Non-ferrous Extractive Metallurgy

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Module No # 06

Lecture No # 21

Extraction of Metals from Sulphides Extraction of Copper

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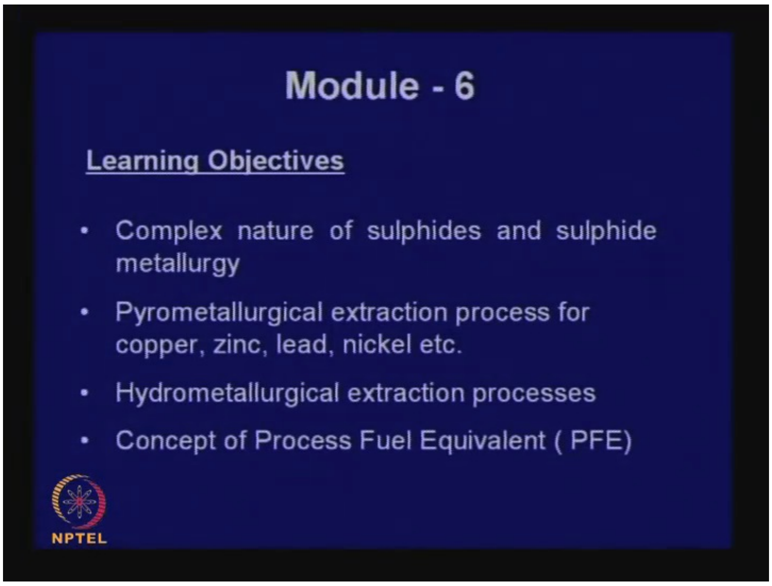

Module - 6

Learning Objectives

- Complex nature of sulphides and sulphide metallurgy
- Pyrometallurgical extraction process for copper, zinc, lead, nickel etc.
- Hydrometallurgical extraction processes
- Concept of Process Fuel Equivalent (PFE)

We are now starting module number 6, which will be about extraction of metals from sulphides and we will start with copper metallurgy. I have already said one or two things, as an introduction during my last lecture, but let me repeat what I have said.

In this module 6, our learning objectives will be following that is regarding the complex nature of sulphides and sulphide metallurgy. Then, we will take on “Pyrometallurgical Extraction Process”, for copper, zinc and lead. These are three very common metals and often called as base metals. We will touch nickel also because nickel is found as sulphides and as well as oxides.

Then, “Hydrometallurgical Extraction Processes”, for copper and zinc, not to (( )) for lead, then we will talk about the concept of Process Fuel Equivalent, which gives us a way of comparing energy requirements.

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Methods of metal recovery

- Thermal decomposition
- Roasting and subsequent reduction
- Controlled roasting → matte → metal
- Flash smelting → matte → metal
- Metallothermic reduction of sulphide
- Hydrometallurgical processing
- Chlorination → chlorides → metal
- Electrolytic refining of matte to pure metal (Commercial process for Ni only)

Now, these are the standard methods of producing metal from sulphides. One is straightforward; it is ‘Thermal Decomposition’. This is applicable in the case of mercury sulphide: Hg S, which can be simply heated and it decomposes to give mercury metal and sulphur. Most common and logical will be to take the sulphide, roast it to make an oxide, and then reduce by carbon, like the way you treat an oxide.

The third one is what we apply in the case of copper, and also in the case of nickel, will see when nickel is in the form of sulphide. In this case, the idea is not to roast copper sulphide to copper oxide and then reduce by carbon. It is a very different technique. Copper sulphides are often associated with iron sulphide, and if you try to roast them, iron gets oxidizing preference with respect to copper and iron will start forming iron oxides. We ensure that not all iron gets oxidized and we leave oxidation of iron incomplete.

The iron oxide that forms F e O is slagged out. We are left with copper sulphide and some residual iron sulphide. These two form what is known as a matte; matte is a mixture of sulphides from there we get metal by very interesting oxidation technique where simply by oxidizing it we make produce copper. How we will do that we will see later. The other will be flash smelting, where roasting, smelting, are combined and speeded up. The process is speeded up. We can also have metallothermic reduction of sulphide; there can be hydrometallurgical processing of sulphide.

A sulphide can be chlorinated, change into a chloride, from which the metal can be extracted by electrolysis or by a metallothermic reduction. Finally, there is also a process, in some cases matte, which is a mixture of sulphides can be refined to produce pure metal by an electrolytic process. The commercial process is for nickel only.

