Non-ferrous Extractive Metallurgy

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Module No. # 01

Lecture No. # 16

Extraction Aluminum (Contd.)

We have been discussing the Bayer's process for production of pure alumina. And I mentioned that this alumina, finds many applications: in medicines, in cosmetics, as a grinding reagent, many others, but its main use is in aluminum electrolytic cell for aluminum production.

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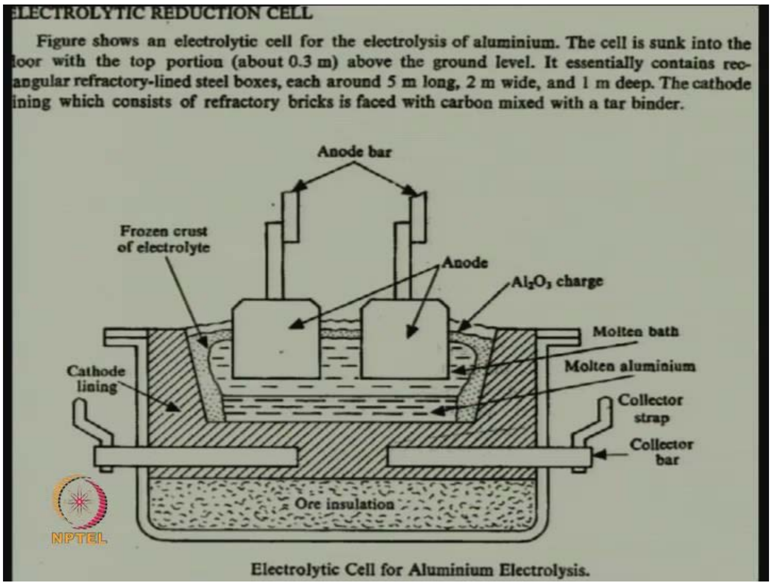

ELECTROLYTIC REDUCTION CELL

Figure shows an electrolytic cell for the electrolysis of aluminium. The cell is sunk into the loor with the top portion (about 0.3 m) above the ground level. It essentially contains recangular refractory-lined steel boxes, each around 5 m long, 2 m wide, and 1 m deep. The cathode ining which consists of refractory bricks is faced with carbon mixed with a tar binder.

Electrolytic Cell for Aluminium Electrolysis.

Now, let us see how a cell looks like. Here, I show schematically, an electrolytic cell. Now, you will find an electrolytic cell. This is the electrolyte, which has Al2O3, dissolved in cryolite. Alumina is continuously charged here, and there is a frozen crust of electrolyte, which is all around, and this floats on top of aluminum that is continuously produced.

Anodes are two graphite blocks. They can be many, but I have shown two graphite blocks. These are anode bars which are supplying current. Two graphite's anodes dipped into cryolite, which has alumina in solution. Aluminum that is produced goes to a graphite cathode, the whole thing lining is a… is the cathode. Aluminum is attracted here, deposited here. This is the basic scheme of.

Now, gases that are produced will bubble out, and there are ways and means, of collecting them, that I will show later. Basically, it is a steel cell, and you will have the ore insulation. There is insulation at the bottom, on top this is the cathode lining, aluminum. Then you have the electrolyte; then you have the solid crust.

Now, it is a very tricky situation. Now, let me read out what is there on top. This is the electrolytic cell for electrolysis of aluminum. The cell is sunk into the floor, with the top portion about point 3 millimeter above the ground level. It essentially consists of rectangular refractive lines, steel boxes each around 5 meter long, 2 meter wide and 1 meter deep. They are not deep. Remember, I have always said that electrodes, you cannot go for depth. And the cathode lining which consist of refractive bricks is faced with carbon mixed with a tar binder.

Sorry, there is a correction here. There is no question of a cathode which is hanging vertically. Here the cathode is horizontal cathode. Sorry, the cathode area is the horizontal cathode area. And the cathode lining which consists of refractive brick is faced with carbon mixed with tar binder. So, this is the basic scheme.

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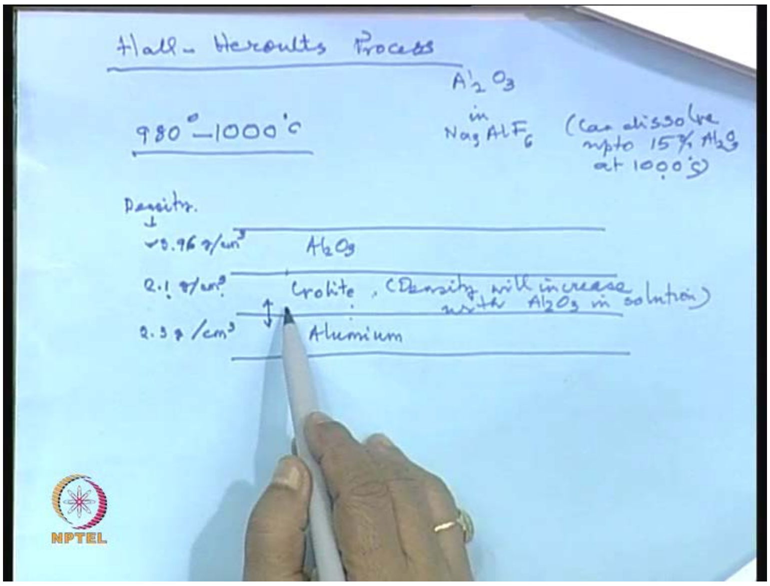

Hall - Heroults Process

Al_2O_3 in Na_3AlF_6 (can dissolve upto 15% Al_2O_3 at 1000°C)

980° - 1000°C

Density
~3.96 g/cm³ Al_2O_3
2.1 g/cm³ Cryolite, (Density will increase with Al_2O_3 in solution)
2.3 g/cm³ Aluminium

Now, there is a it is a very tricky situation, which I am trying to explain to you. We have cryolite, which is a natural mineral. At 1000 degrees when it is molten, its density is just 2.1. Aluminum, which is produced, is slightly heavier than that. So, it goes, it sinks, to the bottom. Alumina will does not dissolve or which do not want to dissolve will form a solid crust, will float because its density is its density is 3.96. So, it is there as a solid crust. Now, the real trick is here that the density of cryolite will go up if more and more alumina going to that because it is of higher density.

If we dissolve more and more alumina, its density will go up, we do not want the density to become too high, and then aluminum will not sink so effectively. Fortunately, we cannot dissolve too much of alumina anyway, because there is a limit. We can at 1000 degrees; we can dissolve only up to 15 percent alumina.

But still nobody will like to go to that. We would like to maintain a density difference. So, one would operate at about 8 percent alumina only, not more than that. So, this is the situation. Temperature will be 980 to 1000 degree centigrade. So, 5, 6, 8 percent alumina and then we have a separation between cryolite and aluminum. Aluminum stays at the bottom above the graphite cathode.

It is also protected from everywhere so that there is no question of it, getting oxidized. This is the basic scheme. Now, there are many requirements that we have to keep in mind in this electrolytic process.

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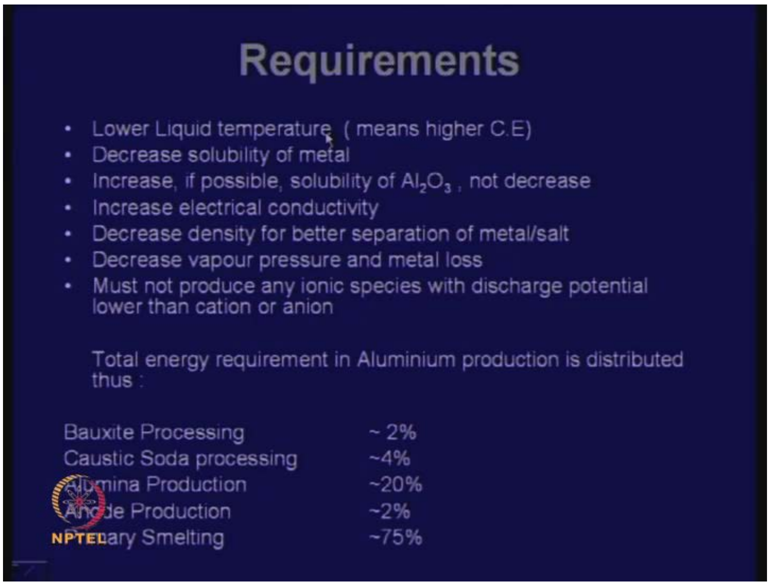

Requirements

- Lower Liquid temperature (means higher C.E)
- Decrease solubility of metal
- Increase, if possible, solubility of Al_2O_3 , not decrease
- Increase electrical conductivity
- Decrease density for better separation of metal/salt
- Decrease vapour pressure and metal loss
- Must not produce any ionic species with discharge potential lower than cation or anion

Total energy requirement in Aluminium production is distributed thus :

Bauxite Processing	~ 2%
Caustic Soda processing	~4%
Alumina Production	~20%
Anode Production	~2%
Primary Smelting	~75%

We want lower liquid temperature means, we have to operate at as lowest temperatures as possible, because then will get a high current efficiency. Otherwise, you will be using current to general heat; we have to decrease solubility of the metal in the few salts. Please remember, I had given some lectures that many metals dissolve in their own salts, and if you do that then it is a metal loss that can be decreased by adding other salts. If you recall that if you at third, fourth, fifth, salts then the solubility of the metal in whole salts goes down.

