Non-ferrous Extractive Metallurgy
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Module No. # 01
Lecture No. # 17
Extraction Aluminum (Contd.)

I have been discussing extraction of aluminum, for last three lectures. Before, I begin today; let me recapitulate one or two important things. I mentioned that the Hall Heroult's process, for extraction of aluminum, through electrolysis of alumina, dissolved in cryolite, came simultaneously in United States and France, in the year 1886. It was very interesting coincidence.

Now, the process needed supply of pure alumina and it so happened that just about that time, Bayer developed a process called Bayer's process, which gave a method of producing pure alumina from bauxite ores. Now, none of these processes, would have made a head way, if electricity was not available. It so happened that just about ten years earlier than that, the commercial electricity became better. So, electricity was available, there was a process for alumina and then there was this Hall Heroult process, where electrolysis of alumina in cryolite.

Now, I have gone through the basics of Bayer's process, and Hall Heroult's process and I have to impress upon you, the fact that everywhere one has to work, within very narrow bands, especially in electrolysis.

In electrolysis, aluminum has to sink to the bottom. So, it has to be heavier than the electrolyte, and the electrolyte therefore, cannot have too much of alumina dissolved in it because then the densities become too close, if the alumina concentration increases, density will increase, at the same time, we really want more alumina, because more alumina will bring down the energy requirement.

Again, if there is too much of alumina, it will not dissolve, because there is a solubility limit for alumina. So, it will form a crust. So, one has to work in a very narrow band of alumina concentration; say around five to eight percent or so. Now, there is a very interesting phenomenon, associated with very low values of alumina in cryolite, and this you must remember, because in the aluminum industry it is a highly discussed topic. It is called anode effect.

Anode effect occurs when alumina concentration falls below 2 percent. If alumina concentration, by any chance falls below 2 percent, then the operation of the electrolytic cell practically seizes. Why does this happen? Firstly, what is the phenomenon, and then secondly, why that phenomenon. I will tell you, what the phenomenon is. The phenomenon observed in the industry, is that if the alumina concentration comes below 2 percent, then the surface of the anode gets covered with bubbles. Bubbles that cover the surface and then prevent further electrolysis.

So, when there are bubbles on the anode surface, causing anode effect, then effectively the resistance, in the bath increases enormously, and therefore, current falls. If the voltage is kept constant, and the resistance has increased then the current will fall. If the current falls, then there is no electrolysis, there is no production of aluminum. Now in the industry, they operate with constant current source, means there are devices which ensure a constant current pass system.

So, if the resistance has gone up, and there is something to ensure constant current passing, then what happens, if the voltage increases. Because you have to get that much of current going through the cell, resistance has gone up. So, the voltage goes up. And the voltage can go up to something like 30 volts. So, the voltage has gone up to 30 volts.

A lot of current is flowing, but there is no electrolysis, and what happens to the current. The current does not cause electrolysis then. It jumps, as sparks, electrical sparks, straight from one electrode to the other electrode. So, it is not going to the electrolyte causing electrolysis. There are electrical sparks, that is completing the circuit and these sparks, all that they can do is cause heating; there is no electrolysis.

And there are multitudes of small electric sparks, small lightening in the cell. So, the current is going, but then nothing is happening. Now, why does it happen? This is found that it happens. There are many theories about why it happens, and I would rather not go into it.

Excepting that, I would say, that apparently it comes out of bonding of fluorine produced with carbon, that if alumina level falls, you deposit fluorine. Fluorine bonds with carbon, produces all kinds of gases, through the decomposition of this carbon-fluorine compounds, and they are on the electrode surface, and they will not go. What does one do then? Very often one has to stop electrolysis, and try to get rid of these bubbles sticking to the surface.

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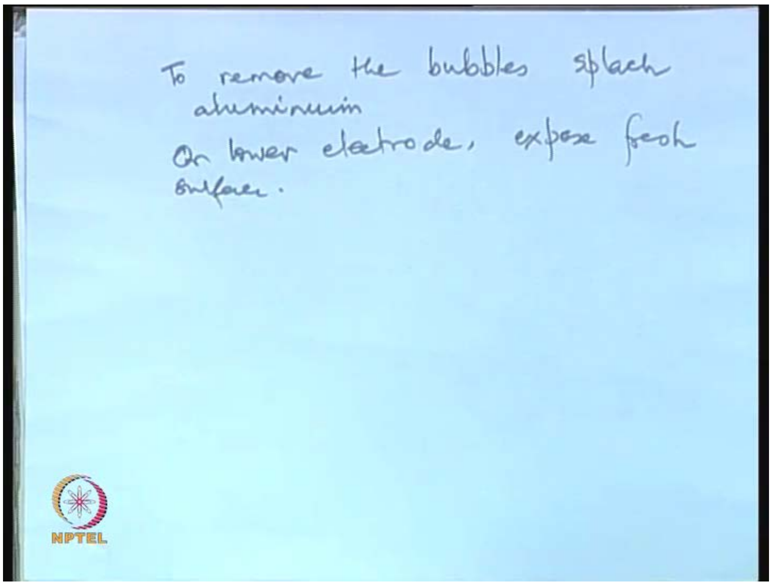

To remove the bubbles splash aluminium
Or lower electrode, expose fresh surface.

And one way to do that, is to splash liquid aluminum on the anode surface, to get rid of the bubbles or one can bring in fresh anode, fresh surface or in the same anode, it can be lowered down, bringing fresh surface on which electrolysis can take place. So, this is what anode effect is.

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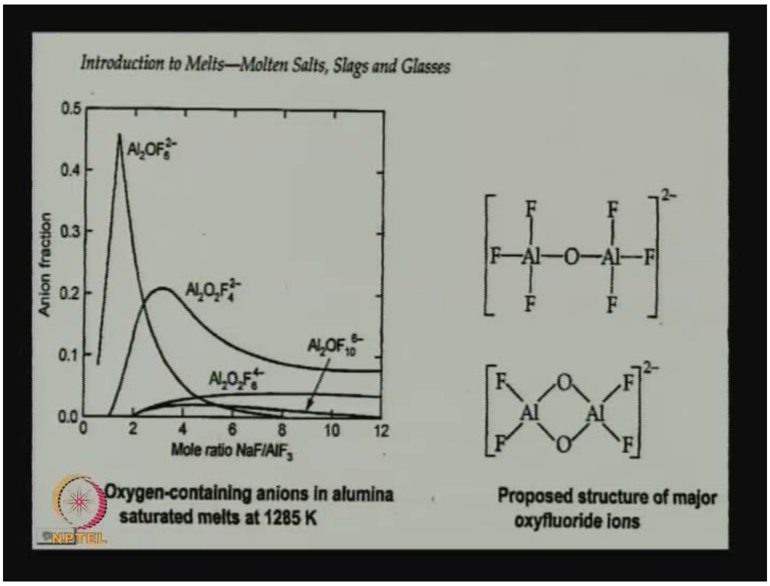
Introduction to Melts—Molten Salts, Slags and Glasses

Oxygen-containing anions in alumina saturated melts at 1285 K

Proposed structure of major oxyfluoride ions

Now, let me go back to the subject again. As I was discussing, I mentioned last time, that although, basically you have alumina in cryolite. And in theory, alumina should give aluminum and oxygen ions, and cryolite should only give you Na F ions and Al F 6 ions.

But in reality, the whole lot of ions, anions exists. They come out of reaction with the oxygen, that has been introduced from alumina or the alumina itself, and many research papers research investigations finally established, that there is coexistence of many anionic species and if they depend on the mole ratio of NaF by Al F 6.

Actually, fluorine comes out of many of these and I will give the reactions little later. So, all these things, the presence of fluorine and depletion of alumina, they all add up to give an anode effect, which virtually stops electrolysis, and they have to be… it has to be eliminated at any cost.

