

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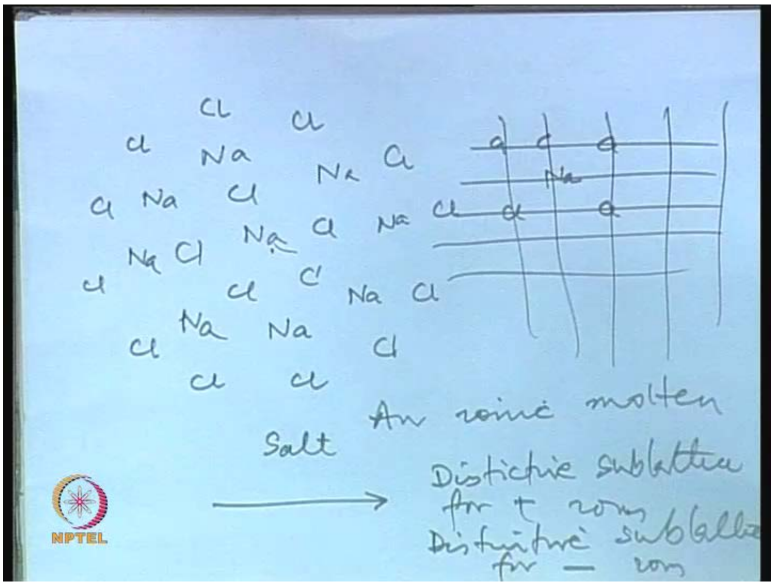

Now, we can represented that in a two dimensional picture like this, that suppose you talk about NaCl we are not going to charge it surrounded by chlorine, then there will be another arrangement of plus ions beyond, then again chlorine ions beyond that.

Now, here if you look at this arrangement, if you look at a sodium ion it is surrounded by chlorine, if you look at chlorine you will find it is surrounded by sodium, if you look at sodium it is surrounded by chlorine, it will look at chlorine it will surrounded by sodium this is happening. Or in other words we had in sodium chloride a lattice, where same lattice positions are occupied by sodium around which, the other lattice positions are taken up by chlorine and then again there are some lattice positions which are occupied by sodium ions.

So, it is said that an ionic liquid, an ionic molten salt is characterized by a lattice where there is a distinctive sublattice for plus ions and there is a distinctive sublattice for negative ions and these are intertwined.

So, let me repeat in a molten salt always for charge neutrality positive ions will be surrounded by negative ions, negative ions will be surrounded by positive ions. The positive ions distribute them in a lattice of their own and in the negative ions distribute in a lattice of their own and these two lattices has the intertwined.

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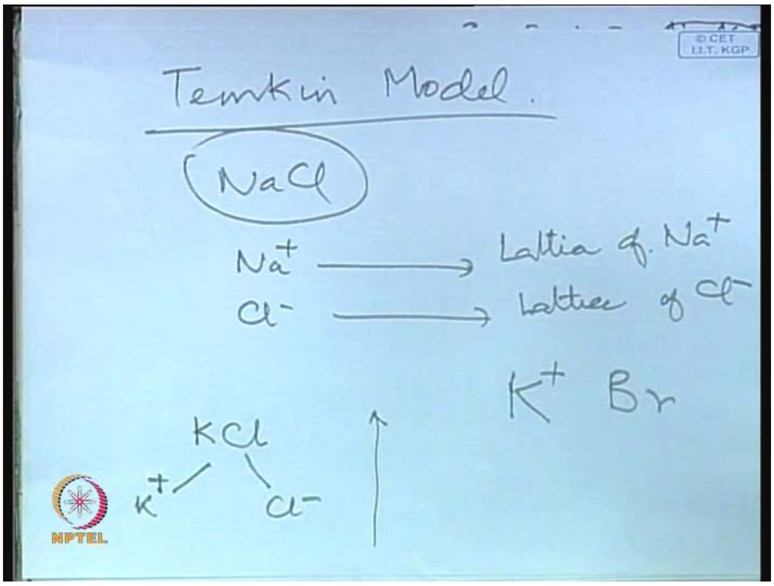

This was the model given by a gentleman called Temkin and it is a very famous model known as Temkin model. And this assumption leads to some conclusions which are very interesting, what it says is that, suppose you have sodium chloride, here sodium ions have a lattice of sodium ions ,chlorine ions are in a lattice or sublattice of chlorine ions.