Increase if possible, solubility of alumina, not decrease. We do not want to decrease alumina solubility beyond 2 percent. There is a minimum limit and now, I discuss why. We have to increase electrical conductivity. There are many requirements; we have to decrease density for better separation of metal and salt. Now, if we increase alumina concentration then you will need less voltage for decomposition, but increasing alumina concentration in cryolite will mean increasing the density, bringing it too close to aluminum for good salt, metal separations.

So, these are contradictory. We do not want too high alumina concentration, because then the density will go up. So, you want to decrease density for better separation of metal and salt. We have to decrease vapor pressure and metal loss. We do not want vapor pressure to be high. It must not produce whatever is been electrolyzed. Any ionic specie will discharge potential lower than cation or anion, all kinds of problems. Before, I go deeper into it, just me give you an idea about where energy is going in aluminum industry. I have been mentioning that it is very energy intensive.

Two percent of energy in bauxite processing, caustic soda processing, and 4 percent alumina production about 20 percent, because it needs grinding, autoclaving, all kinds of pumping. this that… It will require some anode preparation; we have to make graphite anodes. But maximum 75 percent is going into primary smelting, means the electrolytic process that is why maximum energy is concerned.

Now, I have all along been saying that essentially you are adding alumina to make a solution of alumina in cryolite which is Na 3 Al F 6 or 3NaF.Al F 3. But in fact, many other compounds have to be added in some minor amounts.

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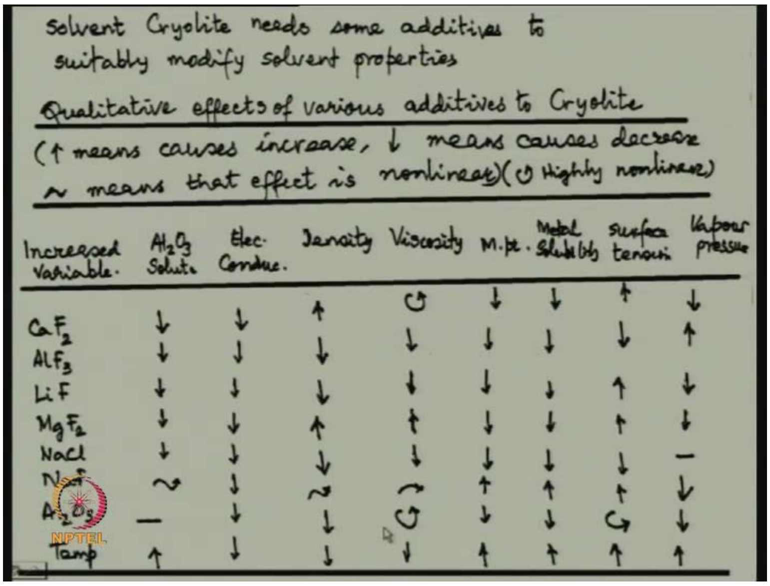

Solvent Cryolite needs some additives to suitably modify solvent properties

Qualitative effects of various additives to Cryolite

(↑ means causes increase, ↓ means causes decrease ~ means that effect is nonlinear)(↻ Highly nonlinear)

Increased Variable.	Al_2O_3 Soluty.	Elec. Conduc.	Density	Viscosity	M.pt.	Metal Solubility	Surface tension	Vapour pressure
CaF_2	↓	↓	↑	↻	↓	↓	↑	↓
AlF_3	↓	↓	↓	↓	↓	↓	↓	↑
LiF	↓	↓	↓	↓	↓	↓	↑	↓
MgF_2	↓	↓	↑	↑	↓	↓	↑	↓
NaCl	↓	↓	↓	↓	↓	↓	↓	—
NaF	~	↓	~	↷	↑	↑	↑	↓
Al_2O_3	—	↓	↓	↻	↓	↓	↻	↓
Temp	↑	↓	↓	↓	↑	↑	↑	↑

Here are some of the things, with which people have experimented for years, why we require smaller amounts of these things, let us consider that. Solvent cryolite needs some additives to suitably modify solvent properties, because there are many requirements of the electrolytic processes, and here we are giving some qualitative effects of various additives to cryolites, what happens when these are added. Now, this means that causes increase, a downward arrow means causes decrease. This means that effect is non-linear and this means highly non-linear. Some of them you should easily understand. Some you cannot understand. They have been found by trial and error. If you increase Al 2 O 3, now this is Al 2 O 3 solubility, please remember, this word is Al 2 O 3 solubility.

Now, if you add calcium fluoride, this solubility will increase…, (( )) will decrease (Refer Slide Time: 11:21), will decrease, this will decrease it, LiF will decrease it. All salts, if you add will decrease Al 2 O 3 solubility, because there are also going into cryolite.

Sodium fluoride, we do not know. If we increase temperature, solubility will increase. So, while it may be necessary to add other solids for various reasons that we see. All these, will decrease solubility of Al 2 O 3 that you want to dissolve in the salt. What will happen to electrical conductivity? Calcium fluoride will decrease it, aluminum fluoride will decrease, lithium fluoride will decrease that, and magnesium fluoride will decrease. All of them will decrease electrical conductivity.

May some will increase density; some will decrease density. You can easily say that if you had something like sodium fluoride which is a very light molecule, then it will decrease. But some others will increase. Viscosity is also important, because on viscosity, will depend, separation of metal and salt of metal will go through, and trickle through how they will be handled. Some increase it; some decrease it. More important is what the effect on melting point is.

Now, all these additions excepting sodium fluoride, is good from the point of view of melting point, because melting point decreasing, is to our advantage. Metal solubility, any foreign ions will decrease metal solubility. So, many of them…, metal solubility this all will decrease. Surface tension affect, vapor pressure effect is also complicated. So, people play around with all these additives, in the industry, and different industries have developed their own formulas, as to what to add and what not to add. Two are very common; one must add some calcium fluoride, some aluminum fluoride. These are the most common things and what they do will see later on.

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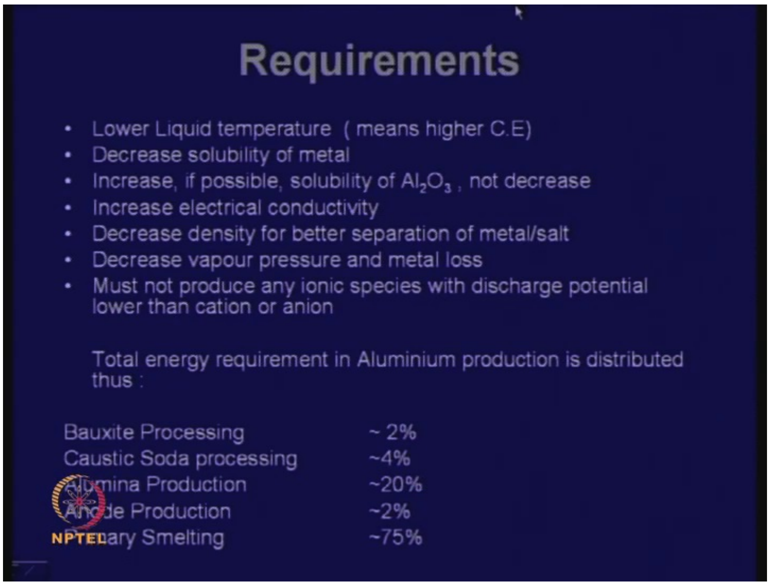

Requirements

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Primary Smelting	~75%

Now, all these additives are to achieve these criteria: lower liquid temperature, decrease solubility of metal, increase possible solubility of Al 2 O 3, increase electrical conductively, etcetera and this has to be achieved in the cell.

