Non-ferrous Extractive Metallurgy

Prof. H. S. Ray
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Lecture No. # 09

Electrometallurgy (Contd.) and Temkin Model for Fused Salts

Friends, I have started discussing principles of electrometallurgy from the last lecture. I realize later, that I kind of rushed through, when I was discussing fused salts. So, I would like to repeat a few things I said in the last lecture.

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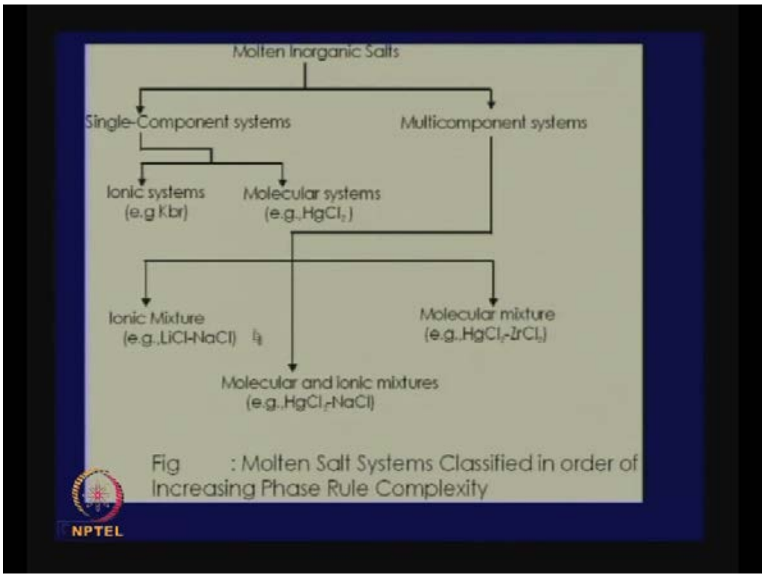

Molten Inorganic Salts

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., $HgCl_2$-$ZrCl_4$)

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

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

We have started talking about molten salts, and before that, I did point out that not all molten inorganic salts are ionic; there can be totally molecular systems; there can be systems which are partly molecular, partly ionic; we are not going to talk about these, because if you want to talk about electrolysis, we need a completely ionic media. So, we are concerning ourselves with ionic mixtures, where the individual components are also ionic, and the media is totally ionic. Now, for ionic molten salts, there is a very interesting model called Temkin model, which now everybody has accepted and I like to discuss it once again.

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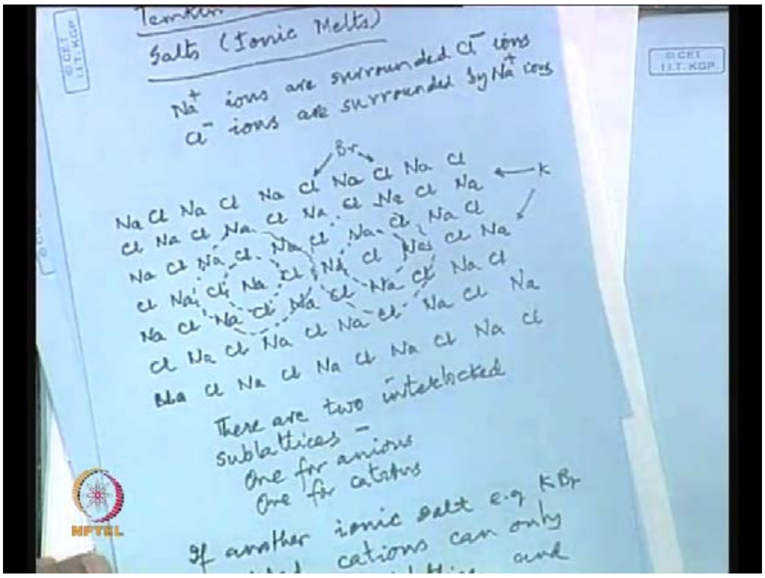

Temkin

Salts (Ionic Melts)

Na^+ ions are surrounded Cl^- ions

Cl^- ions are surrounded by Na^+ ions

There are two interlocked sublattices -
One for anions
One for cations

If another ionic salt e.g KBr
cations can only
and

The Temkin Model for Fused Salts or Ionic Melts says that in the ionic media, there are two sub-lattices: one sublattice for the cations, one sublattice for the anions.

Let us first consider a pure salt sodium chloride. Now, sodium chloride has a crystal lattice and a two-dimensional representation is like this, that every sodium is surrounded by in the first order, first coordination chlorine ions, every chlorine is surrounded by sodium and the other chlorine atoms comes further down.

So, what we can say, that in the liquid state there will be no solid order which goes into infinity but, there is short range order, that when the solid transforms into molten state, this order prevails in short distances. And in the short distances, we will have sodium ions surrounded by chlorine ions, chlorine ions surrounded by sodium ions; this is required for the sake of electro neutrality.

Now, if to this salt that is sodium chloride, we add another salt say potassium bromide, which breaks into potassium and bromine ions. Potassium ions can only occupy some space previously occupied by sodium ions and bromine ion being an anion must find the place somewhere, where there was a chlorine ion. In other words, in other words the anions must go to the anions sub-lattice and cations must go to the cation sub-lattice.

So, there are two interlock sub-lattices, one for the anion and the other for the cation. And in that fused mixture, if another salt is added the cations can only go to the cations sub lattice and anions can only go to the places occupied by anions. Temkin model also says that, the activity of sodium chloride in a fused mixture is defined as probability of finding one sodium ion and one chlorine ion together in the neighborhood, which means, activity will be a product of the cation fraction and the anion fraction.

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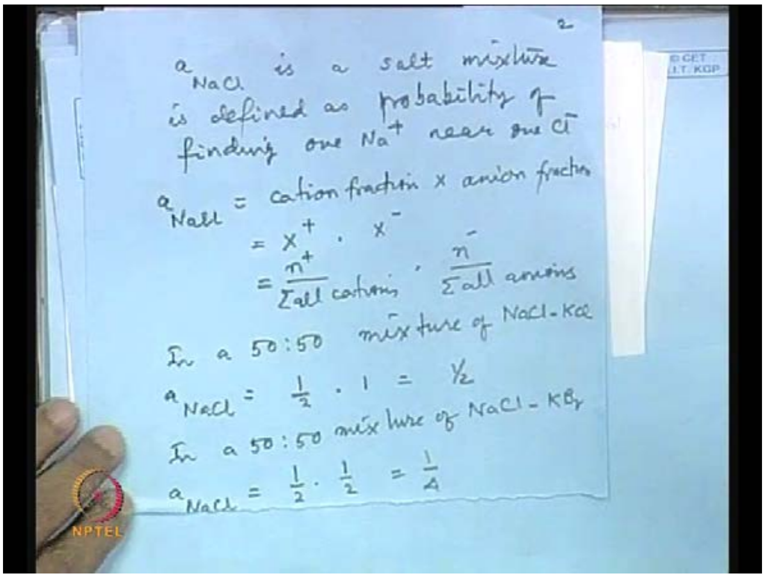

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a_{NaCl} is a salt mixture is defined as probability of finding one Na^+ near one Cl^-

a_{NaCl} = cation fraction x anion fraction

$= X^+ \cdot X^-$

$= \frac{n^+}{\Sigma \text{all cations}} \cdot \frac{n^-}{\Sigma \text{all anions}}$

In a 50:50 mixture of NaCl - KCl

$a_{NaCl} = \frac{1}{2} \cdot 1 = 1/2$

In a 50:50 mixture of NaCl - KBr

$a_{NaCl} = \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4}$

X cation, X anion, which will be represented by number of cations in the entire mixture divided by all cations in the mixture, because this ratio will give us the probability of finding a cation in the cation sub-lattice. And at that point, n minus 1 by all n anions will give us the probability of finding an anion in the anion sub-lattice and the product means that there will be together, so that gives us the probability.