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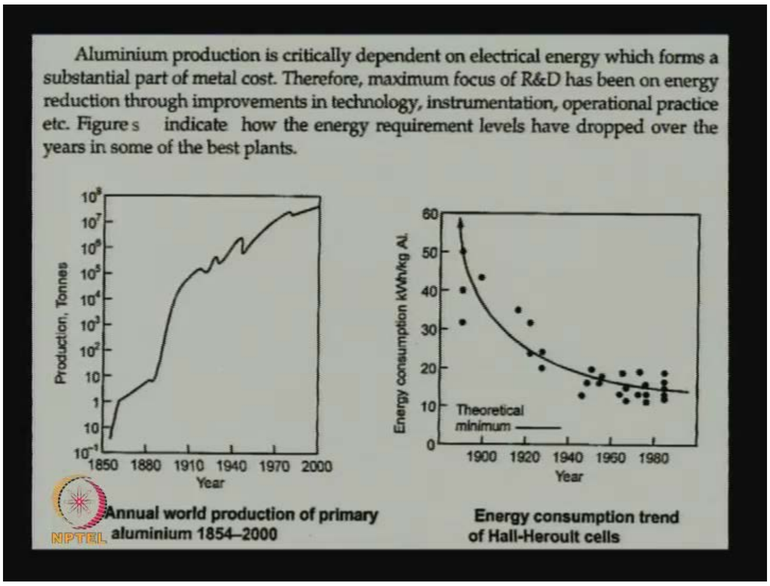

Aluminium production is critically dependent on electrical energy which forms a substantial part of metal cost. Therefore, maximum focus of R&D has been on energy reduction through improvements in technology, instrumentation, operational practice etc. Figures indicate how the energy requirement levels have dropped over the years in some of the best plants.

Annual world production of primary aluminium 1854–2000

Energy consumption trend of Hall-Heroult cells

Now, I had digressed a bit, while showing you this slide last time and I would digress again today. Look at this slide, the way the world production of primary aluminum has gone up from 1854 to 2000. It is now; you know more than a million, some 30… I think I have given you a figure earlier. India produces only around 0.35 million tons, we need to produce lot more, but the industry is on the rise.

And while we are producing more and more aluminum, their efforts to address the question of energy consumption; energy consumption is being continuously decreased, to a value which is the practically minimum, you can never go to the theoretical minimum, because I have mentioned that above the theoretical minimum, which is required for decomposition of alumina. You need little extra to heat up. So, you would, the practical minimum would be somewhere here (Refer Slide Time: 10:43) and we are almost approaching that.

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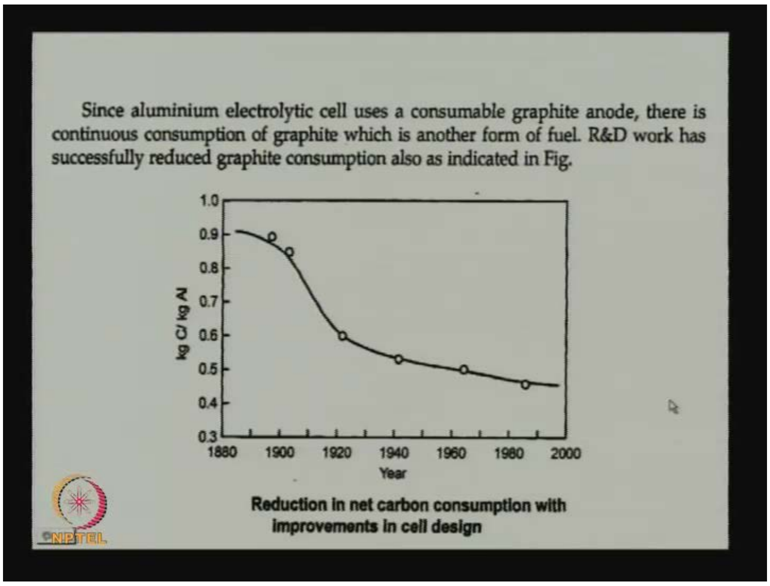

Since aluminium electrolytic cell uses a consumable graphite anode, there is continuous consumption of graphite which is another form of fuel. R&D work has successfully reduced graphite consumption also as indicated in Fig.

Reduction in net carbon consumption with improvements in cell design

The industry is also trying to bring down carbon consumption, where it is a consumable anode and there is nothing you can do, it will be consumed. But there are ways and means of trying to bring it down and there is also a very good trend, in reduction in carbon consumption.

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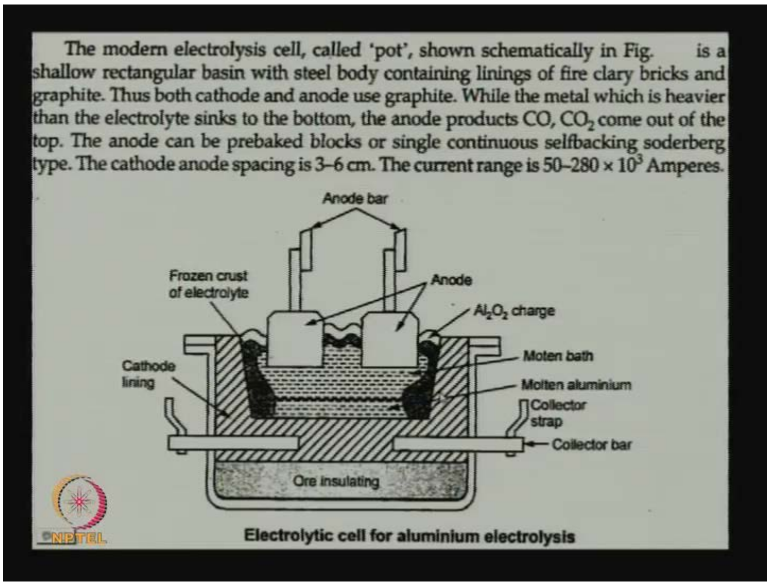

The modern electrolysis cell, called 'pot', shown schematically in Fig. is a shallow rectangular basin with steel body containing linings of fire clary bricks and graphite. Thus both cathode and anode use graphite. While the metal which is heavier than the electrolyte sinks to the bottom, the anode products CO, CO_2 come out of the top. The anode can be prebaked blocks or single continuous selfbacking soderberg type. The cathode anode spacing is 3–6 cm. The current range is 50–280 × 10^3 Amperes.

Electrolytic cell for aluminium electrolysis

Now, before I go back to discussing the cell, let me mention, why I digress last time. Last time I emphasize this point that India has very good reserves of bauxite ores, and there are industrialist would like to set up plants for bauxite mining. Some to go for export and some to be taken in for aluminum production, the government also wants it.

Because, the government that can create jobs, it will create a thriving aluminum industry which can compete in the global market and there is scope for tremendous expansion of the aluminum industry in the country, because bauxite ores are available; knowhow is available; R&D personal are available; engineers are available.

Problem is, we do not have power, and a power has to be produced from thermal power plants, and then a whole world is now against CO, CO 2 generation, which are… which causes global warming, but we have no other source of power now. All we have reached the limit of hydel power. There is no other source of power, and we have to have thermal power plants, but we have to operate them more efficiently. And we have to find out ways of handling this CO 2 that is let off from the power plant.

So, we have to go for higher technologies, but we need power. Look at the western countries; the developed countries, 100 years ago, there was no restriction of what they did with their steam engines, with their power plants, they have produced all the CO 2 in the world.

They have had the feel to themselves and they have progressed. Now, they have bringing in these things, but you cannot blame them. This is now a world problem. So, we cannot follow the technologies of the past. We have to develop our own technologies, but we need power at any cost.

But there are other problems, apart from technological problems. Technological problems are now interfaced with social and environmental problems, and all though this course is about the technology of non-ferrous metals production, I think it is fair that I give the hint of the in those interfaces.

Let us talk about environmental regulations. You know the government has become now very touchy about environmental issues and rightly so. There are now laws, which were not there 20 to 30 years ago, and industry could do whatever it wanted. It could take land, cut forest, set up plants, let of CO 2, bring in toxic streams, put them in river or ponds, but now there are very strong restrictions.

If an industry has to set up, something in an area, which was forested, now the regulation demands that if you are cutting down one thousand trees, you have to find a way of putting twice the amount of trees elsewhere or nearby areas. Even more serious is, at one time mining was done recklessly, because no ore lies on a surface with some exceptions. They are mostly below the surface, and there is a layer of soil on top, which you will call the top soil; means most ocean minerals are found like that.

So, for mining one has to remove the top layer, which may be a meter or two, whatever and then dig for the ores that you want. There was a time that people just did not care. They just threw the top soil anywhere they wanted, did whatever they wanted and when they found there was nothing more to be done, they just abundant their minds and they went away. Like you see, this brick-kin bhattis, you find. You know where the soil is taken out, for making bricks, and after that when they found they have dug enough, they go to another places.

The thing that has been realized now, that suppose you have done that, and abundant a mine, it takes some 200 to 300 years to have a top soil like that again, through a natural process. Nature cannot restore the top soil, so quickly. It takes decades, centuries.