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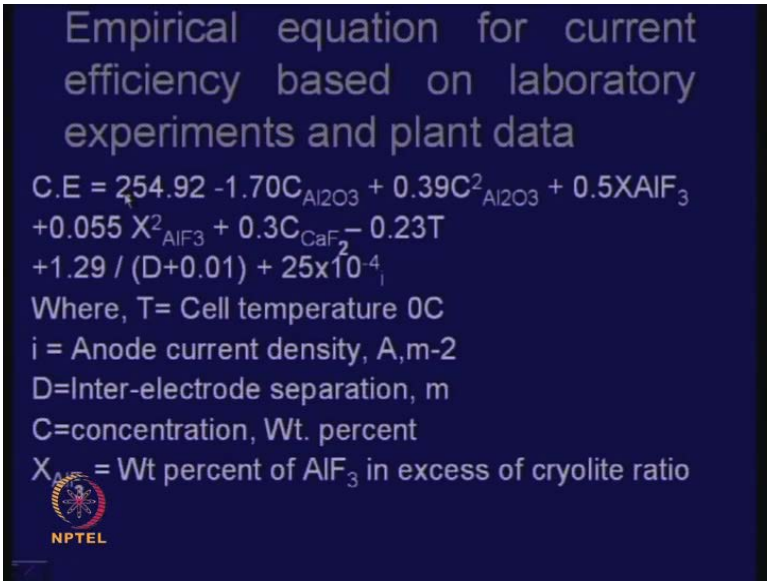

Empirical equation for current efficiency based on laboratory experiments and plant data

$$C.E = 254.92 - 1.70C_{Al2O3} + 0.39C^2_{Al2O3} + 0.5XAlF_3 + 0.055\,X^2_{AlF3} + 0.3C_{CaF_2} - 0.23T + 1.29/(D+0.01) + 25\times10^{-4}\,i$$

Where, T= Cell temperature 0C

i = Anode current density, A,m-2

D=Inter-electrode separation, m

C=concentration, Wt. percent

X_{AlF_3} = Wt percent of AlF_3 in excess of cryolite ratio

Now, the effects of various parameters of current efficiency or energy efficiency have been determined in the industry, by lot of R&D work. Many researchers have worked. Here is an equation that I am giving. I again taking out from a book and this book you must see. The three books, I referred to in the morning, you must see at least for aluminum, discussions on aluminum.

That current efficiency is given empirically by an equation written here. There is a negative term with respect to concentration of alumina, but here is a term alumina concentration square, current efficiency will increase with aluminum fluoride addition, both are plus. Current efficiency increased with calcium fluoride addition, current efficiency decreased with temperature; obviously, and there are some dimensional things also, like inter-electrode separation. If the inter-electrode separation if it increases this term (Refer Slide Time: 15:32) will increase, therefore, current efficiency will drop.

So, the between the distance between the cathode and anode, both graphite's, they have to be minimized. See here (Refer Slide Time: 15:48), they have to be minimized, because if this increases, this term will decrease, current efficiency will decrease. If this is decreased, this will increase; this will increase. So, the two electrodes must come close together, but then, there has to be some distance also. Otherwise, how will you… The resistance of the electrolyte has to provide it. So, there is a kind of compromise they have to work out, different industry do it differently.

And in many cases they can even go to a distance of only about 0.5 centimeter between the one electrode anode and the cathode. So, there are thin layers of cryolite and metal.

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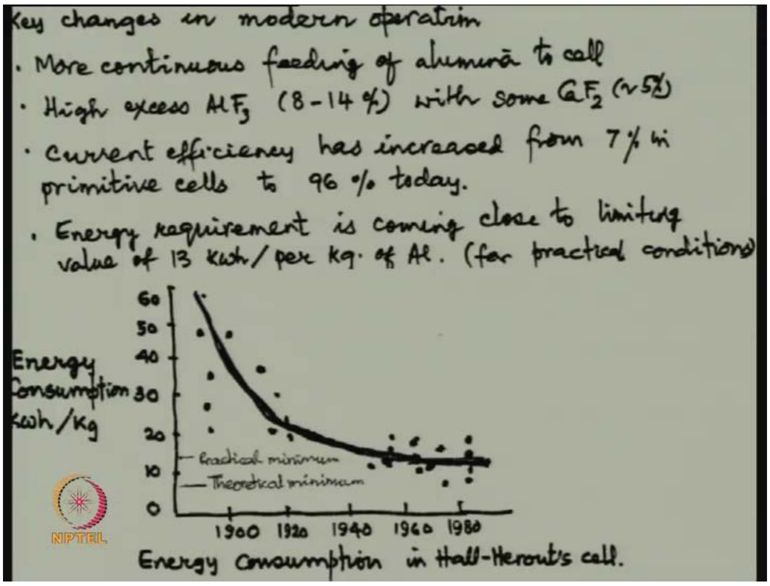

Key changes in modern operation

- More continuous feeding of alumina to cell
- High excess AlF_3 (8-14 %) with some CaF_2 (~5%)
- current efficiency has increased from 7% in primitive cells to 96 % today.
- Energy requirement is coming close to limiting value of 13 kwh / per kg. of Al. (for practical conditions)

Energy Consumption in Hall-Herout's cell.

Now, what are the key changes in modern operations, say compared to what happened in, say hundred years ago. First of all, they have now found out cells where the continuous feeding of alumina to cell, continuous feeding of alumina, continuous removal of aluminum. Higher excess of aluminum fluoride, a lot of aluminum fluoride excess is being added, a lot of calcium fluoride excess 5 percent, is being added.

Current efficiency in the beginning was 7 percent, has gone up to some 96 percent today. Usually 4 percent of the current is going into reactions that you do not want, 96 percent is going into decomposition alumina to aluminum. Energy requirement is coming to gradually a limiting value of 13 kilo watt hour per ton, almost coming to the practical minimum. These two dots are wrong (Refer Slide Time: 17:51). They should not be there. The theoretical minimum is even less. It is above 6. Why theoretical minimum? Only the power required to dissociate aluminum.

But we need some energy also to keep the electrolyte hot. So, the practical minimum is above theoretical minimum, but in the last twenty years or so, industries are almost able to bring it to the practical minimum. I will give you some figures to this effect little later.

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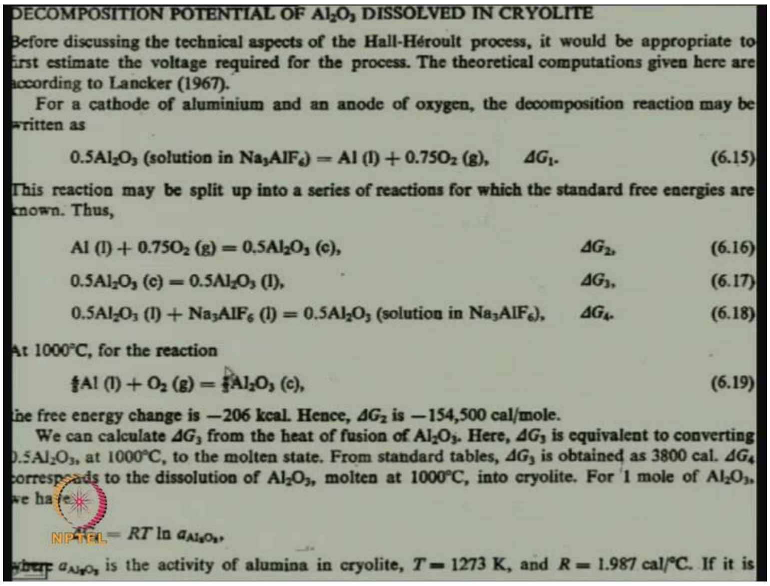

DECOMPOSITION POTENTIAL OF Al_2O_3 DISSOLVED IN CRYOLITE

Before discussing the technical aspects of the Hall-Héroult process, it would be appropriate to first estimate the voltage required for the process. The theoretical computations given here are according to Lancker (1967).

For a cathode of aluminium and an anode of oxygen, the decomposition reaction may be written as

$$0.5Al_2O_3 \text{ (solution in } Na_3AlF_6) = Al\ (l) + 0.75O_2\ (g), \qquad \Delta G_1. \qquad (6.15)$$

This reaction may be split up into a series of reactions for which the standard free energies are known. Thus,

$$Al\ (l) + 0.75O_2\ (g) = 0.5Al_2O_3\ (c), \qquad \Delta G_2, \qquad (6.16)$$

$$0.5Al_2O_3\ (c) = 0.5Al_2O_3\ (l), \qquad \Delta G_3, \qquad (6.17)$$

$$0.5Al_2O_3\ (l) + Na_3AlF_6\ (l) = 0.5Al_2O_3 \text{ (solution in } Na_3AlF_6), \qquad \Delta G_4. \qquad (6.18)$$

At 1000°C, for the reaction

$$\tfrac{4}{3}Al\ (l) + O_2\ (g) = \tfrac{2}{3}Al_2O_3\ (c), \qquad (6.19)$$

the free energy change is -206 kcal. Hence, ΔG_2 is $-154{,}500$ cal/mole.