So, in a 50 50 mixture of sodium chloride and potassium chloride, a NaCl would be half, because in the entire cation sub-lattice, 50 percent positions are occupied by sodium, the other positions are occupied by potassium chloride. So, it will become half but, when we come to the anion chlorine, there is only one kind of anion chlorine, so the probability of finding chlorine in the adjacent side, it is all one there is no other anion, therefore the activity of sodium chloride will be half but, the situation changes. If we have a 50 50 mixture of sodium chloride and potassium bromine, because in this case the cation fraction, that is sodium ion fraction is half, because half the positions are occupied by sodium but, the anion fraction the chlorine is also half, because the other positions are occupied by bromine ions, so a initial would become one fourth.

Even though there is 50 50 mixture of sodium and potassium chloride in the, in the fused mixture activity of sodium chloride is not half, in this, in this case it becomes one forth, if it is N a C l and K B r, I hope you have understood this. Now, let us consider little more complicated situation. We want to find the activity of a salt C d B r 2 in a salt mixture and this activity will be probability of finding one C d in a cation position and two bromine ions, in the nearby anionic positions in the sub-lattice.

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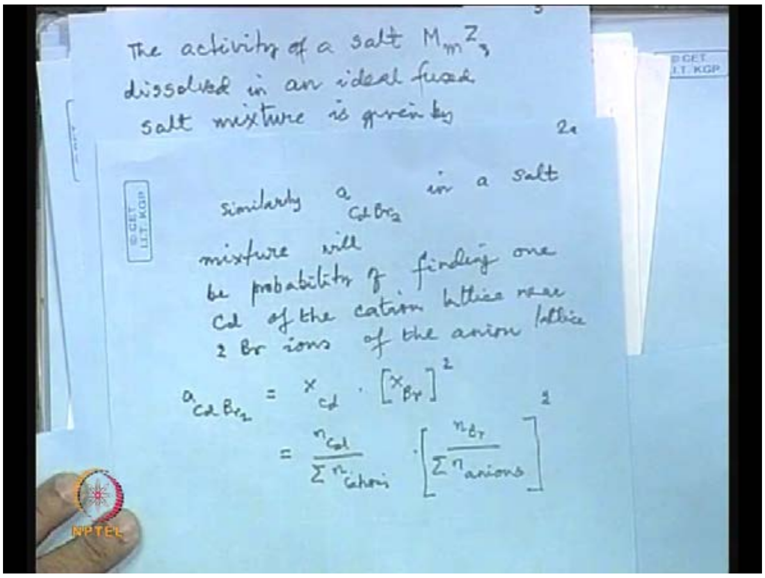

The activity of a salt $M_m Z_z$ dissolved in an ideal fused salt mixture is given by

2a

Similarly a_{CdBr_2} in a salt mixture will be probability of finding one Cd of the cation lattice near 2 Br ions of the anion lattice

$$a_{CdBr_2} = x_{Cd} \cdot [x_{Br}]^2$$

$$= \frac{n_{Cd}}{\Sigma n_{cations}} \cdot \left[\frac{n_{Br}}{\Sigma n_{anions}}\right]^2$$

So, it will be multiplication of cation fraction and square of anion fraction, because you need to have two, x b r gives the probability of finding an bromine ion in the anionic sub-lattice, another one has similar probability, so that has to be squared, so activity of C d B r 2 will be given by atoms of C d in the cationic sub-lattice divided by, not atoms ions of C d in the cationic sub-lattice and total number of cations into number of bromine ions in the anionic sub-lattice, divided by number of all anions to, it is squared, because we are talking probability terms.

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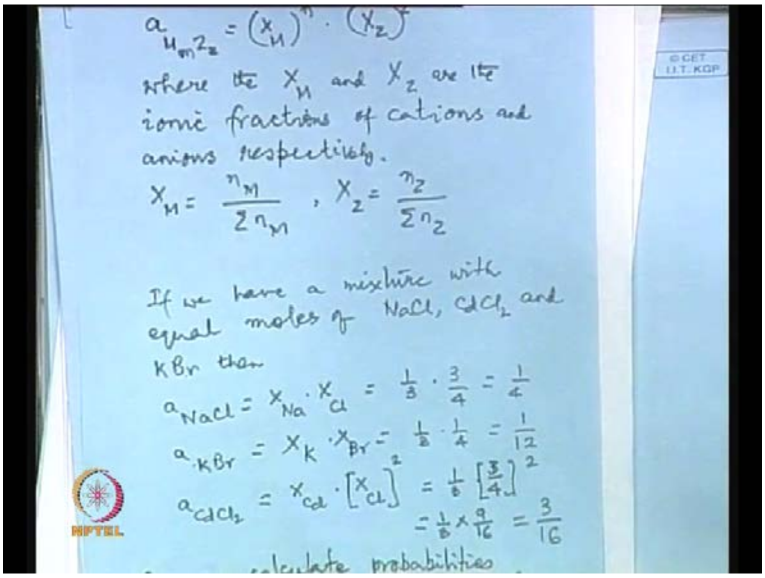

$a_{M_m Z_z} = (X_M)^m \cdot (X_Z)^z$

where the X_M and X_Z are the ionic fractions of cations and anions respectively.

$X_M = \frac{n_M}{\Sigma n_M}$, $X_Z = \frac{n_Z}{\Sigma n_Z}$

If we have a mixture with equal moles of NaCl, $CdCl_2$ and KBr then

$a_{NaCl} = X_{Na} \cdot X_{Cl} = \frac{1}{3} \cdot \frac{3}{4} = \frac{1}{4}$

$a_{KBr} = X_K \cdot X_{Br} = \frac{1}{3} \cdot \frac{1}{4} = \frac{1}{12}$

$a_{CdCl_2} = X_{Cd} \cdot [X_{Cl}]^2 = \frac{1}{3} \left[\frac{3}{4}\right]^2$

$= \frac{1}{3} \times \frac{9}{16} = \frac{3}{16}$

lculate probabilities

Now, the generalized expression for activity of a salt M sub m, Z sub z, dissolved in an ideal fused salt mixture is given by activity term, ionic fraction of M to the power m, ionic fraction of Z to the power z, where X sub M and X sub Z are the ionic fractions of cations and anions respectively, this is the definition of the anion fractions.

Let us solve the simple problem, if we have a mixture with equal moles of N a C l, C d C l 2 and K B r, then activity of N a C l is ion fraction of sodium into ion fraction of chlorine. Ion fraction of sodium is one third, because in the cationic sub-lattice are equal numbers of the cations sodium, cadmium and potassium whereas, the anionic fraction will be 3 by 4, if you if you see there. There is total number of four anions out of which one, three fourth is bromine, three fourth is chlorine, one forth is bromine, so a N a C l is 1 by 4. Activity of potassium bromate would be ionic fraction of potassium into ionic fraction of bromine, so it is one third and this is one fourth, because three positions are occupied by chlorine, one position is occupied by bromine, so activity of potassium bromide is 1 by 12. So, even though they are in equal proportion, we do not get the same activity value.