Let us start with copper. Now I mentioned that there is a beneficiation technique called floatation, which makes it possible to concentrate low grade copper ores to produce a concentrate that will have much higher concentrations of copper. And flotation, as I mentioned, is a technique where we have very fine ores; ores is ground very fine. Then we make a froth, we have that fine suspended, in a medium where there is a froth, and when the bubbles come out, the sulphide particles attach themselves to the bubbles; they float to the surface. The gangue minerals like silica and other oxides which do not attach themselves to the bubbles; they stay behind. So, from the top we can scheme out a layer which will be very rich in the sulphide particles.

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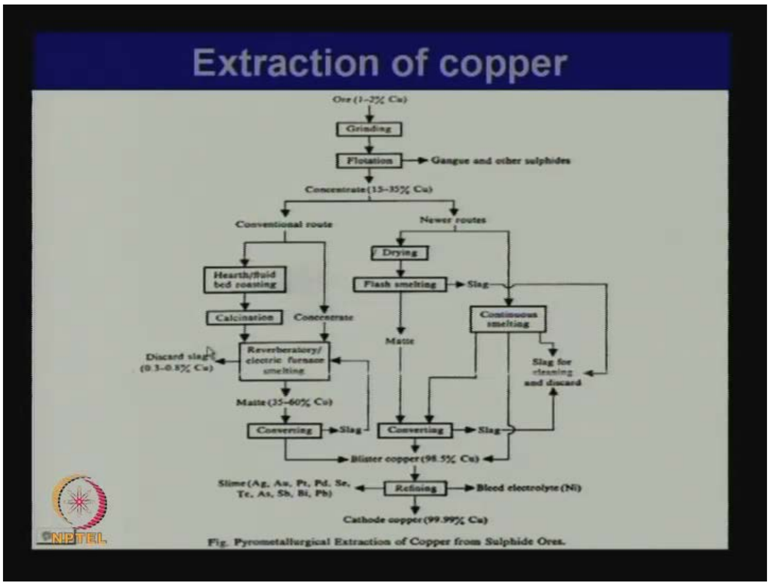

Extraction of copper

Fig. Pyrometallurgical Extraction of Copper from Sulphide Ores.

So, starting with an ore which may contain only one to two percent copper, one can after grinding and flotation, one can produce a concentrate which will have 13 to 35 percent copper, depending on circumstances. And the gangue and the other sulphides which have not been floated will be taken out.

There is a way of doing differential flotation also where we float one sulphide, not the other sulphide, with another state float the other sulphide. So, here we are doing a differential flotation, only to get the copper sulphide mineral floating out of other gangue and other sulphides and there are other sulphides are not floated. So, the conditions are so maintained. So, we will start now with a concentrate, which contains sulphide from15 to 35 percent copper. This is the starting material.

Now, there are several ways which are similar, but they evolved over time. The conventional or traditional route is this (Refer Slide Time: 07:22). The concentrate goes for reverberatory or electric furnace smelting, or it can go from hearth or fluid bed roasting, calcinations and then go for a reverberatory or electric furnace smelting.

Now, in the smelting process, I have mentioned little while ago is the aim is not to produce an oxide, but to have controlled oxidation, so that we produce a matte. Matte is a mixture of copper sulphide and iron sulphide, which means that copper sulphide which was in the concentrate, is left practically untouched. Only the iron sulphide part is oxidized that too incompletely, so that only it goes to the Fe O state. That Fe O is slagged out, and the rest of the iron sulphide and copper sulphide, they form a sulphide solution called matte, which can have 35 to 60 percent copper, the rest will be iron as iron sulphide.

So, all the oxygen has been eliminated from the system, and the slag that comes out, which has most of the iron, slagged out Fe O with silica, limestone, quartz etcetera, in a slag. It will also take out a small amount of copper; obviously, that we cannot ensure. But, basically oxygen is eliminated, from the system. But what we get is a matte, a mixture of iron sulphide and copper sulphide. Then this goes through a process called converting. Converting, a process of oxidation, where as we oxidize iron sulphide and copper sulphide matte, a stage comes where suddenly copper comes out of the system, and there is some slag also. The slag will be put back to the reverberatory furnace because it may contain some iron.