So, there is a very simple solution that we do not destroy the top layer, which sustains life, which sustains flora and fauna. So, these days what the industries are required to do is before mining, they have to remove the top soil. Keep it at one place, dig and do their mining, whatever it is. When that is over, bring the top soil and put it back again.

So, that vegetation can grow again. The flora comes back and fauna comes back. This is being done, in many of our industries, and it is beautiful. We if we there are… I do not want to name, there are many mines, and where you will not believe that mining has been done here, because it looks so beautiful.

Now, this again is a technological problem, that you have a technological solution, but what about social issues. Now, this course is not about social issues; I cannot spend more time, but I cannot neglect it either. You know everywhere industry is demanding land. The land belongs to the government in theory.

But when they go to acquire the land, people who are there, they say what about our interests. We have been living here for centuries. What happens to us, when we get dislocated? To that there are simple answers, we are giving you a fair price for the land you own or may be more than a fair price.

Some industries go one step beyond and say we will provide job to the family's one member per family. Some say we are going to provide you land elsewhere or housing elsewhere. These questions have always been there, but they were not so strongly put forward in the past. Do not forget the Tata's also came to a tribal area, which was forested; there they have a set up an industry. Those people must have been dislocated, somewhere absorbed, somewhere looked after.

You cannot say that in 110 years ago or 100 years ago what Tata's did that was wrong. They have set up a beautiful township. There is an industry which is doing wonders for the economy. Provide jobs, some to the locals, many more to the people, from all over the country. Look at Rourkela steel plant. Look at Durgapur steel plant. Look at wherever; there is a large industry. Land was required, land had to be taken and people had to be relocated. Their interests were sometimes taken care of, sometimes not taken care of.

But now, this question has become up paramount interest, because the so called weaker sections are no longer so weak. They know how to voice their opinion; they want to know how we ensure that their interests are protected, not just for next four years or five years, if you give them lump sum amount of money, many of them simply blow it away.

Because they do not know what to do out of money, they know how to do agriculture. They know how to get products from the forest. Now, to answer that question, I found from a story that a student of mine had told me, and I must share it with you, before I go on with the lecture.

I had a classmate. We were together in this institute forty years ago. He was a civil engineer. Then he went to Germany. He is now settled in America; he sometimes comes and meets me. Some of his friends and he have set up a company, for iron ore mining in northern areas of Canada where Eskimos' live.

Now, who owns those lands on paper? It is a Canadian government, but the Canadian government means what, it was the white settlers who came 200 years ago, and settled there. Now, they say is their territory. But now, the Canadian government recognizes, that those territories, where so much of iron ore belongs as much if not more to the Eskimos' who have lived there for thousands of years. So, now there has been a tripartite agreement between those Eskimos communities, the company that belongs to my friend and his associates, and the government; all are stake holders, all are interested in development there, they want to get something out of the iron ore which is their in abundance and also other minerals.

But now the local community of Eskimos, they have been taken in to confidence, and made a partner in the entire enterprise. So, when the company grows, makes profit; the profit is shared by the government, by the company, by the Eskimos also. Now, the Eskimos and the others who lived there, if they can find jobs well and good, even if they do not get jobs, they have a share of the profit.

Now, whenever an industry is going to go to a place like that, the question comes about is about stake holders. Who are the stake holders? Not only the local community, and the government, and the people in the industries, who are going to bring in the knowhow and the capital and all that technological experiences; it can go even beyond that.

Actually the entire country has a stake in that. So, there are NGOs' who say I may not belong to that place, but I am involved with this kind of work; I am also a stake holder. So, nowadays the approach is to bring all the stake holders at one place, have discussions come to a consensus. So, that we have a win-win situation, that we do set up an industry. It is necessary, because you cannot go on, depending on agriculture or on forest products. Anywhere where countries are progressed, you find number of people working in agriculture they have drastically come down. It is true for china also, very much true for western countries because agricultural methods have also improved; they have become much more efficient.

You have machinery and you have high yielding seeds. So, why do the people go, they have the time now to go into industries. So, we need to answer these questions, and we need to answer them fast, because otherwise our industries cannot grow, and the aluminum industry is already facing this problem and that is why I digressed.

In the east coast in Orissa, Andhra, there are bauxite mines where mining activities cannot begin, because the locals are protesting, the NGOs' are protesting. They want a solution to the question as to who will protect their rights in the long term.

If that can be done, aluminum has a great future. As regards the problem with technology like thermal power plants, the entire world is working on trying to make the technology more efficient and I am sure there will be solutions found.

Now, I have digressed quite a bit. Now, let me go back to the subject properly.

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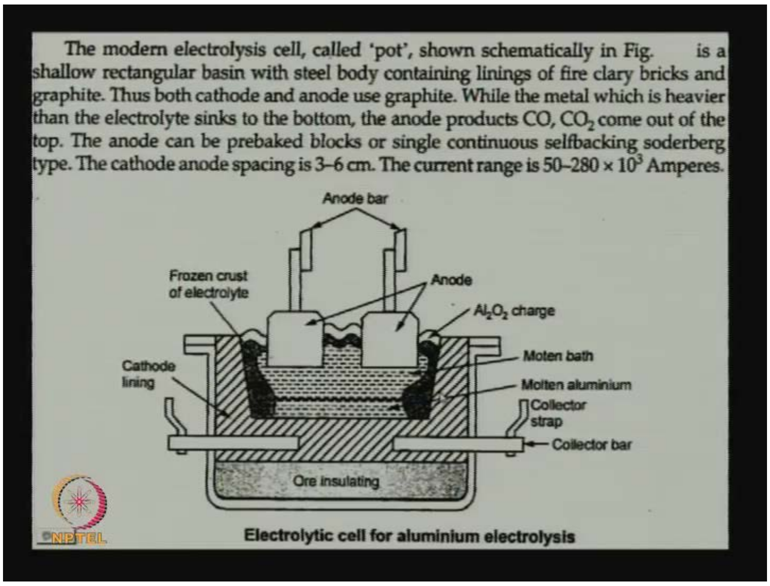

The modern electrolysis cell, called 'pot', shown schematically in Fig. is a shallow rectangular basin with steel body containing linings of fire clary bricks and graphite. Thus both cathode and anode use graphite. While the metal which is heavier than the electrolyte sinks to the bottom, the anode products CO, CO_2 come out of the top. The anode can be prebaked blocks or single continuous selfbacking soderberg type. The cathode anode spacing is 3–6 cm. The current range is 50–280 × 10^3 Amperes.

Electrolytic cell for aluminium electrolysis

Here is the aluminum electrolytic cell; I have shown you the picture once before, let me show it again. This is a basic sketch. We have a layer of aluminum covered by the electrolyte which has alumina dissolve in it and you know there are heat loses from these steel walls, and that is why some of this aluminum and the electrolyte get frozen. And that sort of gives kind of insulation on top with an alumina charge. It is all not all solid because the CO, CO 2 that are here, they have to come out of this also.

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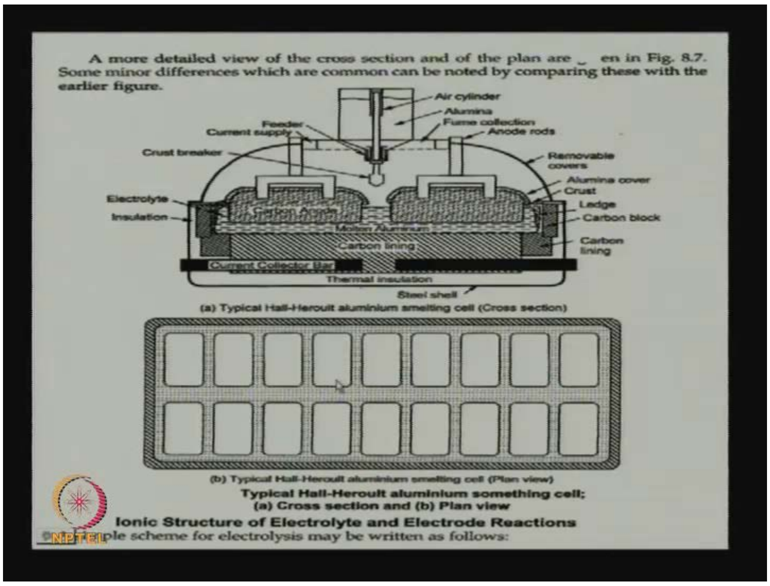

A more detailed view of the cross section and of the plan are _ en in Fig. 8.7. Some minor differences which are common can be noted by comparing these with the earlier figure.