What about activity of C d C l 2? The expression for this is ionic fraction of C d, into ionic fraction of chlorine to the power square, because a C d ion has to find two chlorine ions in the neighborhood and each of them has this probability, so it must be a squared term. So, we get one third for this, three fourth for this, so this becomes 9 by 16, so we end up with 3 by 16.

So, although we have these three source in equal proportions in the mixture, activity of sodium chloride is one fourth, activity of K B r is 1 by 12, activity of C d C l 2 is 3 by 16. This is a very interesting implication of the basic postulate of Temkin model. Of course this is valid, while the mixture is consider to be ideal, very often the mixture may not be ideal and therefore, there can be deviations from these expressions but, we will not go into this.

Now, in a fused mixture remember that, which you have prepared by mixing sodium chloride, cadmium chloride and potassium bromide. The identities of these individual components have disappeared, because there is no sodium chloride there, there is no cadmium chloride there, there is no potassium bromine there, there are only ions of sodium cadmium and potassium chlorine and bromine.

Therefore, we can also say, that it is a salt mixture also of sodium bromide, cadmium bromide, potassium chloride, these are the things which you did not have but, you can always talk about probabilities of these finding them. You can even calculate probabilities of finding C d B r together not B R 2, 1 C d, 1 B R, 1 C d, 1 chlorine neighborhood.

All these activities will add up to one, because then you will exhaust all possibilities of combinations. So, the some substance of saying this is that in a fused slat mixture, the activity of a component is not going to be defined in terms of its relative proportion. It may be there in 50 percent but, this activity may be less than 50 percent, because of the complications of Temkins model but, whatever I have said is for only an ideal situation.

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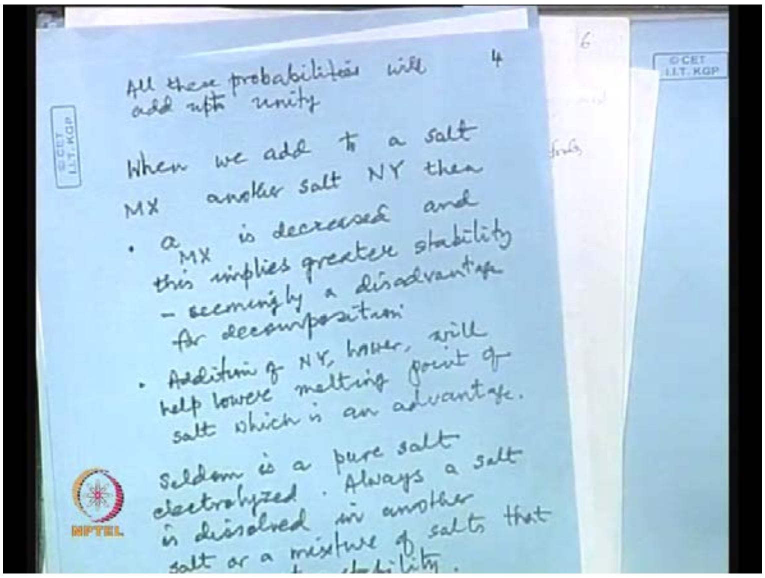

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All these probabilities will add upto unity

When we add to a salt MX another salt NY then

- a_{MX} is decreased and this implies greater stability – seemingly a disadvantage for decomposition
- Addition of NY, however, will help lower melting point of salt which is an advantage.

Seldom is a pure salt electrolyzed. Always a salt is dissolved in another salt or a mixture of salts that

Now, what are some other implications of this this observations? We see that when we add to a salt M X another salt N Y, then activity of M X is decreased obviously, and this implies greatest stability of a X by, so putting another salt, we are stabilizing the the other salt. Now in electrolysis this may seem to be a disadvantage, because when you have stabilized that combination dissociation will be more difficult.

But on the other hand there is an advantage that addition of N Y however, will help lower the melting point of the salt mixture. This is an advantage, because you can carry out the operation at a lower temperature. You should know that seldom is a pure salt electrolysis very rarely, may be may be never. We always take a salt and dissolve it in a solvent, which are other salts and then we electrolyze. Like if you can see the some compositions here, there is some typical data for electro winning for molten salts. See in the case of aluminum, I mentioned that repeatedly that, alumina dissolved in cryolite, which is N a A l F 3, is essentially, you think that should be the system but, now we also had calcium fluoride we also had sodium fluoride.

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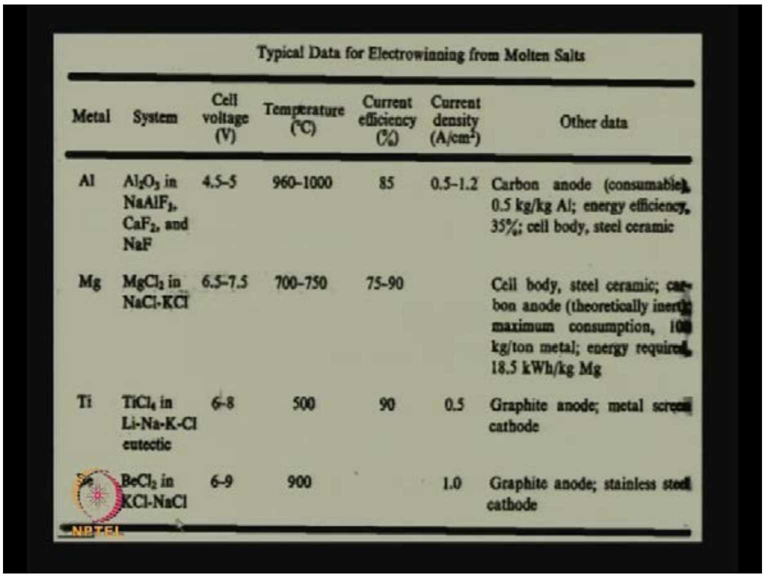

Typical Data for Electrowinning from Molten Salts

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, 100 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 screen cathode
Be	$BeCl_2$ in KCl-NaCl	6-9	900		1.0	Graphite anode; stainless steel cathode

So, this is the media in which A l 2 O 3 has been dissolved, the bath is very very complex this, I will discuss when we come to aluminum in the metallurgy, there are all kinds of ions existing. In the case of magnesium, magnesium chloride is dissolved in sodium chloride and potassium chloride, so we have a ternary magnesium chloride, sodium chloride, potassium chloride.

The only thing we have to ensure is that, when you apply the voltage to decompose magnesium chloride, sodium chloride and potassium chloride should not decompose and they do not, because they are more stable. Titanium can be produced by decomposition of T i C l 4 in a eutectic mixture of lithium, sodium, potassium chloride, this three chlorides make an eutectic system, the melting point goes down and in that, we put titanium tetrachloride, so it is actually a quaternary.

Barium chloride can be decomposed by electrolysis to produce beryllium; supporting electrolyte is potassium chloride, sodium chloride. So, in fused salt electrolysis, we always try to find a stable salt mixture solvent, which will not decompose itself and through that, we will add the salt that we want to decompose.