We can calculate ΔG_3 from the heat of fusion of Al_2O_3. Here, ΔG_3 is equivalent to converting $0.5Al_2O_3$, at 1000°C, to the molten state. From standard tables, ΔG_3 is obtained as 3800 cal. ΔG_4 corresponds to the dissolution of Al_2O_3, molten at 1000°C, into cryolite. For 1 mole of Al_2O_3, we have

$$= RT \ln a_{Al_2O_3},$$

where $a_{Al_2O_3}$ is the activity of alumina in cryolite, $T = 1273$ K, and $R = 1.987$ cal/°C. If it is

Now, let us make some calculations, about decomposition potential, and for that, I would request you to read up, something that I have given in this book on, “Introduction to Melts - Molten Salts, Slags and Glasses” and also “Extraction of Non-ferrous metals”.

How you make some simple calculations to find out what is the theoretical requirement for vortice to dissociate. Now, for that you know a fundamental formula. If you want the free energy of formation say Delta G, then it can be equated to minus z f faraday, and decomposition potential e. Delta G is equal to minus z f e, put the value of z which is valency for aluminum, a faraday constant, you get the decomposition potential in volts. So, there is a co-relation between free energy of formation, calories and decomposition potential in volts.

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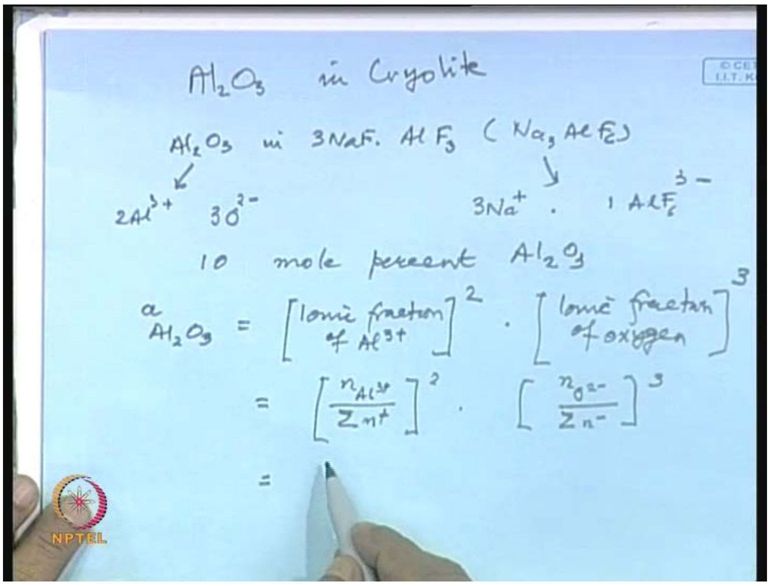

Al_2O_3 in Cryolite

Al_2O_3 in $3NaF \cdot AlF_3$ (Na_3AlF_6)

$2Al^{3+}$ $3O^{2-}$ $3Na^+ \cdot 1\, AlF_6^{3-}$

10 mole percent Al_2O_3

$$a_{Al_2O_3} = \left[\text{Ionic fraction of } Al^{3+}\right]^2 \cdot \left[\text{Ionic fraction of oxygen}\right]^3$$

$$= \left[\frac{n_{Al^{3+}}}{\Sigma n^+}\right]^2 \cdot \left[\frac{n_{O^{2-}}}{\Sigma n^-}\right]^3$$

$$=$$

Now, when you have A1 2 O 3, in cryolite and you are applying voltage to decompose A1 2 O 3, you are not decomposing pure alumina, you are decomposing alumina in solution. So, you have to find out the decomposition voltage required for alumina in solution in cryolite. How do you find that? That calculation is given here, I have lifted it, from one of my books and that is why I left the equation numbers here also, because it will be easier for me to refer today. Sorry it is a long write up, but let me explain what it says; it is not so difficult.

Before discussing the technical aspects of Hall Heroult's process, I am saying, it will be appropriate first to estimate a voltage required for the process of dissociation, the theoretical computations given here are according to somebody have given the reference.

Now, for a cathode of aluminum and an aluminum anode of oxygen, let us consider an ideal situation. This does not happen, that you have alumina in cryolite, you have an electrode where aluminum is getting deposited, another electrode where oxygen is deposited, to produce oxygen ion to oxygen, for that you need platinum.

That is not how it happens in industry, but let us say in the lab, we find out the theoretical voltage required when Al 2 O 3, is decomposing to aluminum and oxygen. So, we need a platinum electrode.

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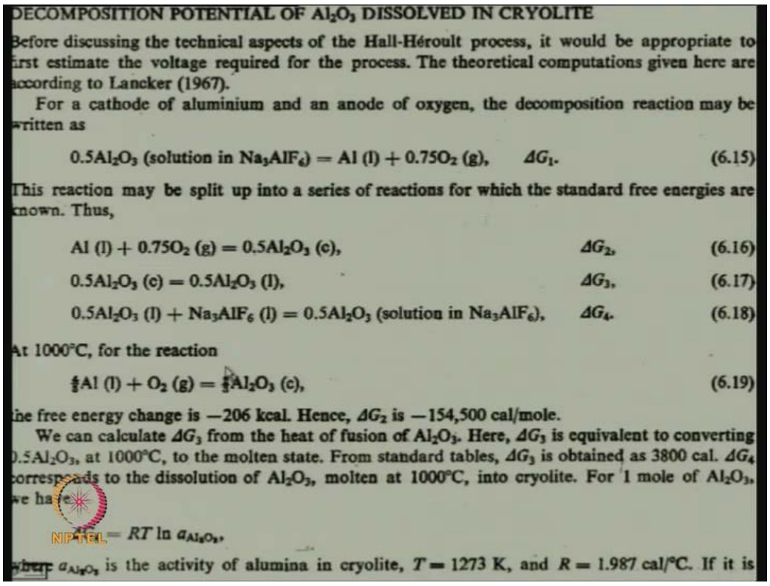

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Now, this is how we calculate, we want to know the decomposition of alumina into aluminum and oxygen. And this alumina is in solution; it is 0.5 Al 2 O 3, aluminum, and 0.75 O 2. I am writing it in this form. So, that we are always getting one atom of alumina. Suppose, the free energy change, for this Delta G 1, the reaction may be split into series of reactions, and this we must understand. Firstly, there is consider pure alumina, the formation reaction is one aluminum, 0.75 oxygen, Al 2 O 3, c means solid.

Now, this solid alumina, assume that it is becoming liquid alumina, and that liquid alumina is dissolving in liquid cryolite to produce this alumina, in solution in cryolite, this is very tricky way of doing things. Now, suppose you are mixing sugar in water. Now in the sugar solution, sugar is not there as solid, it is in a liquid state. So, we can visualize this reaction as solid sugar, first melting to make liquid sugar, then liquid sugar plus liquid water, giving you a liquid solution of sugar in water.

So, in the process of dissolution, somewhere sugar is melting, as of that is how you can also understand. Why when many salts when they dissolve in water, the water becomes cooler. If you take silver nitrate, dissolve it, in water you will find the temperature drops. Why? Because the solid silver nitrate has melted notionally and for melting it has extracted heat from water, and then it has the two liquids are mixed, so the water will be (( )).

So, they say when you have sharbat, in summer, it cools you. It is true, because the moment you have put some sugar in water, sugar has extracted heat from water, to melt. Liquid sugar has dissolved now with water and you have got cooler water. You can actually see it by using a thermometer. Something like this is happening here. You have alumina solid, we visualize it as becoming liquid alumina, and the liquid alumina is reacting with cryolite to become a solution. So, we have split the reaction into three. Firstly (Refer Slide Time: 24:44), the formation reaction, then the state change reaction, then dissolution.

We will find these values, and then add them up, to get this value (Refer Slide Time: 25:01). Now, at 1000 degrees for the reaction, aluminum plus O 2, A1 2 O 3, the c again solid, we get from our Ellingham diagrams, the free energy change there is given per hydrogen molecule.