(a) Typical Hall-Heroult aluminium smelting cell (Cross section)

(b) Typical Hall-Heroult aluminium smelting cell (Plan view)

Typical Hall-Heroult aluminium something cell;
(a) Cross section and (b) Plan view

Ionic Structure of Electrolyte and Electrode Reactions

ple scheme for electrolysis may be written as follows:

Here is a better picture. It shows that you know no two designs are the same. Do not think why it looks different, and this one is looking different. You see there is a cover because the CO, CO 2 that comes, they have to go out in a stream and there are all kind of feeding mechanisms, the currents supply feeders, there is a crust breaker, if there is a very strong crust, which is not allowing gases to escape, this thing will come and break it so that gases can escape.

And there are many other things that details, you can see here. What is more important is you see this, the layout of the pots. Typically Hall Heroults aluminum smelting cell has many pores arranged in series parallel connection, may be in parallel.

There are bus bars going from two sides giving you voltage to all the pots here. Now this part, ionic structure electrolyte, electro reactions will go, to go to the next slides. So, ignore that, read only up to here.

So, we are showing you the cross section and the plan view. So, let us move forward

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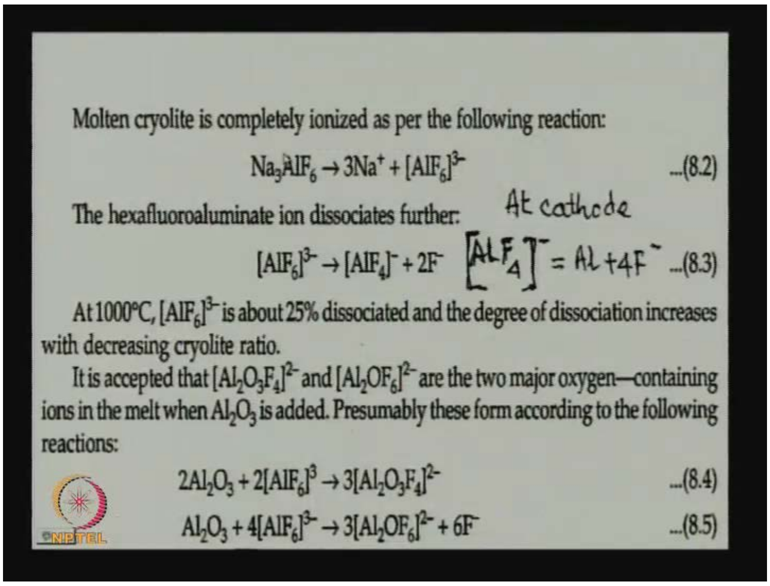

Molten cryolite is completely ionized as per the following reaction:

$$Na_3AlF_6 \rightarrow 3Na^+ + [AlF_6]^{3-} \quad ...(8.2)$$

The hexafluoroaluminate ion dissociates further: At cathode

$$[AlF_6]^{3-} \rightarrow [AlF_4]^- + 2F^- \quad [AlF_4]^- = Al + 4F^- \quad ...(8.3)$$

At 1000°C, $[AlF_6]^{3-}$ is about 25% dissociated and the degree of dissociation increases with decreasing cryolite ratio.

It is accepted that $[Al_2O_3F_4]^{2-}$ and $[Al_2OF_6]^{2-}$ are the two major oxygen—containing ions in the melt when Al_2O_3 is added. Presumably these form according to the following reactions:

$$2Al_2O_3 + 2[AlF_6]^{3} \rightarrow 3[Al_2O_3F_4]^{2-} \quad ...(8.4)$$

$$Al_2O_3 + 4[AlF_6]^{3-} \rightarrow 3[Al_2OF_6]^{2-} + 6F^- \quad ...(8.5)$$

Again, I go back to cryolites. There is no other substitute for cryolite, for dissolution of alumina. Alumina will not dissolve in anything else, no other halide. It can dissolve in some oxides, after all slags have alumina. But you cannot electrolyte slags to produce aluminum. Slags are very viscous; from there you cannot get aluminum, and may be other things will come out of the slags.

So, this is the only electrolyte we have, Na 3 Al F 6. Unfortunately it is not something that is stays unchanged. It also decomposes. Firstly, decomposes to give sodium and aluminum F6 three minus ions. Then the hexafluoroaluminate that is, it dissociates further, and now it is generating fluorine. This F minus can go to the anode and decompose to produce fluorine gas. It produces this ion, when you have produced this ion, it can also dissociate and produce aluminum at the cathode.

Actually at 1000 degrees, Al F 6 3 minus is about 25 percent dissociated and the degree of dissociation increases with decreasing cryolite ratio. Cryolite ratio means Na F and AlFF6. The more you have the Al F 3 part, the cryolite ratio would be lower and therefore, the degree of dissociation will be more. Now, initially, I have shown you, a distribution of various anions that has oxygen. These two are the dominants ones,

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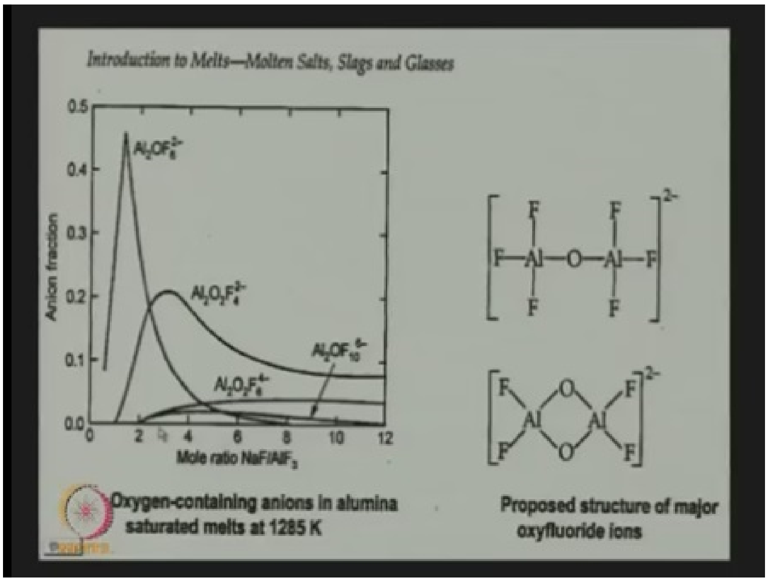
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Oxygen-containing anions in alumina saturated melts at 1285 K

Proposed structure of major oxyfluoride ions

because you will recall, this distribution around here, after all the ratio of Na F by Al F 3 in cryolite is three is to one, it is here.

But we always add little extra NaF. So, you find at this point, these two are the major about 0.2 and 0.2 of this and 0.2 of this. So, these two are the major anions (Refer Slide Time: 28:56), which contain oxygen when Al 2 O 3 is added that is only it forms. It will not form other way, it comes out of the oxygen. Now, there are many theories as to how they found. Here are two equations. Al 2 O 3 reacts with Al F 6 3 minus to produce this ion. Similarly, it also can react with the Al F 6 in slightly different manner to follow the other one. Here there is no fluorine being formed, here fluorine being formed.

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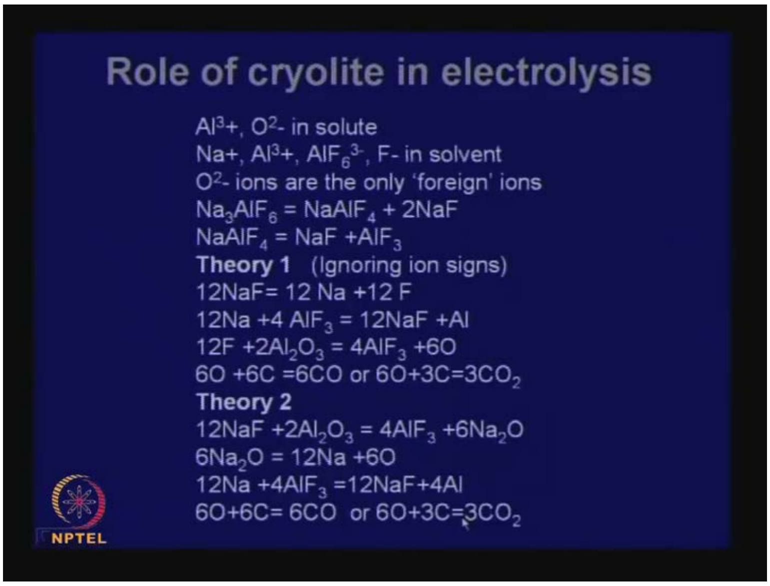

Role of cryolite in electrolysis

$Al^{3}+$, $O^{2}-$ in solute

$Na+$, $Al^{3}+$, AlF_6^{3-}, $F-$ in solvent

$O^{2}-$ ions are the only 'foreign' ions

$Na_3AlF_6 = NaAlF_4 + 2NaF$

$NaAlF_4 = NaF + AlF_3$

Theory 1 (Ignoring ion signs)

$12NaF = 12 Na + 12 F$

$12Na + 4 AlF_3 = 12NaF + Al$

$12F + 2Al_2O_3 = 4AlF_3 + 6O$

$6O + 6C = 6CO$ or $6O + 3C = 3CO_2$

Theory 2

$12NaF + 2Al_2O_3 = 4AlF_3 + 6Na_2O$

$6Na_2O = 12Na + 6O$

$12Na + 4AlF_3 = 12NaF + 4Al$

$6O + 6C = 6CO$ or $6O + 3C = 3CO_2$

So, then many things happened in when Al 2 O 3 goes into cryolite and so cryolite is much more than a supporting electrolyte.