Now in this mixture if you add some other molten salt like say potassium chloride, potassium chloride gives potassium ions it will give chlorine ions.

Now, there is no problem these chlorine ions that are added, they can go into the lattice that is made up of chlorine ions. The potassium ions have to go to the cations lattice; it cannot go and occupy any position where there is chlorine ion. Let us make a little more complicated, suppose we add potassium bromide into sodium chloride, then potassium ions must go to the sublattice where there are cations and bromine ions must go the sublattice where there are anions.

There can never be a situation, where an anion can go into the position occupied by cations because calculations have shown that, to do that if you want to remove a cations from the influence of the surrounding anions, you need energy which would be more then the energy required to completely volatilize the melts. In other words the cations and anions are so strongly bound, that there is no way you can take, you can make an anion take the place of a cations which is surrounded by anions. Now, this takes as to another very interesting conclusion.

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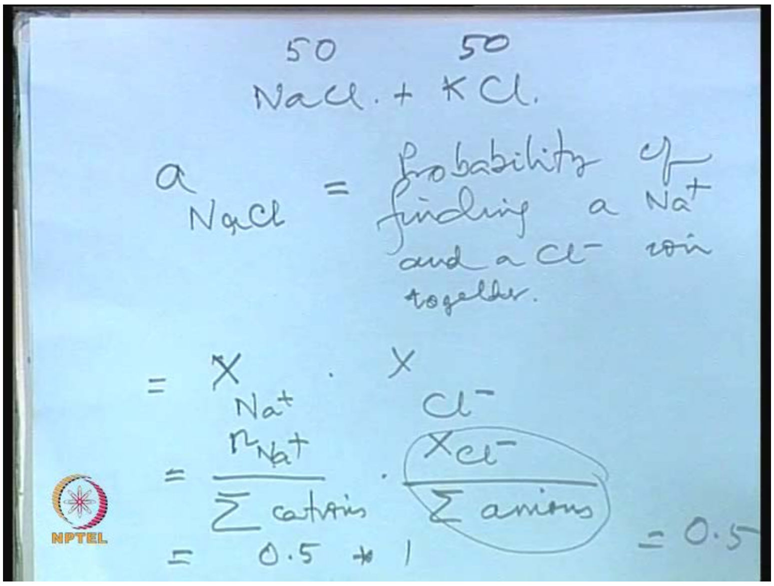

$$\overset{50}{NaCl} + \overset{50}{KCl}$$

a_{NaCl} = probability of finding a Na^+ and a Cl^- ion together.

$$= X_{Na^+} \cdot X_{Cl^-}$$

$$= \frac{n_{Na^+}}{\sum \text{cations}} \cdot \frac{X_{Cl^-}}{\sum \text{anions}} \quad = 0.5$$

$$= 0.5 * 1$$

That conclusion is this, that suppose we have sodium chloride and potassium chloride mixture, we want to know what is the activity of sodium chloride. Now, according to

Timkin model, activity of sodium chloride is really the probability of finding a sodium ion and a chlorine ion together, this is the probability.

Now, we can also write for this, this will be equal to the ionic fraction of sodium into ionic fraction of chlorine. Now this is, this may appear something very obvious, that in the entire body we have to find out what is the ionic fraction of sodium, which means the fraction of sodium ions amongst all the cations and fraction of chlorine ions amongst all the anions. Now, so far it is very simple, now since we only have a chlorine ion this is always one because its only chlorine the fraction of chlorine ions as to be one because there are only anions and anions are chlorine ions.

So, the fraction of sodium ions would be as for the proportion of sodium chloride and chlorine, means if there is fifty percent of by mole of sodium chloride and fifty percent by mole of potassium chloride, this will be point 5 this is 1 therefore, this will be point 5, no problem here 50, 50 sodium chloride and potassium chloride.

So, the ionic fraction of sodium will be 0.5, ionic fraction of chlorine is 1, the product is point 5. It seems very obvious but see the complication we have, if we have sodium chloride and potassium bromide, let be 50 mole percent 50 mole percent.