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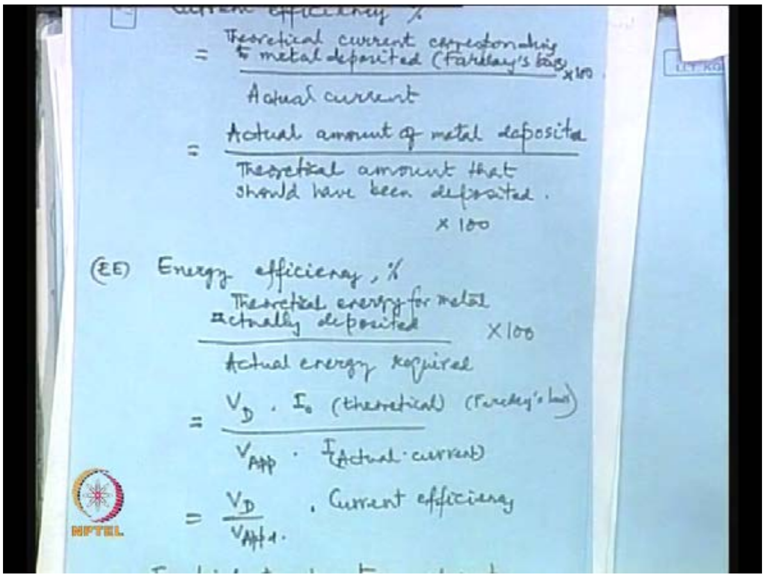

current efficiency %

$$= \frac{\text{Theoretical current corresponding to metal deposited (Faraday's law)}}{\text{Actual current}} \times 100$$

$$= \frac{\text{Actual amount of metal deposited}}{\text{Theoretical amount that should have been deposited.}} \times 100$$

(EE) Energy efficiency, %

$$\frac{\text{Theoretical energy for metal actually deposited}}{\text{Actual energy required}} \times 100$$

$$= \frac{V_D \cdot I_0 \text{ (theoretical) (Faraday's law)}}{V_{APP} \cdot I_{\text{(Actual current)}}}$$

$$= \frac{V_D}{V_{APP}} \cdot \text{Current efficiency}$$

Now we must, when we discuss electro metallurgy define some terms and you should know exactly what they mean, very often we talk about current efficiency, during electrolysis by the word, current efficiency mean, we mean theoretical current corresponding to the amount of metal deposited, you know you have during electrolysis produce certain amount of metal.

Using Faradays laws, we can find out what is the theoretical current requirement and we divided by, what is the actual current requirement. Because you need more than the theoretical current requirement into hundred will give us the current efficiency, we can put it in another way also, what is the actual amount of metal that has deposited, by the current that you have used and what is the theoretical amount that should have been deposited, according to Faradays laws. Now what are Faradays laws? Faradays lays there are two of them; one is more the current more is the production of metal, so there is a direct link which between amount of current and the amount deposited. The second one says qualify the step, that the amount deposited will be proportional to the equivalent weight of the metal.

And if you double the current you will get twice the equivalent weight but, for two metals same amount of current, will not give you same amount of metals. They will be proportional to take their equivalent weights, so again first law says, if you double the current, you double the deposition of metal, second says deposition of the metal would be according to their equivalent weight. So, for a particular same kind of current, the amount of copper that will be deposited in grams will be different from the amount of zinc that is deposited in grams but, in terms of equivalent weights, they will be the same.

Then there is another term called energy efficiency, now before you go to that you you must understand, why the actual current required to deposit a certain amount of metal, is always more than the theoretical current you require to deposit that amount of metal. The explanation is very simple, in the cell, there may be other reactions taking place also, which means some current is doing things, which you do not want the current to do, you are passing the current to dissociate a compound. But it is very difficult to restrict the role of the current, only to that dissociation reaction; the current can go elsewhere for some side reactions.

So, there is wastage of current and that is why, the current efficiency falls below hundred but, then current efficiency values if you see are always better in low temperature operations. You say this is the typical data for electro winning form ecosystems, for copper it is 80 to 90, for cobalt it is 75 to 90, which means here, the rest of the current is going elsewhere, for zinc 90 percent of the current is being used properly, in dissociation of zinc salt dissolved in it but, the 10 percent is going elsewhere.

But in the case of a fused salt electrolysis, the current efficiency values may not be so high, they they they can they can drop to lower values, because there are chances of reactions or the more side reactions at high temperatures.

Now, let us come to the second term called energy efficiency. The word energy efficiency means theoretical energy for metal, that is actually deposited how much of energy you should have used, for deposition of the metal that you have got and the actual energy you have required, the actual energy that you need to deposit a certain amount of metal will always be more, because part of the energy will go elsewhere, we will come to that later on into 100.

Now, what should be the theoretical energy requirement? It will be the theoretical decomposition of voltage, every salt has a theoretical decomposition voltage, decomposition potential, which you can find from thermodynamic data, multiplied by the theoretical current that should be required to deposit that much of metal, that we can calculate from Faradays laws, divided by the actually applied voltage.

The decomposition happens because of a theoretical value but, with that value we cannot operate in an actual self, we have to apply higher voltages, because voltage drops takes place in because of various factors, this I will discuss just now. So, V applied into I actual, so the expression is decomposition voltage theoretical divided by the actual voltage into current efficiency, this is the expression for energy efficiency.

Now, electro metallurgy, these two terms will appear again and again. They would always ask what the energy efficiency is, what is the current efficiency? Now let us talk about the applied voltage, during an actual operation you have to apply a voltage across two electrodes, these voltage is more than the theoretical decomposition of voltage, because there are some other resistance as you have to over come.

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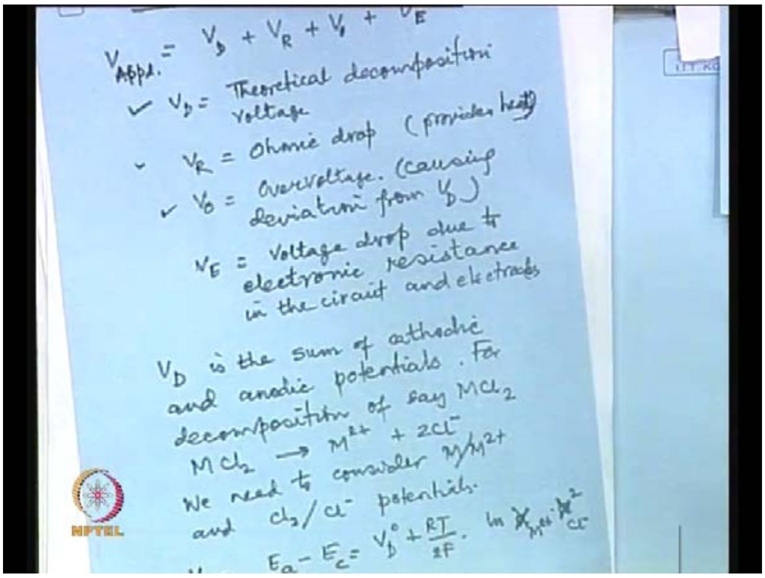

$V_{Appl.} = V_D + V_R + V_O + V_E$

✓ V_D = Theoretical decomposition voltage

✓ V_R = Ohmic drop (provides heat)

✓ V_O = Overvoltage. (causing deviation from V_D)

V_E = Voltage drop due to electronic resistance in the circuit and electrodes

V_D is the sum of cathodic and anodic potentials. For decomposition of say MCl_2

$MCl_2 \rightarrow M^{2+} + 2Cl^-$

We need to consider M/M^{2+} and Cl_2/Cl^- potentials.