First of all from Al 2 O 3 come aluminum ions and oxygen ions. This is the only foreign ion, because aluminum ion was already there, in cryolite. It had sodium, aluminum, A1 F 6 3 minus, F minus. This in a molecular way, you can write them that this breaks into this, this breaks into that. I have given the ionic thing

Then there are many theories are to what all things happened. I do not wish to go through all this accepting saying

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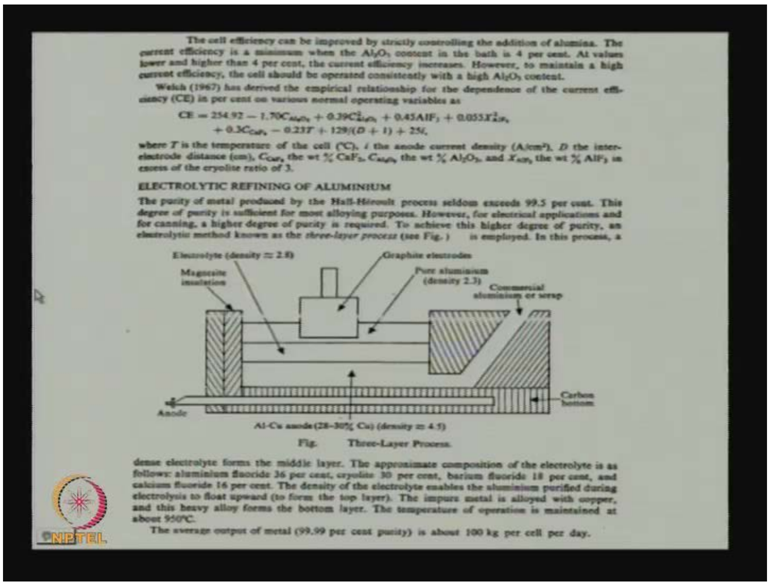

The cell efficiency can be improved by strictly controlling the addition of alumina. The current efficiency is a minimum when the Al_2O_3 content in the bath is 4 per cent. At values lower and higher than 4 per cent, the current efficiency increases. However, to maintain a high current efficiency, the cell should be operated consistently with a high Al_2O_3 content.

Welch (1967) has derived the empirical relationship for the dependence of the current efficiency (CE) in per cent on various normal operating variables as

$$CE = 254.92 - 1.70C_{Al_2O_3} + 0.39C^2_{Al_2O_3} + 0.45AlF_3 + 0.055X^2_{AlF_3} + 0.3C_{CaF_2} - 0.23T + 129/(D + 1) + 25i,$$

where T is the temperature of the cell (°C), i the anode current density (A/cm²), D the inter-electrode distance (cm), C_{CaF_2} the wt % CaF_2, $C_{Al_2O_3}$ the wt % Al_2O_3, and X_{AlF_3} the wt % AlF_3 in excess of the cryolite ratio of 3.

ELECTROLYTIC REFINING OF ALUMINIUM

The purity of metal produced by the Hall-Héroult process seldom exceeds 99.5 per cent. This degree of purity is sufficient for most alloying purposes. However, for electrical applications and for canning, a higher degree of purity is required. To achieve this higher degree of purity, an electrolytic method known as the *three-layer process* (see Fig.) is employed. In this process, a

Fig. Three-Layer Process.

dense electrolyte forms the middle layer. The approximate composition of the electrolyte is as follows: aluminium fluoride 36 per cent, cryolite 30 per cent, barium fluoride 18 per cent, and calcium fluoride 16 per cent. The density of the electrolyte enables the aluminium purified during electrolysis to float upward (to form the top layer). The impure metal is alloyed with copper, and this heavy alloy forms the bottom layer. The temperature of operation is maintained at about 950°C.

The average output of metal (99.99 per cent purity) is about 100 kg per cell per day.

that all the theories say that eventually some fluorine will evolve. So, fluorine evolves at the anode.

Now, we are interested in increasing the current efficiency and also energy efficiency. The cell efficiency can be improved strictly controlling the addition of alumina, and also many additives that I have mentioned earlier. The current efficiency is minimum, when Al 2 O 3 content if the bath is 4 percent to increase current efficiency, we have to increase it at least, around 5 or 8, at various layers and higher than 4 percent, the current efficiency increases; however, to maintain a high current efficiency, this cell should be operated consistently with a high Al 2 O 3 treatment.

The way the cell has to operate, will be under great control that we do not want fluctuations, and actually in many processes, if you can maintain things consistently, you get the highest efficiency. Like when you are driving a car, if you drive at a constant speed, how about 45 kilometers, so you get the fuel efficiency maximum.

But if you know stop and accelerate and stop, fuel efficiency goes down. So, is also true for aluminum electrolysis cell. Try to keep things as uniform as possible, and I have referred to this equation once. I will end with this that many experiments have shown that current efficiency depends on alumina content, depends on Al F 3 content, depends on calcium fluoride, it goes down with increasing temperature, and depends on of course, the inter electrode separation. And all here you saw, the inter electrode separation is very carefully maintained. You see this here.

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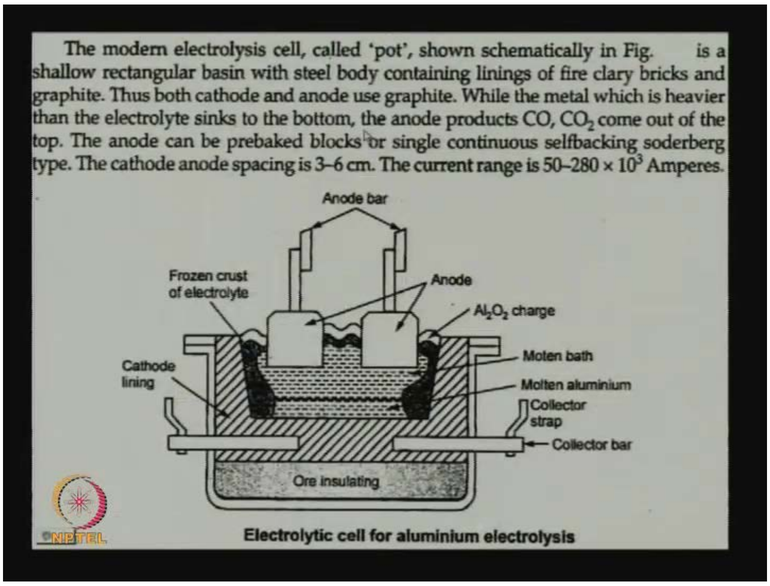

The modern electrolysis cell, called 'pot', shown schematically in Fig. is a shallow rectangular basin with steel body containing linings of fire clary bricks and graphite. Thus both cathode and anode use graphite. While the metal which is heavier than the electrolyte sinks to the bottom, the anode products CO, CO_2 come out of the top. The anode can be prebaked blocks or single continuous selfbacking soderberg type. The cathode anode spacing is 3–6 cm. The current range is 50–280 × 10^3 Amperes.

Electrolytic cell for aluminium electrolysis

Three to six centimeter, is the inter electrode separation. Both cathode and anode use graphite, the metal is heavier than the electrolyte sinks to the bottom, the anode product CO, CO 2 to come out of the top. Anode can be prebaked blocks or single continuous Soderberg type electrodes. Spacing is three to six, and it has to be maintained, as consistent as possible and of course, the current range can vary a bit. Well that is all, I would say about aluminum electrolysis for now.