The copper that has come out goes for refining. Now, a newer route is that which will eliminate reverberatory furnace smelting. We would have and these steps everything is combined into one step called flash smelting, means everything is smelted, calcined and flashed, very fast. It produces a matte, it goes straight for converting, there are even newer processes, where everything is combined; all steps are combined into one continuous smelting process, which can produce either matte for conversion or it can straight away produce the copper, called blister copper. What it is? I will tell you later. And the slag that contains some copper will go for slag cleaning, for copper recovery. After we have produced impure copper called blister copper, which is 98.5 percent copper. It will go for refining.

In the refining process we will produce cathode copper; 99.99 percent copper. But, we will also get whole lot of valuable byproducts in slime. All the precious metals like silver, gold, platinum, palladium, etcetera.

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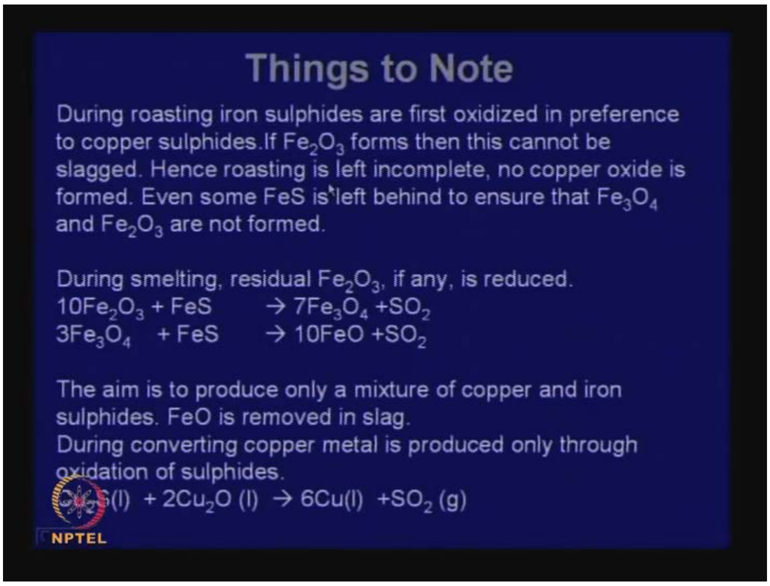

Things to Note

During roasting iron sulphides are first oxidized in preference to copper sulphides. If Fe_2O_3 forms then this cannot be slagged. Hence roasting is left incomplete, no copper oxide is formed. Even some FeS is left behind to ensure that Fe_3O_4 and Fe_2O_3 are not formed.

During smelting, residual Fe_2O_3, if any, is reduced.

$$10Fe_2O_3 + FeS \rightarrow 7Fe_3O_4 + SO_2$$

$$3Fe_3O_4 + FeS \rightarrow 10FeO + SO_2$$

The aim is to produce only a mixture of copper and iron sulphides. FeO is removed in slag.

During converting copper metal is produced only through oxidation of sulphides.

$$Cu_2S(l) + 2Cu_2O (l) \rightarrow 6Cu(l) + SO_2 (g)$$

I will go into the details of the process now and look at these steps, one by one. Now, to understand what happens when we roast the sulphide concentration, the concentrate in a reverberatory furnace, we should note that during roasting sulphides are first oxidized. Iron sulphides are first oxidized in preference to copper sulphides. Now, we do not want iron sulphides to form Fe 2 O 3. Because, if Fe 2 O 3 forms and then this cannot be slagged very easily. It does not dissolve in the slag that you are creating by adding limestone, quartz etcetera. And the gangue, there is a slag phase where Fe_2O_3 does not dissolve very well, but Fe O does.

So, the iron sulphides will be oxidized only up to the Fe O stage, not beyond. Sometimes they say little bit of Fe_3O_4 is ok, because that helps in protecting the refractory, is goes and gets absorbed in the refractory surface. But let us ignore that. We have iron sulphide and copper sulphide in a starting material. We will ensure that one does not go beyond Fe O, which means we will have to leave much of Fe S not oxidized and that is accepted.

So, the Fe O that forms will go into the slag face. No copper oxide is formed, because we have not even completed oxidation of iron sulphide. Copper sulphide cannot be oxidized and yes we have oxidized the whole of iron sulphide. We are not oxidizing whole of iron sulphide. Only part of that is oxidized, only up to Fe O stage, which is taken out iron sulphide and copper sulphide left behind will form matte.

No copper oxide is formed. So, the slag will not have copper oxide. We have mentioned only a very minor amount of copper oxide, which will go into the slag and we are deliberately leaving Fe S behind to ensure that Fe_2O_4 and Fe_2O_3 are not formed. This is the basic technique. Now, during smelting like this subsequently, if there is subsequent if there is some Fe_2O_3 left, if supposing by somehow Fe_2O_3 forms, then in the subsequent step, the residual Fe S that we have will reduce Fe_2O_3 and Fe_3O_4 to low Fe O state and that will be slagged off.