$E_a - E_c = V_D^{\circ} + \frac{RT}{2F} \cdot \ln a_{M^{2+}} \cdot a^2_{Cl^-}$

The expression is applied voltage is sum total of four terms first of course, is a theoretical decomposition voltage, which you must exceed to decompose the metal then there is a ohmic drop. There is a resistance in the bath, which because of which there is a voltage drop called V sub R, then there is that over voltage phenomena.

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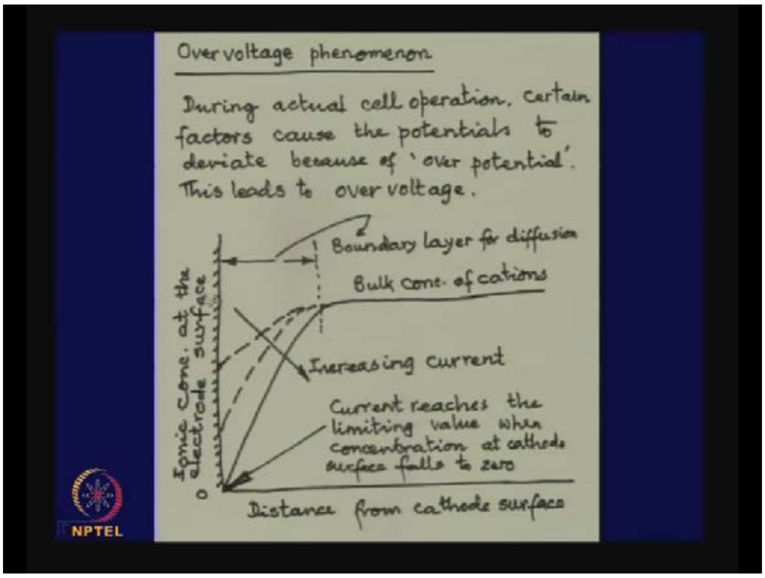

Overvoltage phenomenon

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

Current reaches the limiting value when concentration at cathode surface falls to zero

You will remember that I discussed that, there are concentration gradients near an electro surface, because while the cations are coming and depositing, as the current increases the concentration profile near the electro surface changes, so the metal metal ion concentration, voltage changes. If initially there was a certain amount, this this was a concentration of metal ion some metal metal ion concentration, give some voltage but, when current starts passing the the metal ion concentration of the surface changes, this gives rise to deviations from the electrode potential.

Another reason for electrode potential is from, what happens in the surface, that after all at the surface the the metal ion has to deposit, so there is a surface reaction and over voltage due to that is called activation over potential.

So, the V O, that is over voltage comes from both activation over potential and concentration over potential, which and this cause deviations from V D. V E is the voltage drop due to electronic resistance in the circuit. There are all kinds of electrical connections and everywhere there is an electronic resistance that causes a voltage drop, there is also voltage drop at the electrodes.

And V D, the theoretical decomposition of voltage you know, is the sum of the anodic and cathodic potentials. There are two potentials are the cathode, and the anode, when you sum them up you get the theoretical decomposition of voltage, to that you have to add whatever deviations have taken place, because of activation over potential and concentration over potential. This can be calculated from thermodynamic data the V D very easily.

For example, if it is salt M C l 2 decomposing into M 2, 2 C l minus, it will be derived by adding, the two electrode potentials M M 2 plus and C l 2 minus and for that, there is a straight cut expression like this.

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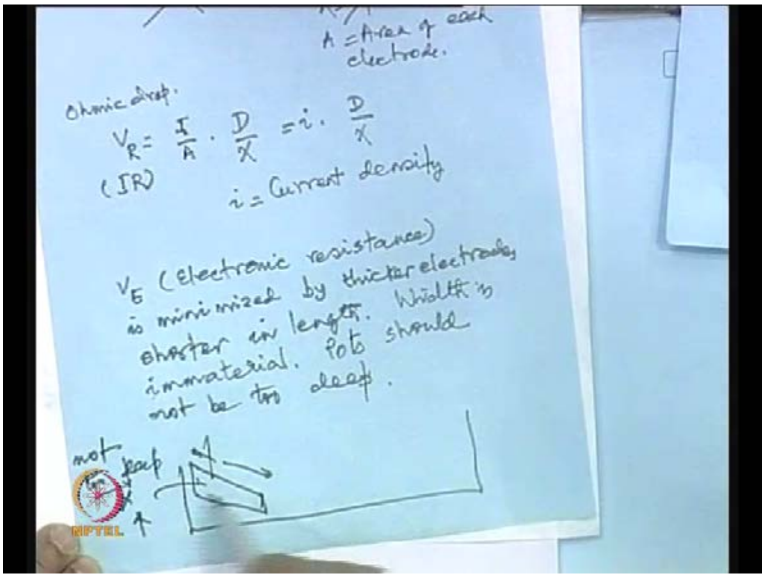

A = Area of each electrode.

Ohmic drop.

$V_R = \frac{I}{A} \cdot \frac{D}{\chi} = i \cdot \frac{D}{\chi}$

(IR)

i = Current density

V_E (Electronic resistance) is minimized by thicker electrodes, shorter in length. Width is immaterial. Pots should not be too deep.

Now, the ohmic drop between two electrodes also is because of the electrical resistance in the circuits, as well as in the electrode bodies themselves. And we express it by writing as electronic voltage drop is current passing and resistance in the circuit, which is written as one by conductance into D is the distance, sorry I am talking about the other term, now ignore this part.

We talk about the resistance due to electronic resistance in the circuit that will be because of the circuit and also because of the resistances in the electrodes. Now it can be shown by simple logic, the thicker electrodes will give you lesser resistance. If the electrodes are thin the electronic resistance will be more and also, there is more resistance if they become too deep, it has been found that electrode should be thick and there should be width, the width does not matter but, depth matters.

So, an an electrolytic cell one one tries to see, that the electrodes are wide. This does not matter, but this depth matters, it should not be too deep not too deep. So, there are all kinds of things to be taken into account, so that to minimize the applied voltage, because if the applied voltage is high, then you have you need more power, voltage into current will go up.

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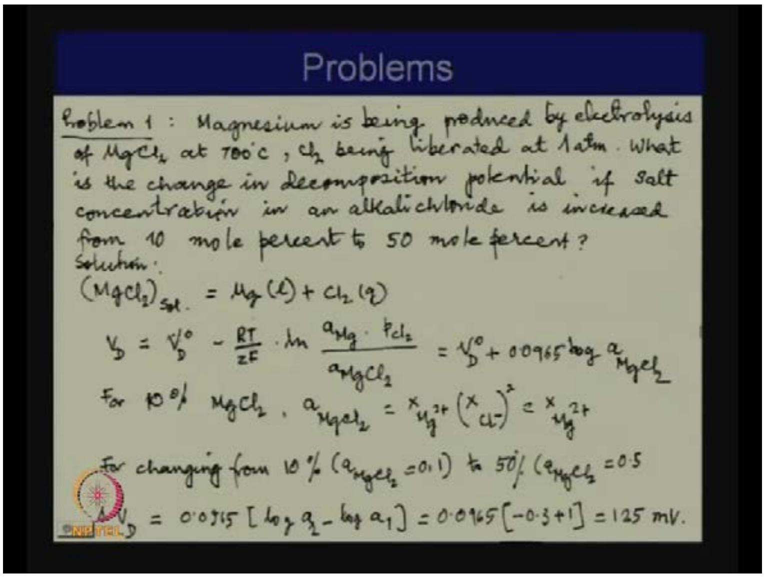

Problems

Problem 1 : Magnesium is being produced by electrolysis of $MgCl_2$ at 700°C, Cl_2 being liberated at 1 atm. What is the change in decomposition potential if salt concentration in an alkali chloride is increased from 10 mole percent to 50 mole percent?