I want to mention at the end something about electrolytic refining of aluminum. Now, you will recall that in the case of copper what we did we took an impure copper anode, which was thick and a thin copper cathode, and we did electrolysis, like we do electrolysis for deposition of copper.

If you have an aqueous solution, a copper salt, which are copper ions and you have a thick copper anode and thin copper cathode. Start electrolysis, copper will get transferred from anode to cathode. So, this will thin down this will become thick you will produce pure copper, some impurities will dissolve into solution, and some will become in soluble slag. I will come to that later on.

This is the principle of electro refining. Something like that is done in the case of aluminum also. But here there is a trick, and the trick is this. In electrolysis, aluminum goes to the bottom, because it is heavier than the electrolyte.

In electro refining, there is a scheme, where aluminum floats, to the top; pure aluminum, and impure aluminum stays at the bottom, how will it stay at the bottom, aluminum is alloyed with something, made in to very heavy. So, that the heavy alloy will stay at the bottom, in pure aluminum, in between there is an electrolyte, and through electro refining very fine, a purified aluminum will come to the top.

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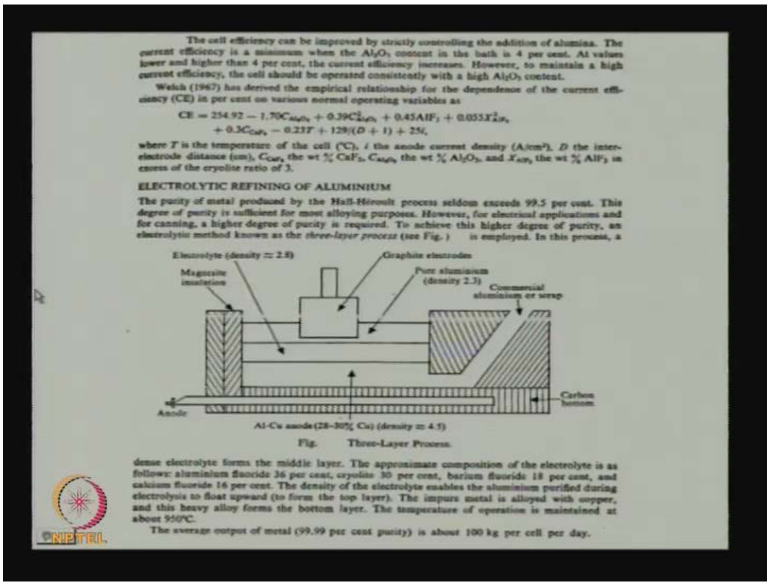

The cell efficiency can be improved by strictly controlling the addition of alumina. The current efficiency is a minimum when the Al_2O_3 content in the bath is 4 per cent. At values lower and higher than 4 per cent, the current efficiency increases. However, to maintain a high current efficiency, the cell should be operated consistently with a high Al_2O_3 content.

Welch (1967) has derived the empirical relationship for the dependence of the current efficiency (CE) in per cent on various normal operating variables as

$$CE = 254.92 - 1.70C_{Al_2O_3} + 0.39C^2_{Al_2O_3} + 0.45AlF_3 + 0.055X^2_{AlF_3} + 0.3C_{CaF_2} - 0.23T + 129/(D+1) + 25i,$$

where T is the temperature of the cell (°C), i the anode current density (A/cm²), D the inter-electrode distance (cm), C_{CaF_2} the wt % CaF_2, $C_{Al_2O_3}$ the wt % Al_2O_3, and X_{AlF_3} the wt % AlF_3 in excess of the cryolite ratio of 3.

ELECTROLYTIC REFINING OF ALUMINIUM

The purity of metal produced by the Hall-Héroult process seldom exceeds 99.5 per cent. This degree of purity is sufficient for most alloying purposes. However, for electrical applications and for canning, a higher degree of purity is required. To achieve this higher degree of purity, an electrolytic method known as the *three-layer process* (see Fig.) is employed. In this process, a

Fig. Three-Layer Process.

dense electrolyte forms the middle layer. The approximate composition of the electrolyte is as follows: aluminium fluoride 36 per cent, cryolite 30 per cent, barium fluoride 18 per cent, and calcium fluoride 16 per cent. The density of the electrolyte enables the aluminium purified during electrolysis to float upward (to form the top layer). The impure metal is alloyed with copper, and this heavy alloy forms the bottom layer. The temperature of operation is maintained at about 950°C.

The average output of metal (99.99 per cent purity) is about 100 kg per cell per day.

Here is the scheme, the purity of metal produced by a Hall Heroult process is 99.5 percent. Now, this purity, is sufficient for most alloying purposes, but for electrical applications, and for canning, which requires lot more improvement of mechanical properties; formability, one needs a higher purity, and to achieve this higher degree of purity, there is an electrical electrolytic method, call the three layer process.

In this three layer process, these are the layers. We make an alloy of impure aluminum and copper. This is 28 to 30 percent copper that makes the density of the alloy about 4.5, copper is very heavy. So, this alloy of aluminum which is actually the impure aluminum, we are calling it, stays at the bottom. We find an electrolyte, which is lighter than this and it is adjusted to 2.8 and on top of that, aluminum; pure aluminum which is 2.3 density, will float.

Scheme is similar; there is a graphite electrode here. There is an anode, this is now cathode, it is no longer anode, is cathode, because aluminum will go there and this is the anode. This is also graphite at the bottom. Commercial aluminum or scrap can be continuously fed into this alloy from here (Refer Slide Time: 36:48). We have to find a way of adding copper also, because, so that we maintain this density, and there is magnesite insulation and so of during electro refining, copper, aluminum will go from the impure layer to the pure aluminum layer.

A dense electrolyte is what you need in the middle, the approximate composition of the dense electrolyte, is now different from simple cryolite. It is made up of aluminum fluoride 36 percent, cryolite only 30 percent and barium fluoride, barium is a heavy, 18 percent, calcium fluoride 16 percent, and the density of the electrolyte enables aluminum purified during electrolysis to float upwards to form a top layer.

So, we have these 3 layers now. The impure metal is alloyed with copper and this heavy alloy forms the bottom layer. The entire thing will happen at about 950 degrees, and from impure aluminum, which we alloyed with copper; we can produce here, very pure aluminum of purity of about 99.99 percent. And this kind of cell, it operates on a smaller scale, it produces about 100 k g per cell per day. Principle is very similar; we have changed the electrolyte made it heavier. So, that aluminum can float in during aluminum electrolysis, aluminum was sinking, but here aluminum has to float. The impure aluminum in the form of an alloy is kept at the bottom.

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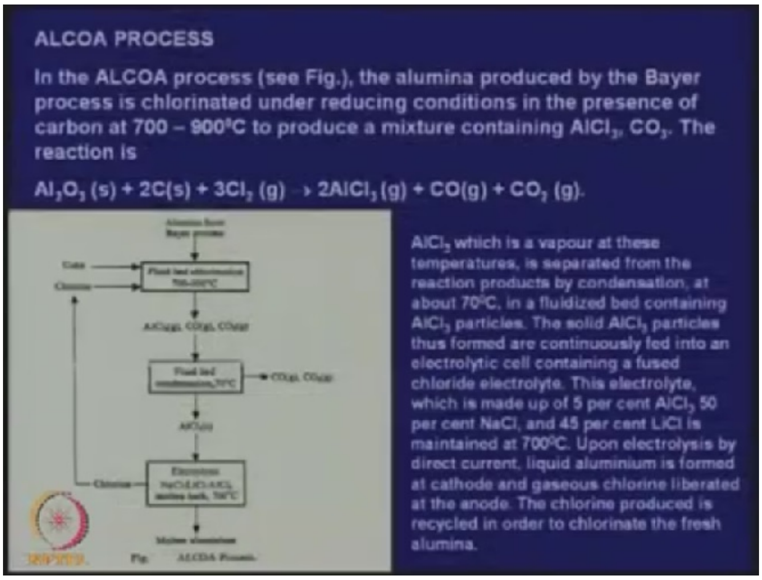

ALCOA PROCESS

In the ALCOA process (see Fig.), the alumina produced by the Bayer process is chlorinated under reducing conditions in the presence of carbon at 700 – 900°C to produce a mixture containing $AlCl_3$, CO_2. The reaction is

$$Al_2O_3\,(s) + 2C(s) + 3Cl_2\,(g) \rightarrow 2AlCl_3\,(g) + CO(g) + CO_2\,(g).$$

$AlCl_3$ which is a vapour at these temperatures, is separated from the reaction products by condensation, at about 70°C, in a fluidized bed containing $AlCl_3$ particles. The solid $AlCl_3$ particles thus formed are continuously fed into an electrolytic cell containing a fused chloride electrolyte. This electrolyte, which is made up of 5 per cent $AlCl_3$, 50 per cent NaCl, and 45 per cent LiCl is maintained at 700°C. Upon electrolysis by direct current, liquid aluminium is formed at cathode and gaseous chlorine liberated at the anode. The chlorine produced is recycled in order to chlorinate the fresh alumina.