So, you have to recalculate it here, for 0.57 have to take. That is given as minus 207 kilo calories. So, Delta G 2 is this. We can calculate Delta G 3, means solid going to liquid from the heat of fusion of alumina. Here Delta G 3 is equivalent to converting 0.5 Al 2 O 3 at 1000 degrees, to the molten state and from standard tables we obtained it as 3800 kilo calorie. Delta G 4 corresponds to dissolution of Al 2 O 3, molten at 1000 degrees into cryolite. For 1 mole of Al 2 O 3, we have Delta G 4 is RT Log activity of Al 2 O 3 because this will depend on activity of Al 2 O 3.

Al 2 O 3 is the activity of alumina in cryolite. Temperature is this, R is this, if it is assumed that the bath contains 8 percent alumina, and the rest cryolite, then the mole fraction of alumina works out to be 0.15, if you take the molecule of weight mole fraction is 0.15. Assuming that the solution is ideal and also the activity of alumina is equal to its mole fraction we get Delta G 4 is equal to R T l n this by 2 this (Refer Slide Time: 26:47).

So, now you add up all these, to get the final value, and that is equal to Faraday constant, Z, which is 3 valency, into E. This E will give us the decomposition potential and by doing this calculation decomposition potential, theoretical, for a solute containing 8 percent alumina comes out to be 2.22 volts. This theoretically calculated value compares with experimentally obtained values between aluminum and platinum oxygen electrodes which lie in the range 2.1- 2.15V.

So, theoretically we have calculated the value which is very similar to what can be experimentally obtained in a lab using platinum electrode and aluminum electrode. Now, there is a little bit of error in this calculation, because we are assuming that when the mole fraction for 8 percent aluminum is 0.15, we are taking the activity is equal to 0.15. Actually this is not quite so. You go back to my discussions on Temkin model for fuse salts.

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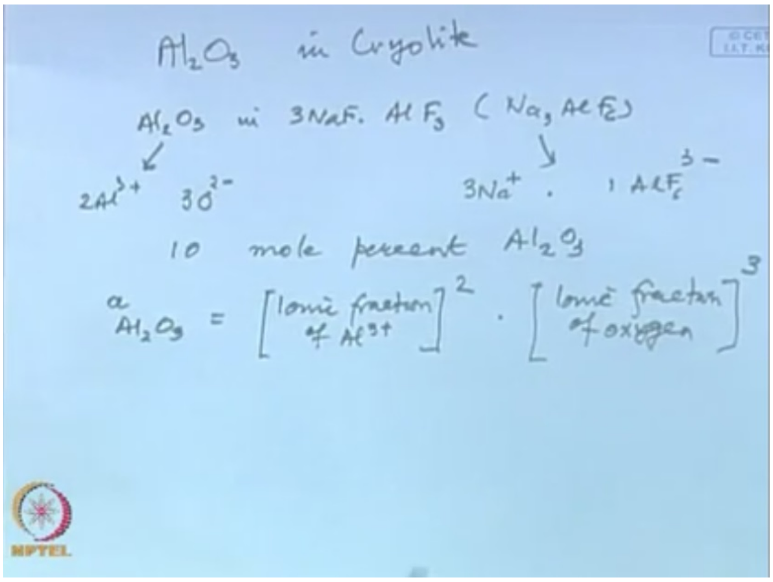


Al_2O_3 in Cryolite

Al_2O_3 in $3NaF \cdot AlF_3$ (Na_3AlF_6)

$2Al^{3+}$ $3O^{2-}$ $3Na^{+} \cdot 1\,AlF_6^{3-}$

10 mole percent Al_2O_3

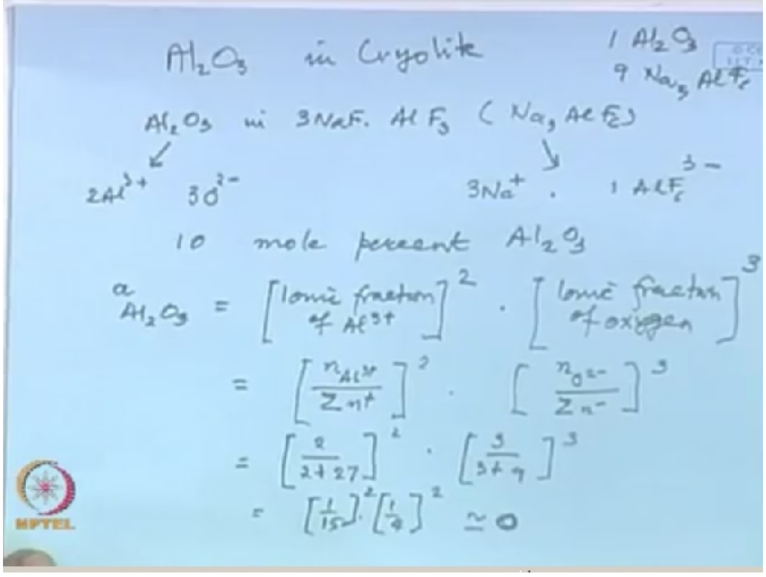
$$a_{Al_2O_3} = \left[\text{Ionic fraction of } Al^{3+}\right]^2 \cdot \left[\text{Ionic fraction of oxygen}\right]^3$$

If we consider Al 2 O 3 in 3 Na F into Al F 3, that is Na 3 Al F 6. This is giving us 2 aluminum ions and 3 oxygen ions. This is giving us 3 sodium ions, one Al F 6 3 minus ions. So, ideally these are the species in the melt. Now, assume make it simple that we have 10 mole percent Al 2 O 3, the earlier calculation was for 15 mole percent, but let us say 10 mole percent, means for one molecule of Al 2 O 3, we have 10 molecules of cryolite. Now, what is according to Temkin's equation, activity of Al 2 O 3, it will be ionic fraction of aluminum 3 plus ions, square into ionic fraction of oxygen cube.

Now, remember what I had said about Temkin's equation. I had said the Temkin proposes that in an ionic melt, we have 2 sub lattices; 1 lattice for cations, 1 lattice for anions. They are mixed together, intermixed. Cations can move in the cation sub lattice, anions move in the anion sub lattice. Such that a cation is always surrounded by anions and anions always surround by cations. When we say activity of alumina, we really mean the probability of finding two aluminum atoms in close proximity of three oxygen atoms. Two aluminum atoms in close proximity of three oxygen atoms.

Now, the probability of finding two aluminum ions will have to be calculated with reference to only the cation sub lattice. Probability of finding oxygen anions, three of them in nearby areas, will be in reference to only the anions sub lattice. And because we are calculating probability, we are talking about two aluminum, so it will be ionic fraction of aluminum to the power square (Refer Slide Time: 31:38), and this will be ionic fraction of oxygen to the power cube.

(Refer Slide Time: 31:45)



Al_2O_3 in Cryolite

1 Al_2O_3
9 Na_3AlF_6

Al_2O_3 in $3NaF \cdot AlF_3$ (Na_3AlF_6)

$\swarrow$ $\searrow$

$2Al^{3+}$ $3O^{2-}$ $3Na^+ \cdot 1\,AlF_6^{3-}$

10 mole percent Al_2O_3

$$a_{Al_2O_3} = \left[\text{Ionic fraction of } Al^{3+}\right]^2 \cdot \left[\text{Ionic fraction of oxygen}\right]^3$$

$$= \left[\frac{n_{Al^{3+}}}{\Sigma n^+}\right]^2 \cdot \left[\frac{n_{O^{2-}}}{\Sigma n^-}\right]^3$$

$$= \left[\frac{2}{2+27}\right]^2 \cdot \left[\frac{3}{3+9}\right]^3$$

$$= \left[\frac{1}{15}\right]^2 \cdot \left[\frac{1}{4}\right]^2 \simeq 0$$

What it will be, instead, we can write it like this. Moles of aluminum ions, divided by all cations, aluminum cations, all cations to the power square, this will be moles of oxygen anions divided by all anions to the power cube. If you are considering one alumina, and nine this, we are going to get out of one two aluminum. Two aluminum is there and there is how many more cations will come there, it will be 2 plus 10 so. So, we have one Al 2 O 3 and 9 Na 3 Al F 6.