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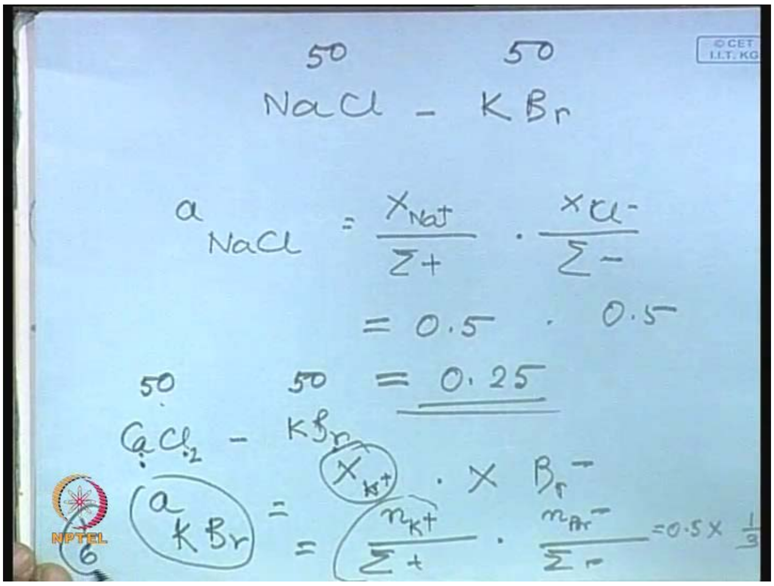

$$\overset{50}{NaCl} - \overset{50}{KBr}$$

$$a_{NaCl} = \frac{x_{Na^+}}{\Sigma +} \cdot \frac{x_{Cl^-}}{\Sigma -}$$

$$= 0.5 \cdot 0.5$$

$$= \underline{\underline{0.25}}$$

$$\overset{50}{CaCl_2} - \overset{50}{KBr}$$

$$\boxed{a_{KBr}} = \boxed{x_{K^+}} \cdot x_{Br^-}$$

$$= \frac{n_{K^+}}{\Sigma +} \cdot \frac{n_{Br^-}}{\Sigma -} = 0.5 \times \frac{1}{3}$$

We want to know the activity of sodium chloride; it will be ionic fraction of sodium multiplied by ionic fraction of chlorine, which means number of sodium ions in the cations lattice, now here 50 percent of the cations are accounted by sodium other 50 is by potassium, so this will be 0.5. Now, see here now this bromine that you have put it has gone into the anionic lattice and it is occupying 50 percent of the positions, so this will now also become 0.5. So, the activity of sodium chloride will now become point 25.

So, the Temkin model gave a revolutionary twist to our picture of the ionic network, in fused media and this concept we will make use of later on, when we discuss a complex salts with lots of components. Let us make it little more complicated, suppose we have a mixture of calcium chloride and potassium bromide, again we have 50 mole percent, 50 mole percent. We want to find out the activity of potassium bromide it will be ionic fraction of potassium into the ionic fraction of bromine and this is number of cations divide by all cations, into number of anions minus n divided by all an ions.

Now here, if you see that we have now in the cations lattice, 50 percent potassium, 50 percent calcium, no problem there both going to cations lattice. See it will be 0.5 but what about here in the anion lattice, now there are twice as many chlorine ions than you have bromine ions. So the fraction of bromine ions become one third, so the activity of this in 50, 50 solution calcium chloride and potassium bromide will become 1 by 6. It is a very interesting, that you have 50 percent of this 50 percent of this.

But, in the case of sodium chloride, potassium chloride 50, 50 will still mean activity of sodium chloride is half but when you start bringing in other ions then the Temkin's activity expression begin to give you all kinds of things. Interestingly let us end this discussion by looking at a mixture of say calcium chloride and potassium bromide.

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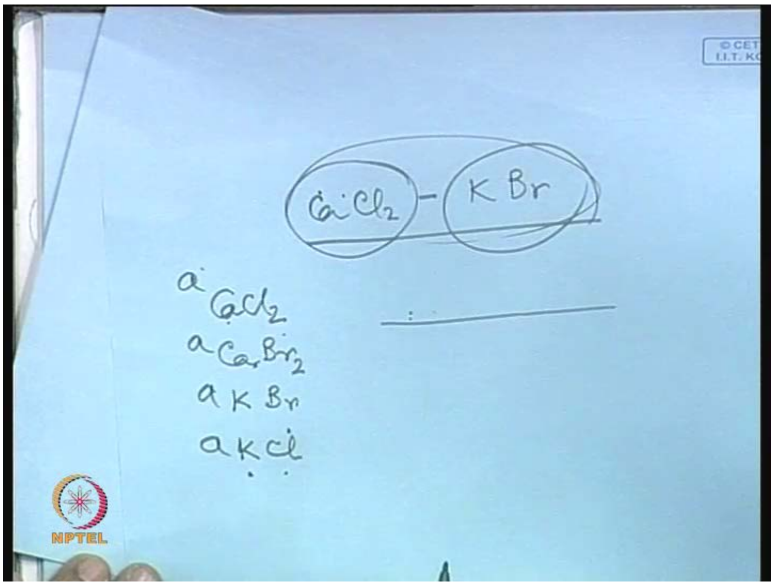

What we can say, that we can think in this media, we actually have a mixture of not only calcium chloride, concept of calcium chloride, we have a concept of calcium bromide, we have a concept of potassium bromide, we have a concept of potassium chloride.