Solution:

$(MgCl_2)_{sol.} = Mg(l) + Cl_2(g)$

$$V_D = V_D^0 - \frac{RT}{zF} \cdot \ln \frac{a_{Mg} \cdot p_{Cl_2}}{a_{MgCl_2}} = V_D^0 + 0.0965 \log a_{MgCl_2}$$

For 10% $MgCl_2$, $a_{MgCl_2} = x_{Mg^{2+}} (x_{Cl^-})^2 = x_{Mg^{2+}}$

For changing from 10% ($a_{MgCl_2} = 0.1$) to 50% ($a_{MgCl_2} = 0.5$

$$\Delta V_D = 0.0965 [\log a_2 - \log a_1] = 0.0965 [-0.3+1] = 125 \text{ mV.}$$

Let us end this lecture with one or two very simple problems that will make use of some principles we have discussed. Here is a problem that magnesium is being produced by electrolysis of magnesium chloride at 700 degrees, chlorine being liberated at one atmosphere. What is the change in decomposition potential, if salt concentration in a alkali chloride is increased from 10 mole percent to 50 mole percent.

Now, it should be quite obvious, that decomposition would be easier, when there is more magnesium chloride one is 50 percent, then when it is 10 moles percent it should be obvious. But, you have to calculate that, we write the decomposition potential in this manner, in the C l 2 in solution giving you magnesium liquid and chlorine gas.

The decomposition potential for that can be written as V D naught, which is standard decomposition potential for pure salt minus R T by Z F. Then we have this activity terms long a M g P C l 2 and this, that is long k this is the equilibrium constant here.

So, the expression we can ignore P C l 2, because it is we have say this one atmosphere. We assume that the activity of magnesium is unity, because it is pure magnesium coming out, so the expression only has activity of magnesium chloride.

So, for 10 percent M g C l 2, what will be the activity using Temkins equation, we say it is more fractional M g 2, into ionic fraction of M g 2, into ionic fraction of chlorine square. Fortunately there is no other anion therefore, this is one, so it becomes X M g 2 plus and so from changing from changing from 10 percent, where activity of M g C l 2 is 0.1 to 50 percent 0.5, we easily calculate that the there will be 125 millivolt change, you will have an advantage, when you have the 50 mole percent you need less voltage.

Whereas simple problem that, one may have to deal with in in in a copper electrolysis plant, we are not talking about electrolysis is an eco solution, the the problem says, question is 100 tons of copper concentrate, are to be processed in 6 months approximately, it is approximately 21 percent copper. 25 working hours per month 8 hour per day, leaching is by H 2 S O 4 estimate minimum rating, this is not fating it should be rating and rating means voltage and current of power supply unit for 12 cells in series, there are too many mistake series. Given the E naught for the cathode and E naught for the anode.

Now, solution would be first we find out the processing rate, the processing rate will be 3500 kilogram of copper per month, then according to Faradays law 96500 coulombs will produce 31.5 gram of copper, that is 1 equivalent weight, hence the deposition of this, we calculate how much of current will be require for deposition of this.

We multiply this by coulombs divided by equivalent weight we find; so many coulombs would be required. Total working time available with us in 1 month is obtained by finding out working days and hours per day, so many seconds. Hence current I is easily found by a ratio, that this divided by that this is the total current requirement. So, 1 rating is we have found out, what is the current requirement, voltage requirement the standard voltage requirement will be E naught cathode minus E naught anode and which is this plus this 0.893 voltage. (Refer Slide Time: 33:48)

Now, since there are 12 cells in series, each cell would need so much of voltage, so V multiply by twelve, this will be the voltage required, now this is a problem we always are faced with in electrolytic plants.

If you put cells in series, that the same current is flowing through all the electrolysis cells but, the voltages are added, so you need more voltage one current is flowing through, if you put the cells in parallel, then we can operate with the same voltage. Because from 2 busbars, we can apply the same voltage in each cell but, the current will be more, because the main current we will have to go through, this go through another channel another channel, they all add up.

So, you have a choice between using more current less voltage or more voltage and less current in either case the energy requirement be ore but, technology will be the same but, the technological requirements are different.

There is one last problem, I have listed here that we have given the operational variables in other data for an electrolytic plant; the conductance of the electrolyte inter-electrode separation over voltages is at the electrodes decomposition voltage theoretical decomposition sorry. The decomposition voltage is not this, I will correct it. The current density is given voltage drop from cathode plate, voltage drop from anode plate to busbar is given, current efficiency is given, equivalent weight of metal is given, we have to calculate kilowatt hour per kg of metal deposited. Actually the it is very simple things have been listed, total voltage drop we have to calculate we have to calculate electricity, sorry yeah. We have to calculate a total voltage drop.

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And actually you are talking in terms of copper it is not in a problem. So, we can consume the, calculate the energy consumed to by by the steps shown I do not want to go through them in detail.

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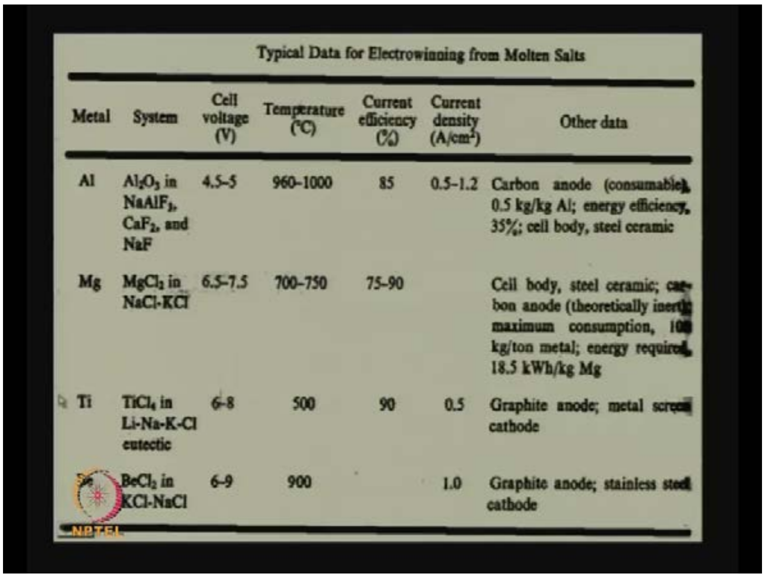

Typical Data for Electrowinning from Molten Salts

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, 100 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 screen cathode
Be	$BeCl_2$ in KCl-NaCl	6–9	900		1.0	Graphite anode; stainless steel cathode

Now, I like to say at the end, that in the industry they use both a cost electrolysis as well as fused salt electrolysis, there are metals which cannot be produced by electrolysis of eco solutions, because they far to reactive.