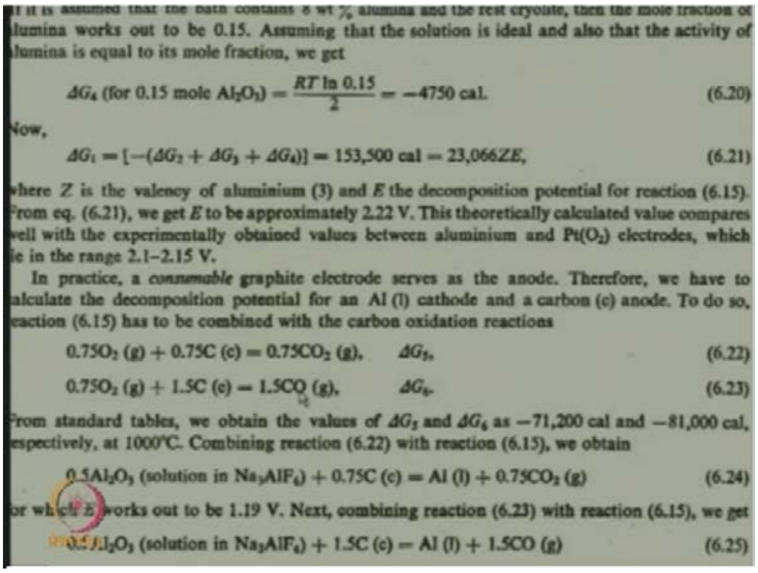
So, 9 into 3 are 27 sodium cations are there and whole square. Oxygen is 3 divided 3 plus 9 since there are 9. We have nine of these, 3 plus 9 and this is cube. Assume this is almost thirty. So, it becomes 1 by 15, approximately and it is 1 by 4; square, cube. This is very small; it is very small. So, there we had said that for an ideal solution 15 mole percent means 0.15, therefore, activity 0.15 that is not true.

According to Temkin's equation, this assumption is not valid that we say that 8 weight percent aluminum, and the rest cryolite works out to be 0.15, means 15 mole percent, mole fraction is 0.15. So, he said if the solution is ideal, reactivity of aluminum is equal to mole fraction 0.15, is not true. This actually should be practically, very small. It cannot be 0.15; according to Temkin equation would be almost near zero, which means it will be much smaller. If it is much smaller then this value that you are calculating (Refer Slide Time: 34:31) will be smaller still and perhaps it will be much closer to this what you are finding.

Whatever, it is. I am just going into the finer things, because I want to relate something I am doing now, to something we have done earlier, just to show you the interesting aspect of Temkin's equation. But what it come tells us now, we can calculate theoretically, and it is fine that if you had platinum electrodes, then you will need about say 2.1 to 2.15, which means little more than 2 volts. But in reality, we need less than 2 volts, why? It is because we are modifying the anode reaction, cathode reaction is remaining the same. Aluminums ions coming to the aluminum electrode getting discharged, but we do not have platinum for discharge of oxygen.

Oxygen is now getting discharged on graphite, but graphite is not a neutral electrode, it is a consumable electrode that oxygen ions when it reacts deposits on carbon, it consumes oxygen, carbon to produce CO or CO 2, depending on the temperature. And because oxygen is consumed, the decomposition reaction is aided, made simpler, lets calculate that.

(Refer Slide Time: 36:14)



f it is assumed that the bath contains 8 wt % alumina and the rest cryolite, then the mole fraction of lumina works out to be 0.15. Assuming that the solution is ideal and also that the activity of lumina is equal to its mole fraction, we get

$$\Delta G_4 \text{ (for 0.15 mole } Al_2O_3) = \frac{RT \ln 0.15}{2} = -4750 \text{ cal.} \tag{6.20}$$

Now,

$$\Delta G_1 = [-(\Delta G_2 + \Delta G_3 + \Delta G_4)] = 153{,}500 \text{ cal} = 23{,}066ZE, \tag{6.21}$$

where Z is the valency of aluminium (3) and E the decomposition potential for reaction (6.15). rom eq. (6.21), we get E to be approximately 2.22 V. This theoretically calculated value compares ell with the experimentally obtained values between aluminium and $Pt(O_2)$ electrodes, which e in the range 2.1–2.15 V.

In practice, a *consumable* graphite electrode serves as the anode. Therefore, we have to lculate the decomposition potential for an Al (l) cathode and a carbon (c) anode. To do so, eaction (6.15) has to be combined with the carbon oxidation reactions

$$0.75O_2 \text{ (g)} + 0.75C \text{ (c)} = 0.75CO_2 \text{ (g)}, \qquad \Delta G_5, \tag{6.22}$$

$$0.75O_2 \text{ (g)} + 1.5C \text{ (c)} = 1.5CO \text{ (g)}, \qquad \Delta G_6. \tag{6.23}$$

rom standard tables, we obtain the values of ΔG_5 and ΔG_6 as −71,200 cal and −81,000 cal, espectively, at 1000°C. Combining reaction (6.22) with reaction (6.15), we obtain

$$0.5Al_2O_3 \text{ (solution in } Na_3AlF_6) + 0.75C \text{ (c)} = Al \text{ (l)} + 0.75CO_2 \text{ (g)} \tag{6.24}$$

or which E works out to be 1.19 V. Next, combining reaction (6.23) with reaction (6.15), we get

$$0.5Al_2O_3 \text{ (solution in } Na_3AlF_6) + 1.5C \text{ (c)} = Al \text{ (l)} + 1.5CO \text{ (g)} \tag{6.25}$$

We say that in practice a consumable graphite electrode serves as the anode. Therefore, we have to calculate the decomposition potential for an aluminum liquid cathode, and a carbon, this crystal is solid anode. To do so, this reaction number 6.15, that I had shown earlier has to be combined with carbon oxidation reactions.

0.75 of O2 with 0.75 of carbon giving you CO2, similarly, oxygen reacting to carbon giving you CO.

Which means now, we will get two more values of Delta G, five Delta G, six, which has these values, these will have to combine with the reactions, which I have written earlier and then we get this is the final reaction. Alumina in solution, in cryolite, reacting with carbon, in the anode produces, aluminum metal and CO 2 or alumina in solution reacts with carbon in the anode, produces alumina metal and CO, whether it will be CO or CO 2, it will depend on temperature. You know the higher the temperature, more the CO, lower the temperature, more the CO 2.

For this, our decomposition potential would be 1.19 volt, which means carbon coming into the picture, eating away oxygen, has made the decomposition easier. Had it been only aluminum and oxygen, they were certain voltage, but this oxygen is now consumed by carbon. So, the dissociation is made easier. So, the voltage is almost made half.

If it is forming CO, which is more likely, because you are operating at 1000 degrees, but there is more CO than CO 2, it is even lower than 1.05, this is a big advantage of a consumable carbon electrode, but there is a disadvantage.

You are not producing life giving oxygen, you are producing life threatening carbon monoxide and carbon dioxide, this is a fact in the industry we have an advantage on one side. You are consuming less energy by using less voltage, less energy means somewhere you are producing less CO, CO 2, in the power station, but here you are producing more CO, CO 2, what to do?

Unfortunately, there is no other way of doing it. People have taught of getting rid of this carbon, lot of work has been done, and almost successful has been of what we called an anode, which is not consumable, inert. Not platinum, if we had tons of platinum, for the industry, it will be a beautiful process. We need little more voltage, but you will produce oxygen, there is always use for oxygen.

People are using this titanium dioxide, inert anode. People have tried this, but it is still not become industrially successful. If that is there you will not use carbon for anode or cathode, whatever. And we will produce oxygen, and we will have an inert electrode, but there the voltage will again go back to more than 2. Now, so, what we have today in this process, where you have graphite anode, and a graphite bottom layer as cathode.

Now, so, from the foregoing discussion, it is evident that graphite aids the decomposition of the Al 2 O 3, because it reacts with oxygen to form CO and CO 2, under normal operating conditions, about 50 percent by volume of CO is produced. The percentage may increase considerably at low current density; it depends on current density also. In general, we assume the value is calculated from reactions. This and this, we take an average. So, theoretical decomposition voltage using graphite electrodes comes to 1.125.