Because in the entire thing we have potassium ions, chlorine ions, bromine ions and calcium ions, so you can always think of activity of calcium chloride which is a one chlorine, one a calcium in the neighborhood of two chlorine, one calcium ion in the neighborhood of two bromine, potassium bromide means, one potassium in the neighborhood of one bromine, one potassium ion in the neighborhood of one chlorine ion.

So, in this mixture we can talk about activities of this, activities of this, activities of this, activities of this. If we make the calculations all these activities however, will have to come to 1 because this will take care of all possibilities, this is the probability of finding calcium chloride together with this, this, this, this, etcetera.

So, we can do all kinds of calculations, some of which I will do later but this must be remembered, that in a fused salt medium, when you bring in another salt then we reduce its activity very effectively, not in proportional anymore to its reality abundance but in terms of its ionic distribution. We can have tremendous effect on the activity of these pieces, maybe I will I will do some problems on this later.

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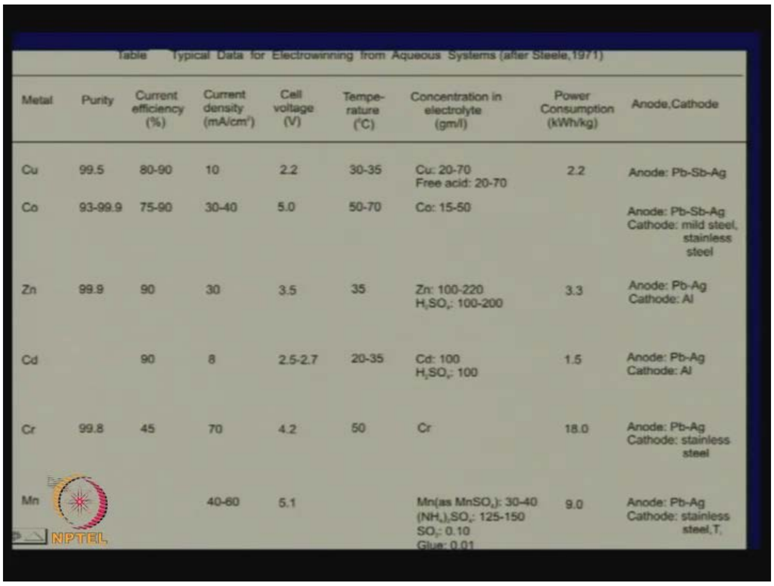

Table Typical Data for Electrowinning from Aqueous Systems (after Steele,1971)

Metal	Purity	Current efficiency (%)	Current density (mA/cm^2)	Cell voltage (V)	Tempe-rature (°C)	Concentration in electrolyte (gm/l)	Power Consumption (kWh/kg)	Anode,Cathode
Cu	99.5	80-90	10	2.2	30-35	Cu: 20-70 Free acid: 20-70	2.2	Anode: Pb-Sb-Ag
Co	93-99.9	75-90	30-40	5.0	50-70	Co: 15-50		Anode: Pb-Sb-Ag Cathode: mild steel, stainless steel
Zn	99.9	90	30	3.5	35	Zn: 100-220 H_2SO_4: 100-200	3.3	Anode: Pb-Ag Cathode: Al
Cd		90	8	2.5-2.7	20-35	Cd: 100 H_2SO_4: 100	1.5	Anode: Pb-Ag Cathode: Al
Cr	99.8	45	70	4.2	50	Cr	18.0	Anode: Pb-Ag Cathode: stainless steel
Mn			40-60	5.1		Mn(as $MnSO_4$): 30-40 $(NH_4)_2SO_4$: 125-150 SO_2: 0.10 Glue: 0.01	9.0	Anode: Pb-Ag Cathode: stainless steel,T,

Now, I would like to come to an end of this by pointing out a few figures to you which is to illustrate some features of electrowinning from ecosolutions and electrowinning from fused salts. Here are some typical data for electrowinning of ecosystems.