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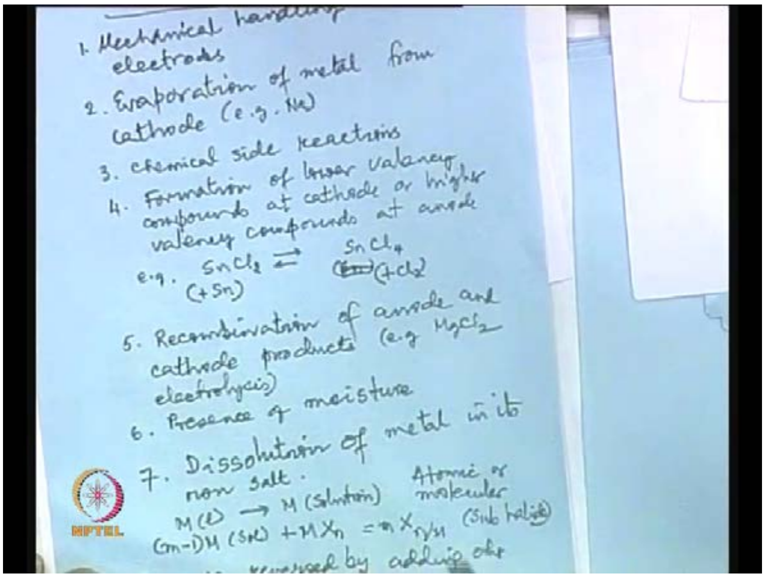

1. Mechanical handling
electrodes
2. Evaporation of metal from
cathode (e.g. Na)
3. chemical side reactions
4. Formation of lower valency
compounds at cathode or higher
valency compounds at anode
e.g. $SnCl_2 \rightleftarrows SnCl_4$
(+Sn) ~~(+Sn)~~ (+Cl_2)
5. Recombination of anode and
cathode products (e.g $MgCl_2$
electrolysis)
6. Presence of moisture
7. Dissolution of metal in its
own salt. Atomic or molecular
$M(l) \rightarrow M(\text{Solution})$
$(m-1)M(\text{sol}) + MX_n = m X_{n/m}$ (Sub halide)
reversed by adding oth

Now, when we are doing fused salt electrolysis, there can be a problem that we do not, we will not get the current efficiency we want because, so many things can happen what are the things that can happen?

Firstly, there can be mechanical handling losses at the electrodes, means you have got the products at the electrodes but, the metal you are not able to collect for one reason or other. So, you think you have not got the amount of metal, you should have got, just because of mechanical handling problems, you are not able to collect the metal, because high temperature operations have their own problems.

Metals can evaporate form the cathode, like if we are trying to produce sodium by electrolysis, sodium may evaporate escaping to the atmosphere. There can be chemical side reactions, that there are some species which are getting electrolyzed other than the main salt, that you want to dissociate.

Then, there can be another very interesting phenomenon that suppose you are trying to produce, you are trying to produce sodium tin by electrolysis of tin chloride. What can happen is that, you may end up producing sodium tin tetrachloride, if chlorine liberated at the anode reacts with this to produce S n C l 4 or in the cell, if you start with S n C l 4 and tin comes in contact with S n C l 4, it may produce S n C l 2. See you can have a situation, where you are producing tin but, the tin is reacting, so no tin is deposited or you can have a situation that you are producing chlorine but, you are not getting any chlorine, because chlorine is reacting, if the bath was S n C l 2 to produce S n C l 4.

So, if you start with S n C l 2 you would lose chlorine, if you start with S n C l 4 you may loss tin, so in such situations 1 has to take precautions of immediately taking out the anode products or cathode products. Sometimes the anode product and the cathode product may recombine, like if we are trying to produce magnesium by electrolysis of magnesium chloride, we have got magnesium, we have got chlorine, but if they come in contact they will react again and produce magnesium chloride. So we have to have cells, where magnesium when it is produced is taken out, separated out using a right right kind of device and chlorine does not allow to come in contact with magnesium.

If there is moisture, a fused salt media, then the lot of current will be lost simply to first remove that moisture, so we will pass current but, no metal will be deposited. Lastly in many few salt baths a very interesting phenomenon takes place that the metal is deposited but, the metal re-dissolves not completely but, at least partly into the fused salt bath.

See you have passed current and you know this much of metal should have come, because of faradays laws metal did get produced but, then metal re-dissolved into the bath. This has been studied very thoroughly and the present theory is, of course metal can dissolve like this, that it reacts with the bath but, we are not talking about a situation where the metal is reacting with the bath.

The metal say, it is a liquid metal that has produce can actually dissolve atomically, means that going to the atomic spaces in the supporting bath. It could be atomic or it could be molecular, then from that state of solution, it reacts with the salt that we are trying to decompose to produce a sub halide.

For example, suppose you are trying to produce magnesium chloride, we have produced magnesium. Magnesium may dissolve atomically react with magnesium chloride to produce certain amount of M g C l. You may say such a compound does not exist but, it may exist in the salt bath. This situation does take place in some few salt media; this will be eliminated or at least reduced very much, if we have other salts in the fused salt bath.

For example, if this is happening, if you add another salt or a third salt, then you will reduce the activity of the main salt you are trying to reduce, try to dissociate, because its activity must go down there are other salts and if that happens, this reaction will go to the left, and then this reaction will also go to the left.

So, we can sub, we can reduce or eliminate sub halide formation by adding a second or a third salt in the fused media. This is another reason why we seldom produce a metal in a pure salt medium, we produce other things to ensure there is no sub halide formation, because both the reactions will be will go to the left direction.

I think, I would try to wind up the discussions on pyrometallurgy, hydrometallurgy and electrometallurgy now. Last couple of lectures we have discussed principles of production of metals using pyrometallurgical operations, hydrometallurgical operations and electrometallurgical operations, all these operations need energy and all these operations have adverse effect on the environment.

Now, in today circumstances, we have to always think of ways and means of reducing energy requirements and reducing adverse impact on the environment. Now much of the impact on the environment comes from use of energy, because if you are using energy you are creating a problem in the environment, so let us just quickly look at the kind of energy requirement, the energy needed for production of metals.

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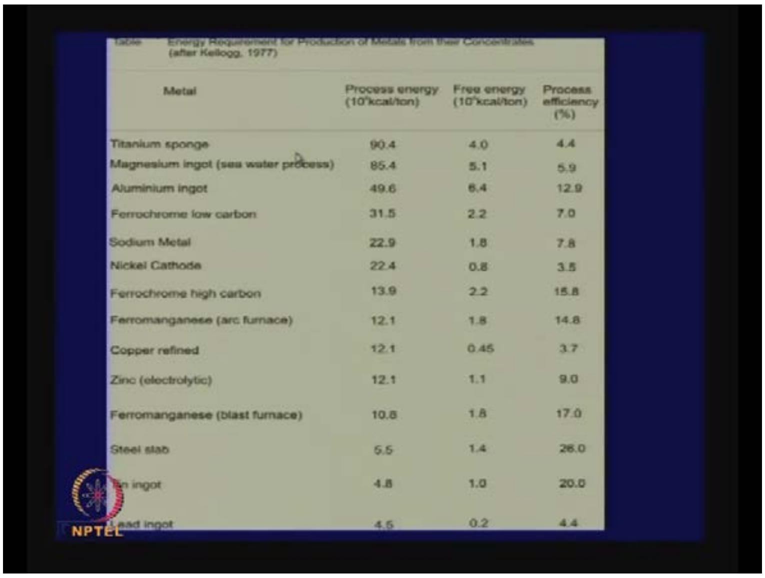