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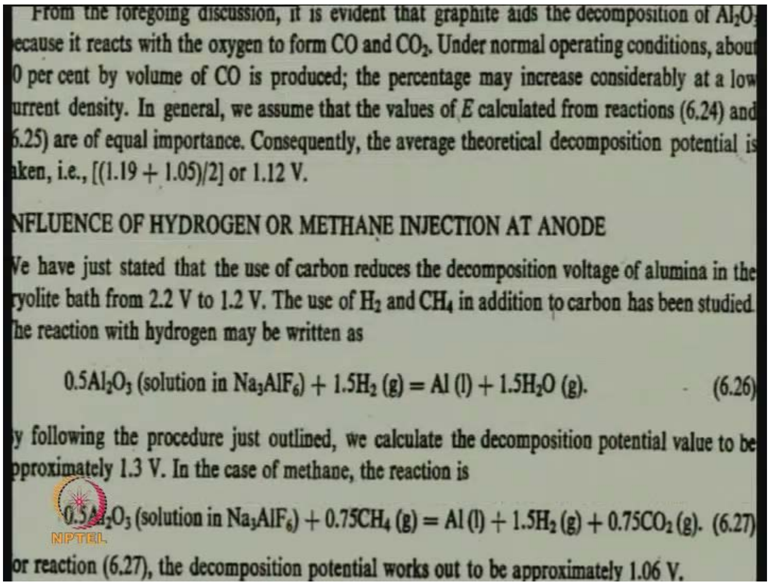

From the foregoing discussion, it is evident that graphite aids the decomposition of Al_2O ecause it reacts with the oxygen to form CO and CO_2. Under normal operating conditions, abou 0 per cent by volume of CO is produced; the percentage may increase considerably at a low urrent density. In general, we assume that the values of *E* calculated from reactions (6.24) and .25) are of equal importance. Consequently, the average theoretical decomposition potential is aken, i.e., [(1.19 + 1.05)/2] or 1.12 V.

NFLUENCE OF HYDROGEN OR METHANE INJECTION AT ANODE

Ve have just stated that the use of carbon reduces the decomposition voltage of alumina in the yolite bath from 2.2 V to 1.2 V. The use of H_2 and CH_4 in addition to carbon has been studied he reaction with hydrogen may be written as

$$0.5Al_2O_3 \text{ (solution in } Na_3AlF_6) + 1.5H_2 \text{ (g)} = Al \text{ (l)} + 1.5H_2O \text{ (g)}. \qquad (6.26)$$

y following the procedure just outlined, we calculate the decomposition potential value to be pproximately 1.3 V. In the case of methane, the reaction is

$$0.5Al_2O_3 \text{ (solution in } Na_3AlF_6) + 0.75CH_4 \text{ (g)} = Al \text{ (l)} + 1.5H_2 \text{ (g)} + 0.75CO_2 \text{ (g)}. \qquad (6.27)$$

or reaction (6.27), the decomposition potential works out to be approximately 1.06 V.

Now, somebody had another interesting idea. They say that if we can consume that oxygen, by consumable graphite then we are bringing down the voltage, but two problems are coming. We are using CO and CO 2, plus you are consuming carbon, means you have to continuously recharge that anode, and that is a problem in the industry; I will come to.

Actually, what happens if the anode is continuously consumed? So, either it keep on changing it from time to time, from the top this is what is done. Electrolysis stopped, a small amount is removed, a new anode is screwed again, and the process started or we have a continuous anode called Soderberg electrode that a carbon paste is pushed from the top, and as the paste keeps going down, its gets dried up, and become the solid anode which is consumable.

So, it is getting consumed here, at the bottom, but from the top it is being continuously checked; it is called Soderberg consumable anode. Some industries used Soderberg process, some use changeable anode. Whatever is in either case, you consume carbon, and that carbon should not be any carbon, it has to be special kind of graphite, to be anode. It needs strength, it needs purity; it needs these kind of things.

Somebody has an idea that if the idea, is to bring down the decomposition voltage, by consuming the oxygen that is coming towards the anode, why we cannot inject hydrogen near the anode. Let that oxygen ion react with hydrogen, just produce nice pure water. So, your product would be water of course, as in the form of steam, and you will produce aluminum as metal and your graphite will be protected also. You will lower the consumption of graphite because bulk of the oxygen that is coming reacts with this hydrogen. It is very good in theory.

So, we can calculate that we have one reaction, this to that, we will combine that. What happens if you bring in hydrogen, so this will react with hydrogen producing (Refer Slide Time: 43:37), we can calculate this voltage will come to about 1.3 volts, which means, it is not very much better than what we had for graphite.

It is only advantage would be surely that it will lower the consumption of graphite, but it will not bring down the voltage. The other idea could be injection of methane that you can calculate, what will the decomposition potential be, if we allow the oxygen that is coming out to react with methane. So, overall reaction is this. You get hydrogen and CO 2, this works out to be 1.06. So, there is no advantage. First of all, technologically, these may not be feasible. We cannot inject hydrogen at this high temperature, but interesting to look at the theory.

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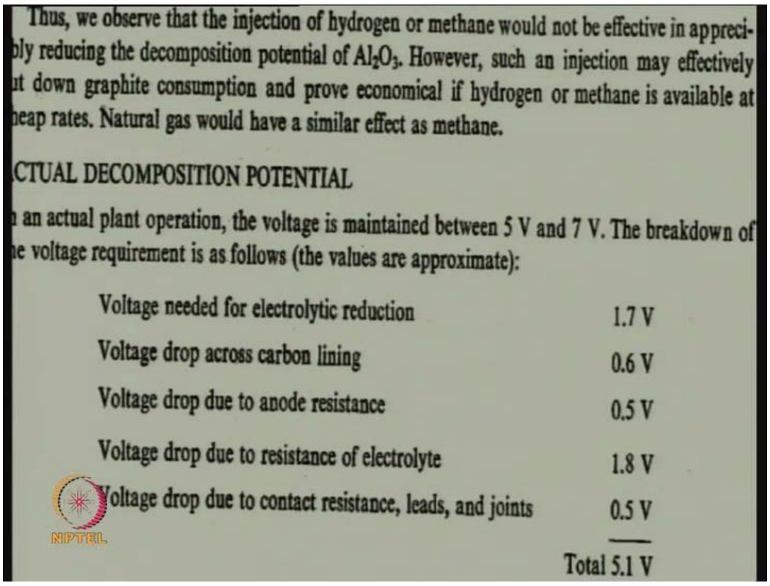

Thus, we observe that the injection of hydrogen or methane would not be effective in appreci-
bly reducing the decomposition potential of Al_2O_3. However, such an injection may effectively
t down graphite consumption and prove economical if hydrogen or methane is available at
eap rates. Natural gas would have a similar effect as methane.

CTUAL DECOMPOSITION POTENTIAL

an actual plant operation, the voltage is maintained between 5 V and 7 V. The breakdown of
e voltage requirement is as follows (the values are approximate):

Voltage needed for electrolytic reduction	1.7 V
Voltage drop across carbon lining	0.6 V
Voltage drop due to anode resistance	0.5 V
Voltage drop due to resistance of electrolyte	1.8 V
Voltage drop due to contact resistance, leads, and joints	0.5 V
Total	5.1 V

But these could be the ways of lowering the consumption of, if we can inject methane or hydrogen. But nobody would like to try it out it. It is good. So, the conclusion is that injection of hydrogen or methane is not effective, would not be effective in appreciably reducing decomposition potential alumina. However, such an injection may effectively cut down graphite consumption, and prove economically hydrogen or methane is available at cheap rates, and there is technology to use them the way which we suggested. Same thing goes with Natural gas.

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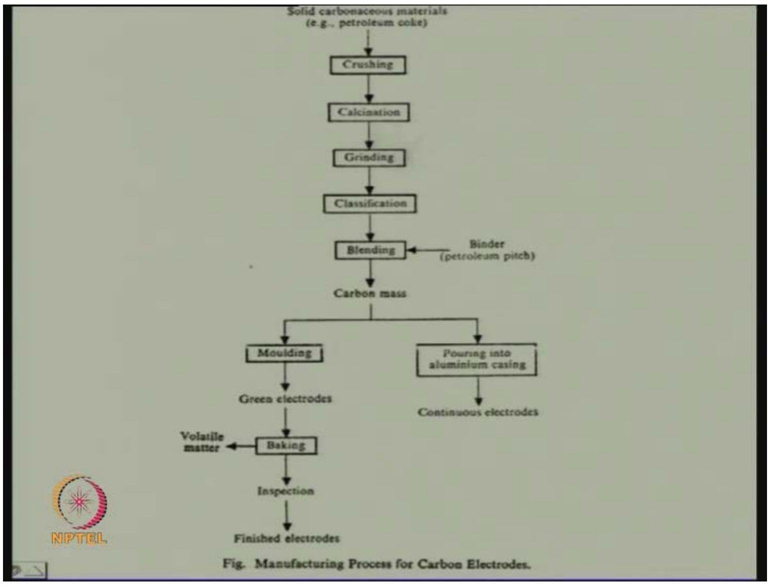

Solid carbonaceous materials
(e.g., petroleum coke)

Crushing

Calcination

Grinding

Classification

Blending

Binder
(petroleum pitch)

Carbon mass

Moulding

Pouring into
aluminium casing

Green electrodes

Continuous electrodes

Volatile
matter

Baking

Inspection

Finished electrodes

Fig. Manufacturing Process for Carbon Electrodes.