Now, let us now end this lecture, by discussing what the future methods in alumina production are. By now, I am sure you know that the Hall Heroults process, invented and introduced in 1886 has gone on and on and on, for more than 125 years now. And people have been constantly searching, for an alternate way of making aluminum. One or two are being discussed; still they have not become industrially viable. The most important development that was announced about 15 years ago, and people thought that is the solution, but it did not prove it to be so, is the AlCOA process.

Alcoa is an aluminum company of America. It is a very big aluminum company; in this process the idea is to abundant alumina in cryolite electrolysis. They wanted some other solute in some other solvent. And the aim was to produce aluminum trichloride for subsequent electrolysis. So, the alumina produce by the Bayer's process is still required. That is the starting point; we get pure Al 2 O 3 that has come from Bayer process.

Now, it will be chlorinated. Now you know, I have discussed during general principle there are two ways of chlorinating oxides. One is direct chlorination. That you chlorinate by Cl 2 or chlorine containing compounds, but in most cases we go for indirect chlorination or reduction chlorination, you bring in a reducing agent also. This is what is required in this case as well.

So, we say chlorinated under reducing conditions, which means in presence of carbon at 700 to 900 degrees, to produce a mixture of Al 2 Al Cl 3 and CO 2 (Refer Slide Time: 41:09). The reaction is this. aluminum Alumina from Bayer's process, in presence of carbon, it will react will Cl 2 to produce aluminum trichloride vapor, carob monoxide and CO 2.

Here is the flow sheet. The chlorination done in a fluidized bed, and in the fluid bed, if there is, we can bring in the temperature to 70 degrees, aluminum trichloride solidifies, thus aluminum trichloride goes for electrolysis in a molten bath, comprising sodium chloride, potassium chloride and an aluminum chloride will be solid.

So, basically it is a sodium chloride, lithium chloride bath. Here electrolysis can occur at a lower temperature or 700 degrees only. Aluminum will no longer be liquid, I guess. But then the entire process would be at a lower temperature. Here, I have given more details that by condensation we separates Al Cl 3 particles, this particles are continuously fed into an electrolytic cell with fused chloride electrolyte.

It has only 5 percent Al Cl 3, 50 percent sodium chloride, 45 percent Li Cl, temperature is 700 degrees. Up on electrolysis by direct current, liquid aluminum, sorry, it will be liquid. Yes just above the melting point.

Liquid aluminum is formed at cathode and gaseous chlorine liberated at the anode, the chlorine produced is recycled, in order for chlorinate the fresh alumina. Now, during electrolysis chlorine will come out, it will go back for chlorination of alumina, it seems to be very attractive process.

How it is done, the electrolytic cell is also very attractive. I will come to that.

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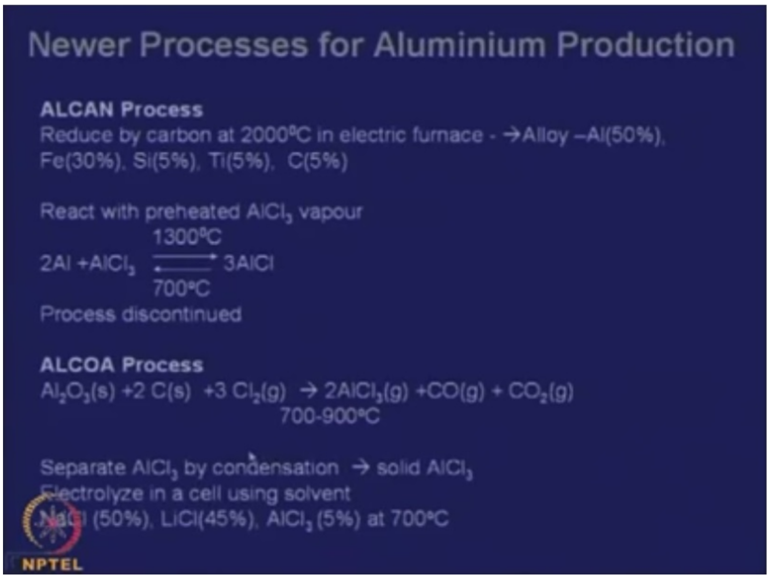

Newer Processes for Aluminium Production

ALCAN Process

Reduce by carbon at 2000°C in electric furnace - →Alloy –Al(50%), Fe(30%), Si(5%), Ti(5%), C(5%)

React with preheated $AlCl_3$ vapour

$$2Al + AlCl_3 \underset{700°C}{\overset{1300°C}{\rightleftarrows}} 3AlCl$$

Process discontinued

ALCOA Process

$$Al_2O_3(s) + 2\,C(s) + 3\,Cl_2(g) \rightarrow 2AlCl_3(g) + CO(g) + CO_2(g)$$
700-900°C

Separate $AlCl_3$ by condensation → solid $AlCl_3$

Electrolyze in a cell using solvent

NaCl (50%), LiCl(45%), $AlCl_3$ (5%) at 700°C

But before that, yeah, this is what the Alcoa process. This is how we can write it, Al Cl 3 by condensation, solid aluminum etcetera.

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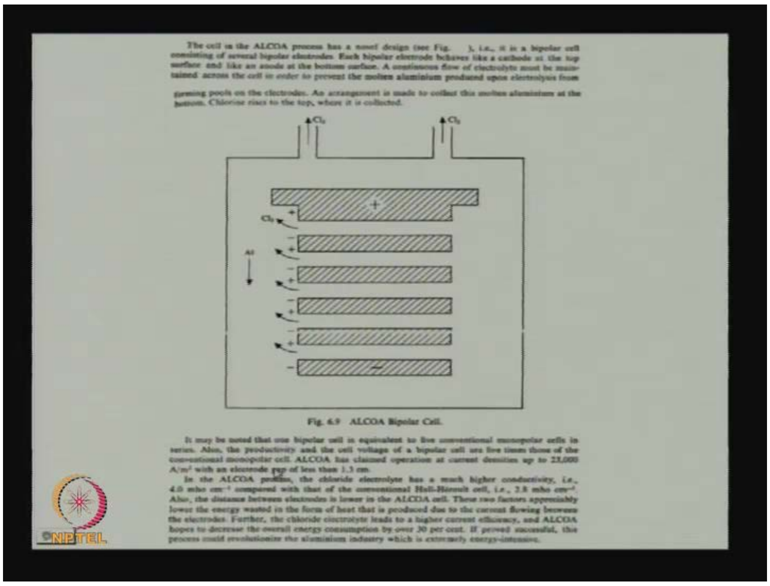

The cell in the ALCOA process has a novel design (see Fig.), i.e., it is a bipolar cell consisting of several bipolar electrodes. Each bipolar electrode behaves like a cathode at the top surface and like an anode at the bottom surface. A continuous flow of electrolyte must be maintained across the cell in order to prevent the molten aluminium produced upon electrolysis from forming pools on the electrodes. An arrangement is made to collect this molten aluminium at the bottom. Chlorine rises to the top, where it is collected.

Fig. 6.9 ALCOA Bipolar Cell.

It may be noted that one bipolar cell is equivalent to five conventional monopolar cells in series. Also, the productivity and the cell voltage of a bipolar cell are five times those of the conventional monopolar cell. ALCOA has claimed operation at current densities up to 23,000 A/m^2 with an electrode gap of less than 1.3 cm.

In the ALCOA process, the chloride electrolyte has a much higher conductivity, *i.e.*, 4.0 mho cm^{-1} compared with that of the conventional Hall-Héroult cell, *i.e.*, 2.8 mho cm^{-1}. Also, the distance between electrodes is lower in the ALCOA cell. These two factors appreciably lower the energy wasted in the form of heat that is produced due to the current flowing between the electrodes. Further, the chloride electrolyte leads to a higher current efficiency, and ALCOA hopes to decrease the overall energy consumption by over 30 per cent. If proved successful, this process could revolutionize the aluminium industry which is extremely energy-intensive.