You see the kind of purity obtained, copper 99.5, cobalt 93 to 99.9, zinc 99.9 or more, chromium 99.8. In aqueous electrowinning the current efficiencies are also high. Generally what do you mean by current efficiency? By current efficiency and whichever defined properly later, we mean the fraction of current that is used for the electrolytic deposition, electrolytic dissociation we have in mind, mean the current should go only for electrolyzing the solute which is going to deposit the metal, it should not be consumed of other reactions. The cell voltages are low because aqueous systems do not need high voltage, especially say copper 2 volts and zinc 3.5.

Power consumptions figures are given and anode cathode I will discuss later. When you come to electrorefining, you will find that the, where is it did you go our cell voltages will be low, look at this cell voltage point 1 5, 1 point 5, 1 point 5 very low. Why do we have low voltages when you talk about electrorefining?

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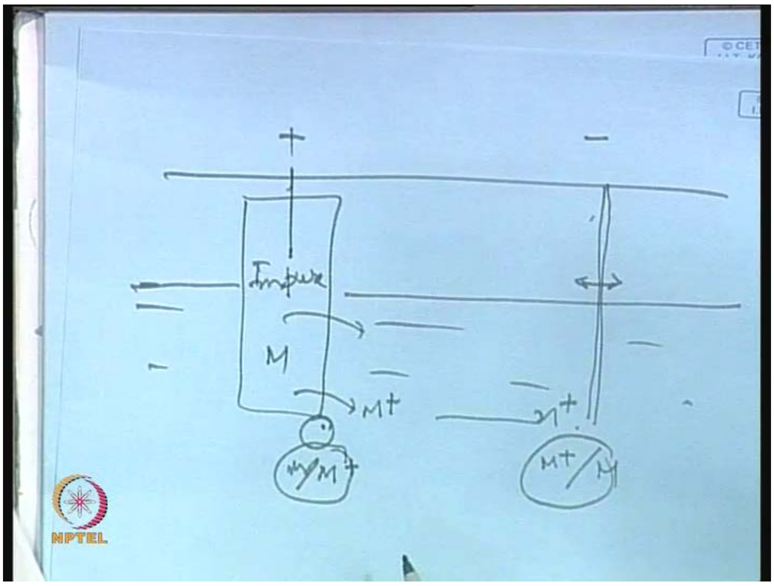

See in basically in electrorefining what we do, is that we will have an impure anode, impure slab of the metal as anode and a pure thin sheet as cathode and when we have a medium or we are doing the electrolysis, say we want metal ions to dissolve here and metal ions to deposit there, so this thin sheet will gradually becomes thick as a pure sheet whereas, this impure metal will dissolve, may essentially in such a process here we have metal, metal ion potential, here also we have metal ion metal potential.

Essentially, there are other things where the essentially, we are dealing with two potentials which are very much near each other and therefore, the electrorefining will not lead high voltages whereas, in the other cases when we electrolyze, we have a anode which is different from the cathode and the voltage required is high. So, in these cases you will find the process is like electrolysis, will have the same kind of materials and electrolyze and other things but voltage required would be low.

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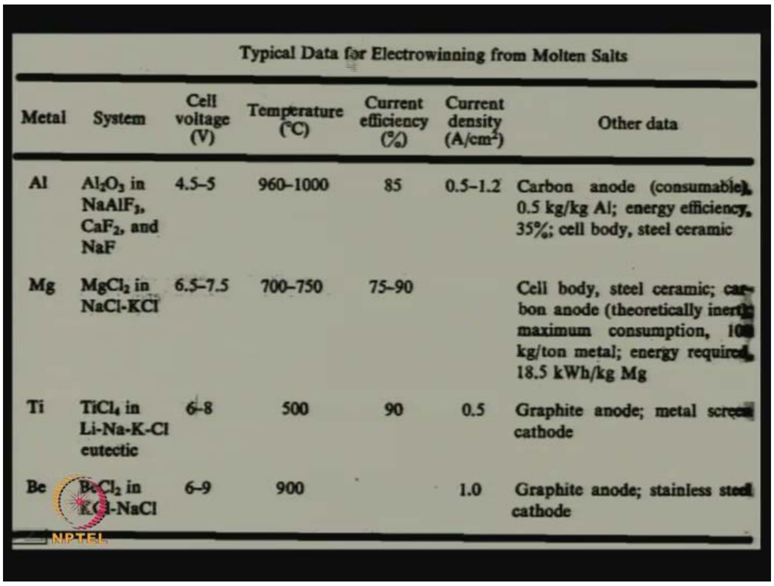