Table Energy Requirement for Production of Metals from their Concentrates (after Kellogg, 1977)

Metal	Process energy (10^6 kcal/ton)	Free energy (10^6 kcal/ton)	Process efficiency (%)
Titanium sponge	90.4	4.0	4.4
Magnesium ingot (sea water process)	85.4	5.1	5.9
Aluminium ingot	49.6	6.4	12.9
Ferrochrome low carbon	31.5	2.2	7.0
Sodium Metal	22.9	1.8	7.8
Nickel Cathode	22.4	0.8	3.5
Ferrochrome high carbon	13.9	2.2	15.8
Ferromanganese (arc furnace)	12.1	1.8	14.8
Copper refined	12.1	0.45	3.7
Zinc (electrolytic)	12.1	1.1	9.0
Ferromanganese (blast furnace)	10.8	1.8	17.0
Steel slab	5.5	1.4	26.0
n ingot	4.8	1.0	20.0
Lead ingot	4.5	0.2	4.4

Now here, is a table that gives the energy requirement for production of metals from their concentrates from their concentrates mind you. Now, we can compare the process energy that is what is normally record to produce the metal form the concentrate, with what should have been the ideal energy required simply to dissociate a pure compound. Now titanium sponge, suppose we could we we could produce it from pure Ti O 2, take pure Ti O 2 break it to produce titanium.

That energy should have been just the opposite of the free energy of formation of Ti O 2, all these oxides are found, we have the free energy of formation, metal plus oxygen that oxide, if we could get the opposite energy, we produce oxygen and titanium.

Now, the free energy of formation is 4.0, 10 to the power 6 kilo calorie per ton but, the process energy requirement is so much higher, almost more than 20 times higher. Why are we requiring, so much energy to break the compound to get the metal, the answer should be obvious, that you are not dealing with a pure compound.

To get Ti, we have to treat a concentrate in which, which has come from an ore, which has come from the mines, so when you are getting the ore form the mines, then going through mineral dressing processes. Then going through pyrometallurgical, hydrometallurgical electrometallurgical operations, whatever to get finally titanium, you are spending a lot of energy in many operations, other than that required for breaking of the I o 2, that is why it this energy is very high.

In the case of magnesium the process energy is 85, whereas the free energy requirement should have, should have been met only by 5, process energy in this case is 4, in this case is 5, in the case of aluminum ingot almost 50 percent with the process energy is 49.6, again in terms of free energy it is small process energy is 12. Only when we come to compounds which are not very stable and which are found in relatively purer forms, which are easier to break like lead ingot, that we find our process efficiency are higher. It is because say in the case of ion, we can get ion ores which are relatively almost very close to the F e 2 O 3 composition, plus the energy requirement in excess of the breaking down of the oxide is not that much.

So, whereas the process energy is 5.5 into 10 to the power 6 kilo calorie per ton, from the free energy point of view of should have been 1.4, so process energy is 26, 26 percent. So, what I am trying to say is that, you can look at the free energies of formation of the pure compounds but, this pure compounds are not available in nature as such, the minerals are available in the form of ores and minerals, where you do not have the pure compounds in this much more energy and that is why, we have to spend, so much of energy to extract metals from ores and minerals.

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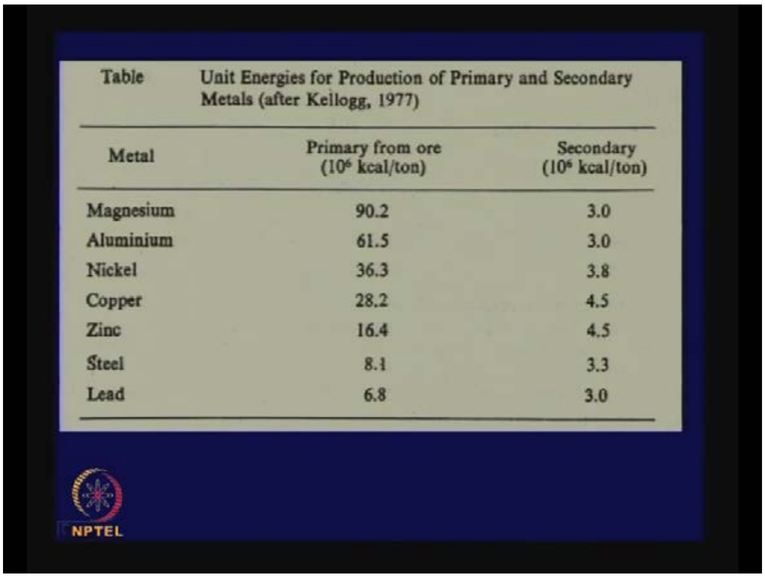

Table Unit Energies for Production of Primary and Secondary Metals (after Kellogg, 1977)

Metal	Primary from ore (10^6 kcal/ton)	Secondary (10^6 kcal/ton)
Magnesium	90.2	3.0
Aluminium	61.5	3.0
Nickel	36.3	3.8
Copper	28.2	4.5
Zinc	16.4	4.5
Steel	8.1	3.3
Lead	6.8	3.0

However, if we can look at the secondary metals, like suppose you have produce aluminum which is gone into the consumer market and after some time it is discarded, there aluminum is in a form from which to get again pure aluminum, you will not need more energy; obviously, because you are not going to extract it from the ore, you have not to going to decompose A l 2 O 3, all you have to do is to take that impure metal and purify it. So, the unit energy is for production of secondary metals would be much lower than the primary metals, by the word primary metals we mean metals extracted form ores. By secondary metals we mean metals extracted from scrap, so the secondary metals come as a result of refining of the metal scrap.

And here are some figures, the primary from ore for magnesium 90 units, secondary would be only 3, aluminum while it will be 61.5 into 10 to the power 6 kilo calories per ton, from the scrap if we produce pure aluminum again it will be only 3. Actually it is only a process of refining, I am going, going to and indecently if a metal like aluminum the energy compound need is 30 to 40 percent, much of the cost of the metal is the cost of energy. So we have to give a lot of attention to processing of scrap.

Look at nickel, primary energy 36.3 units, these these units secondary 3.8, copper 28.2, 4.6 zinc is also one fourth steel is almost half and lead is also similar. If we need 6.8 units from primary and in this case this fairly low, because lead sulphide is an unstable, is not very stable, mineral and it is easily roasted and easily reduced but, if you produce from the secondary source, so much so much easier.

And metals like lead are very easy to be reprocessed; you know many of the car batteries that use lead. The lead goes back and it is refined cleaned of and it comes back into the market. So, I think now, I will conclude by saying that, so far we have not discussed production of any metal as such specifically, we have gone through general principles of pyrometallurgy, hydrometallurgy then electrometallurgy.

The idea has been to produce the metal; we have not specifically talked about producing pure metal. Although, we produced with very pure metal in electrometallurgical operations and sometimes in hydrometallurgical operations also but, we have so far concentrated on production of bulk metal.

In the next lecture, I will try to discuss principles of refining of impure metals. When there are impurities in the metal produced, how we remove the impurities, we will quickly go through that in the next two lectures, thank you.