Now, this cell that Alcoa tried was also very interesting. This cell had, what we call bipolar electrodes, means these are the graphite electrodes, suspended horizontally, in this electrolytic cell, and they were bipolar, means one side of this was negative, other positive, negative, positive, negative, positive, negative, positive, negative.

So, this is the cathode which draws aluminum, but aluminum is drawn everywhere on the cathode side and after getting aluminum ion getting discharged, it falls down to the bottom. So, in the bottom alumina is aluminum collects and the plus sign mean the anodes, chlorine is liberated, and it is liberated here, liberated there, liberated there, and liberated there. All the chlorine being liberated will come out from here.

Now these electrodes are called bipolar electrodes, when the same piece of graphite is serving both as anode and cathode. Let me read what is here. It is a bipolar cell consisting of several bipolar electrodes; each bipolar electrode behaves like a cathode at the top surface and like an anode at the bottom surface.

A continuous flow of electrolyte must be maintained across the cell, in order to prevent the molten aluminum, produced upon electrolysis, from forming pools on the electrode. They should not hang on the electrodes. It must be made to fall to the bottom and arrangement is made to collect the molten aluminum at the bottom. Chlorine rises to the top from where it is collected and it goes for chlorination again.

Now, it may be noted that one bipolar cell is equivalent to, as shown here, is equal to five conventional monopolar cells in series. These are monopolar cells in series; also the productivity and the cell voltage, at the bipolar cell, are five times more than those have the conventional monopolar cell.

Alcoa has claimed operation at current densities up to 23000 ampere per meter square, with an electrode gap of less than 1.3 centimeter. You need less electrode gap now, because you need less heating, but this bipolar arrangement enhances the surface area of the electrode enormously.

Now, the advantages of Alcoa process are listed here (Refer Slide Time: 46:34). The chloride electrode has much higher conductivity, compared with that of convention Hall Heroult cell; distance between the electrodes is lower. These two factors appreciably lower the energy wasted in the form of heat that is produced due to current flowing between electrodes. You need some heat, but you are wasting less heat.

Further, the chloride electrolysis leads to a higher current efficiency and Alcoa hopes to decrease the overall energy consumption by over 30 percent. It proves successfully, this process could revolutionize the aluminum industry which is extremely energy intensive.

So, it would give rise to several advantages. Operation would be at a lower temperature, energy requirement should be always 30 percent lower, and there is no consumable graphite electrode. These electrodes that you see placed horizontally bipolar electrodes have not been consumed.

So, you are not consuming you are not producing any CO, CO 2. You are producing at the anodes, chlorine, which is reused for chlorination of c o two o three. So, on the whole you are simply producing aluminum, from alumina, without consumption of the electrolyte, without consumption of electrodes with lower energy.

Now, it sounded very exciting, but there is a negative side. So, the negative side is aluminum trichloride is an extremely toxic and reactive substance. Like I myself have had an accident, with aluminum trichloride when I opened a bottle without knowing it was aluminum trichloride. I opened the bottle immediately; the aluminum trichloride powders reacted with moisture to produce acid vapors, HCl. The entire room was covered with fumes and I did not know what was happening. I should have been careful, but I had not studied earlier the properties of aluminum trichloride. You open the bottle and boom, there is an explosion, the whole room is full of fumes, and actually then the fire fighting engine came in.

Now, if this is the chemical that you want to handle in an industry everything has to be done under sealed conditions, under covered conditions, with extreme care that makes the technology a very difficult thing to adopt. I suspect, it is because of this that extremely sophisticated arrangement required for handling aluminum trichloride that the technology has not come into the market. it has remained as an R and D project, it has been demonstrate in a pilot plan scale.

But there is no industry, which is operating based on aluminum trichloride electrolysis. Whereas, see the way, you can handle alumina, there is no problem with alumina. It works with the cell. Anybody can operate and everything is going on, there were no problem at all anywhere, but aluminum trichloride, in theory is very good, but it does not quite workout.

What are the other processes that have had been proposed and on which people worked also is called the AlCAN process (Refer Slide Time: 50:17). The AlCAN process is based on the simple thing that if you take alumina, and reduce by carbon, pyrometallurgical reduction by carbon. It should produce aluminum, but that does not happen, because it forms carbide.

So, what the AlCAN process says is let’s form the carbide and see what can be done. So, in the AlCAN process you reduce alumina by carbon at 2000 degree centigrade, in an electric arc furnace. You produced an alloy which has 50 percent aluminum, 30 percent iron, because you know there is always in bauxite, there is and you are not starting with Bayer’s process alumina. You are starting with the ore, bauxite as such.

So, you get iron, you produce you have some silicon, you have some titanium, you have carbon, because there is some carbide, then react with preheated aluminum, then we go back to, once I discussed how you purified aluminum by using an intermediate gas, we go back to that method.

You should have pre-heated aluminum trichloride vapor is made to react with impure aluminum, with that alloy and it is a reversible process. You produce monochloride, take it out, cool it, you produce pure alumina. So, we take that impure aluminum as that alloy with iron and carbide etcetera; react with aluminum trichloride, for mono chloride separate that mono chloride, cool and you get Alcan process that is what this process is.

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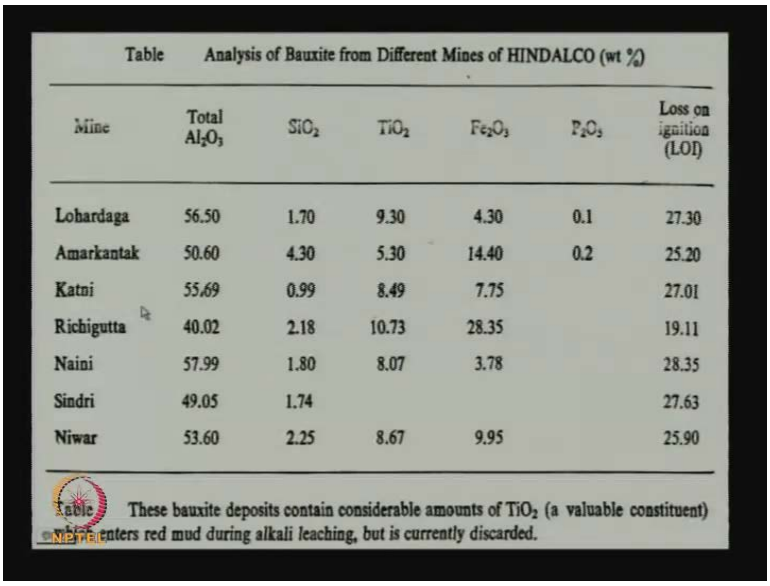

Table Analysis of Bauxite from Different Mines of HINDALCO (wt %)

Mine	Total Al_2O_3	SiO_2	TiO_2	Fe_2O_3	P_2O_5	Loss on ignition (LOI)
Lohardaga	56.50	1.70	9.30	4.30	0.1	27.30
Amarkantak	50.60	4.30	5.30	14.40	0.2	25.20
Katni	55.69	0.99	8.49	7.75		27.01
Richigutta	40.02	2.18	10.73	28.35		19.11
Naini	57.99	1.80	8.07	3.78		28.35
Sindri	49.05	1.74				27.63
Niwar	53.60	2.25	8.67	9.95		25.90

Table These bauxite deposits contain considerable amounts of TiO_2 (a valuable constituent) which enters red mud during alkali leaching, but is currently discarded.

Now, I will end this by one just one comment. I have been mentioning that no two industries operate in the same manner, not only because cells are designed, they supply by different people, also because the raw materials with which they operate are also not the same.

See, these are the compositions of Indian bauxite. This is the analysis of bauxite from different mines of Hidalgo, in one company itself, owns these mines and you see the variation in alumina, silica, TiO 2, Fe 2 O 3, P 2 O 5.

So, now a company would like to try to have a blend where the composition does not change very much. Another company may be using another blend, depending on the accessibility to the mines. So, the raw materials coming to the different aluminum compressor are not the same, and when they are not the same the process has to be different.

I think, I will end this now. In my next lecture I would touch up on the Indian scene. Start to talk about what some aluminum companies are doing in India. What they are saying are the requirements of the aluminum industry? What should be done? What should not be done? What a plus points, what a minus points?

So, this completes my general discussion on aluminum. I would request you to please refer to the three books I have shown to you. You must read them, you need not own all the two books, but if you can own the book call non-ferrous metal production book, it will be good, and the other one also you should have is energy in metals and minerals industries.

Thank you.