Typical Data for Electrowinning from Molten Salts

Metal	System	Cell voltage (V)	Temperature (°C)	Current efficiency (%)	Current density (A/cm^2)	Other data
Al	Al_2O_3 in $NaAlF_3$, CaF_2, and NaF	4.5–5	960–1000	85	0.5–1.2	Carbon anode (consumable), 0.5 kg/kg Al; energy efficiency, 35%; cell body, steel ceramic
Mg	$MgCl_2$ in NaCl-KCl	6.5–7.5	700–750	75–90		Cell body, steel ceramic; carbon anode (theoretically inert; maximum consumption, 10 kg/ton metal; energy required, 18.5 kWh/kg Mg
Ti	$TiCl_4$ in Li-Na-K-Cl eutectic	6–8	500	90	0.5	Graphite anode; metal scree cathode
Be	$BeCl_2$ in KCl-NaCl	6–9	900		1.0	Graphite anode; stainless steel cathode

Now, here are some typical data for electro winning from molten salts, now molten salts would mean high temperatures aluminum electrolysis will be at 960 to 1000, magnesium more than 700, titanium 500, beryllium 900.

So, when you have high temperatures, your current efficiency cannot be, can be high but your energy efficiencies will be low because part of the energy will go into the heating of the cell. Cell voltages will be on the high side because fused salts are stabler than ecosolutions. So, these are the essential difference between aqueous electrolysis and fused salts electrolysis.

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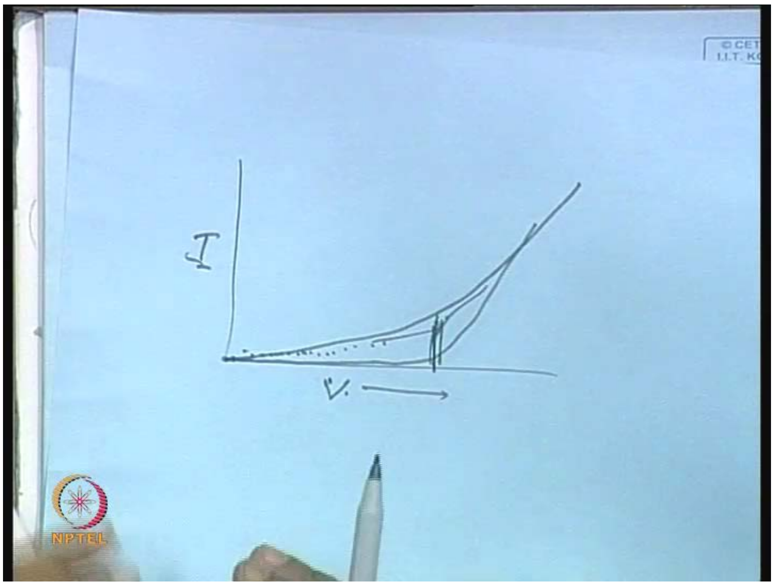

Now, in much system there is a very simple method of finding out what is the voltage required for electrolysis and that is that we will pass through two electrodes, a current and will plot, will apply voltage and gradually increase the voltage and see the current passing through the medium.

Initially, there will be hardly anything any current but there point will come where we will find a current is begun to flow, this indicates the decomposition voltage. The voltage required to decompose the medium. In the case of fused salts, generally this takes a different kind of shape, because many other kinds of residual reactions can take place and we can say, that we still we can get guidance as to what will be the decomposition of potential.

Now, in the data I have shown, I have made a mention of zinc electrolysis and you need to ask this question, that we have always been told that when zinc is in an acid media, hydrogen will evolve and zinc will dissolve, zinc is reactive more reactive than hydrogen and that is why, when we try to precipitate zinc by hydrogen we found it was impossible, even in highly alkaline thing it was impossible, perhaps you need very high pressures of hydrogen to precipitate zinc.

But, during electrolysis we can take out zinc from solution, all the in electrochemical series zinc is above hydrogen and normally, zinc in acid solution will dissolve to bring out hydrogen, we can produce zinc by electrolysis of acid solutions, how is it possible?