So, these are trials, people try and try to see what to do, what not to do, but it does not matter. Now, let me wind up to these things by saying two other things, aluminum electrolysis has a cell that is continuously being fed by alumina. It has to be continuously fed by graphite also for making an anode, which is consumable and the manufacturing process for carbon electrodes is a very elaborate thing. I have given a flow sheet that you take solid carbonaceous materials like petroleum, very pure crush, calcined, grind, classify, and blend, with petroleum pitch so that it can be given a shape.

Then you get a carbon mass, you mold, you get green electrodes. They have to be baked, they have to go for inspections then you have finished electrodes, or in Soderberg electrode, is the paste which straight away is poured into aluminum casing, and its continuously fed into the cell, and it gets dried up, as it get lower down so that by the time, the bottom comes in touch with the electrolyte, it has been baked. But look at all the elaborate processing that is required, you have to start with petrol.

So, it is not only an expensive raw material, it is also an energy consumable thing. You had seen I have given you some data that the whole process consumes some energy. Here somewhere, I gave how much it will be required. Here anode production (Refer Slide Time: 47:31), two percent of the energy of aluminum electrolysis is involved in that anode production, because of all those problems.

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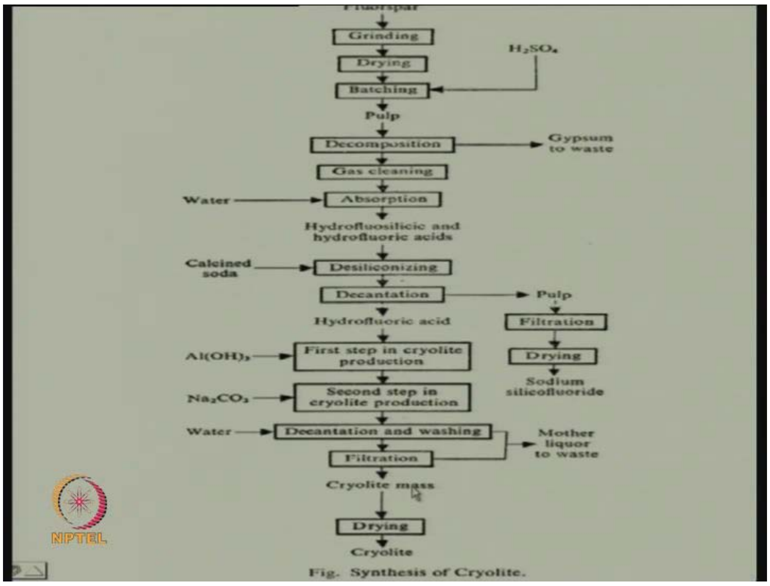

Fig. Synthesis of Cryolite.

Then there is the question of cryolite, now cryolite is a synthetic mineral, which is not available very widely. It will be available in the places like Greenland and in one or two other places. And you might think that once you have put in a cryolite, because it is only the solvent alumina is coming, it is getting decomposed, cryolites stays as such, which is not true.

Cryolite is not so innocent solute, it also takes part in reaction, small amounts of cryolite also decomposes producing all kinds of things, which I will discuss next, which means you need a continuous supply of cryolite also. Although it is not really supposed to be consumed, it is only a supporting electrolyte, for the solute, but you need cryolite. People have tried very hard to manufacture cryolite. Where natural cryolite is not available, they have been successful also.

Here is a flow sheet, again we do not have to remember the flow sheet, but I must tell you that cryolite can be manufactured. If you cannot simply add three molecules of sodium fluoride and one molecule of aluminum fluoride, say it is 3 Na F plus Al F 3; it is now cryolite, no. We are writing cryolite like that, 3 Na F dot Al F 3, to show it is notionally a combination of 2 minerals, but actual mineral is Na3 F Al F 6, and it is not a mechanical mixture of sodium fluoride and aluminum fluoride.

So, it has to be manufactured specially. The process is like this (Refer Slide Time: 49:40), we will start with fluorspar which is calcium fluoride grinding, drying, batching, pulp, sulphuric acid treatment, decomposition, gypsum to waste gas cleaning, absorption, then hydrofluorosilicic acid and hydrofluoric acid treatment, desiliconization, decantation, hydrofluoric acid, etcetera, whole lot of things, finally, we will get cryolite.

We will add sodium carbonate here, somewhere to get the sodium part; the calcium fluoride part is coming from the top. So, you see it is very complicated thing. Aluminum is coming from aluminum hydroxide. So, to produce synthesized cryolite one needs a very elaborate setup, but some countries have to do it. Suppose they are in aluminum production and cryolite is not available in the market, natural cryolite, one has to manufacture. So, this is another research.

Now, I mentioned just now that cryolite although it is a supporting electrolyte, it is not sitting there doing nothing, its main job is to be molten at about 980 degrees or so, dissolve alumina. So, that it can be electrolyzed, that is its main job.

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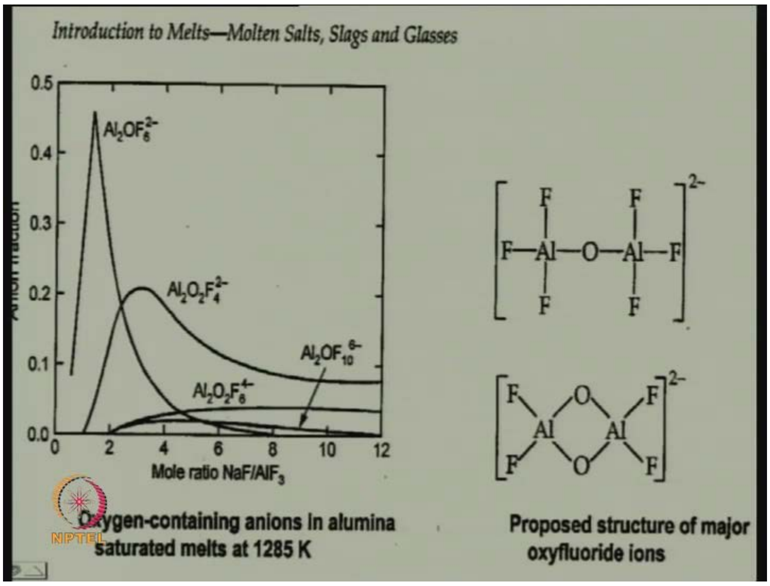

Introduction to Melts—Molten Salts, Slags and Glasses

Oxygen-containing anions in alumina saturated melts at 1285 K

Proposed structure of major oxyfluoride ions

But unintentionally it gets also involved in many decomposition reactions, and we get in the melt whole lot of ions, which has come through reactions of alumina and the fluoride ions, these are some of the ions. Oxygen containing anions and alumina saturated melts. Oxygen has come from alumina because there is no oxygen in cryolite, but we do get Al 2 O F 6 2 minus, this ion, that ion that ion, and this depends on mole ratio of Na F Al F 3.

The mole ratio in cryolite is 3 Na F Al F 3 means 3. So, if we are in this ratio, we will have about 0.1 of Al 2 O 2 F 8, 4 minus. We will have Al 2 O 2 F 4 2 minus about 0.2 percent; we will have a little bit of these two ions also.

If you go below that means, if you add extra Al F 3, then we get this ion, if we go more than that means, if we add extra Na F, then we tend to get more of these ions. Again, having the presence of these ions have some implications, we show here the proposed structure of some major OX fluoride ions.

These are unavoidable, but their proportion can be controlled, by controlling mole ratio of Na F Al O 3, different industries operate differently. Some would like to go more on this side, some would like to go more on this side, because they have develop their processes. I think, I will stop here for now, and take off from here in my next lecture, and carry on. I would need another two, three lectures to talk about aluminum production in general.

Then I would also devote some time to the aluminum productions in India, and this will be one of the exceptions, where I will discuss the Indians in particular. I will do that, because for India aluminum is vitally important. It is an industry, which sees expansion, which in the bid to expand is running into a lot of problems, because you know in Orissa there are huge deposits of bauxite, and there are many companies which are coming forward for mining. And they have to now then occupy those areas. Many of these areas happen to be tribal areas, where tribals have been living for many generations.

They say they may not be agricultural land. They may be land lying, because in this aluminum and silicates and alumina silicates, things may not grow, but the land belongs to them.

So, they said what compensation do they get when these mines grow, actually I will start with this what some other countries have done, about setting up such industries in areas where there have been people living for generations.

Thank you very much.