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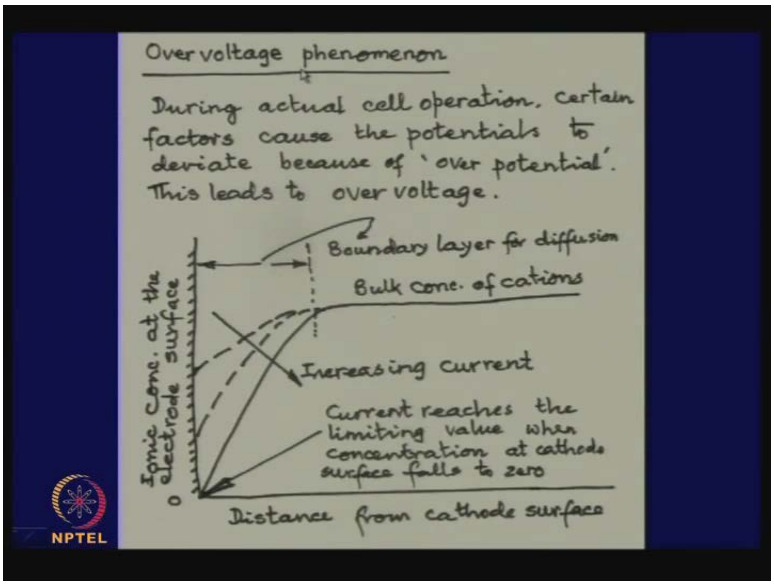

Over voltage phenomenon

During actual cell operation, certain factors cause the potentials to deviate because of 'over potential'. This leads to over voltage.

The explanation to this phenomena rise in what we called, the over voltage phenomenon over voltage phenomenon is the phenomenon which changes the normal zinc, zinc ion potential. Means the electrode potential will no longer be what you have seen in the electrode potential series.

It will be dropped to below hydrogen or you can say the hydrogen will go above zinc, why should this happen? There are the two reasons behind such phenomenon, now assume a general situation where during an actual operation, the cations are coming to the surface of the electrode surface, where they are going to be discharge and deposited as metal.

Now, you have seen in the case of leaching or cementation, whenever ions are moving towards a surface, they have to they are going because of two reasons, first of all there is an electrical voltage applied, so there is pressure on the cations to move from this side to that side, but they must come through a process or defuse through the aqueous media and when they come from here to here, they have to go across a boundary layer and this is where a concentration gradient is set up.

Now, when we increase the current increasing the current means, you are pushing more cations per unit time which, means you are trying to forcing cations to go and get discharged in increasing amounts. So, when that happens that gradient increases because if you want more diffusion of cations from this side to that side to this surface, the gradient has to be more. So, it is said that as you gradually increase the current the diffusion profile changes.

And finally, a situation comes where the surface concentration of cations will fall to zero; we call this situation a situation of a limiting current density that you cannot pass any more current, you cannot produce for the given area at the metal, at a higher at anymore, because the gradient cannot increase anymore. And here also there are two sub steps, one is diffusion and then whatever happens at this surface metal ion getting discharge, so two steps are involved, the diffusional step and the surface reaction step.

Now, you see the potential between metal and metal ion, depends on the metal ion concentration here, when this phenomenon is going on, then there can be a different metal, metal ion potential because metal ion concentration as a surface as changed. Similarly, when we look at the phenomenon of metal ion coming into in equilibrium with the metal surface, that reaction step is also important. So, we actually during actually electrolysis these two steps are disturbed and zinc, zinc ion potential is no longer what it was in the electrochemical series, we say there is an over voltage zinc, zinc ion voltage as changed.

As a matter of fact, it changes to an extent when hydrogen becomes more reactive than zinc and hydrogen replaces zinc from solution and zinc ion deposits. Well, I will try to explain this again if necessary, when we come to discuss the subject. But I will conclude today by saying that Electrometallurgy came much later than Pyrometallurgy and Hydrometallurgy but it is, in a sense more sophisticated because electricity is an invention of modern times, and electrolytic processes produce very pure metals Electrometallurgy means many things as I have said because it means, you will have electricity and electrolytical effects but we are restricting ourselves in this course only to discussion of electrolysis and electrorefining, where the process is not spontaneous we have to apply a voltage, pass a current, make ions move from this side to that side, make metal cations deposit to produce a metal.

I will continue with the subject because it is very vital, a metal production and I will also try to discuss some problems, thank you very much.