So, we want that Fe S to play this role also. We must have some Fe S that subsequent if there are higher oxides; they will be reducing to the Fe O stage for slagging. This stage, smelting is coming after or now. So, our aim is to produce only a mixture of copper and iron sulphides. Fe O is removed in slag. Then we will go for what is known as converting. Converting is where we start oxidizing the matte. First that iron sulphide is oxidized to produce Fe O. That is removed in a converter and then copper sulphide starts getting oxidized. Once it reaches the Cu_2O and when it forms Cu_2O then there is a very interesting reaction between Cu_2S and Cu_2O that forms copper straight away. The reaction is written as Cu_2S plus 2 Cu_2O to produce copper and SO_2.

So, what is it we had? Starting with a sulphide concentrate, we have roasted it to ensure that we are left with incomplete roasting of iron sulphide, we will produce a matte, and then we will have a smelting process. In the smelting process residual Fe S will ensure that Fe 2 O 3, Fe 3 O 4 forms Fe O and that is slagged off. Then we have left up with the matte, which will go for the converting step, where in a converter oxygen will be blown to oxidize iron sulphide to Fe O stage and it is slagged off. And once copper starts getting oxidized, once it form Cu 2 O, these two will reacts and it will produce copper straight away. Now, all the reactions that are taking place are exothermic. So, in theory you are not supplying any energy, but in practice that is not so. Because when you have a reverberatory furnace or in electric furnace where you do the smelting operation, obviously there will be lot of energy losses. So, energy will have to be supplied. But, the converting step where you have a molten matte and oxygen is being injected, it is a highly exothermic process, no external heat supply is required.

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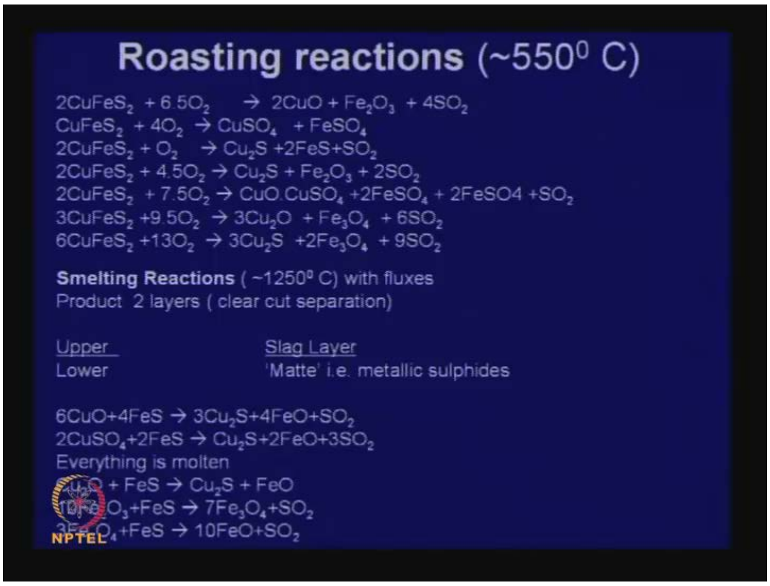

Roasting reactions (~550⁰ C)

$2CuFeS_2 + 6.5O_2 \rightarrow 2CuO + Fe_2O_3 + 4SO_2$
$CuFeS_2 + 4O_2 \rightarrow CuSO_4 + FeSO_4$
$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$
$2CuFeS_2 + 4.5O_2 \rightarrow Cu_2S + Fe_2O_3 + 2SO_2$
$2CuFeS_2 + 7.5O_2 \rightarrow CuO.CuSO_4 + 2FeSO_4 + 2FeSO4 + SO_2$
$3CuFeS_2 + 9.5O_2 \rightarrow 3Cu_2O + Fe_3O_4 + 6SO_2$
$6CuFeS_2 + 13O_2 \rightarrow 3Cu_2S + 2Fe_3O_4 + 9SO_2$

Smelting Reactions (~1250⁰ C) with fluxes
Product 2 layers (clear cut separation)

Upper	Slag Layer
Lower	'Matte' i.e. metallic sulphides

$6CuO + 4FeS \rightarrow 3Cu_2S + 4FeO + SO_2$
$2CuSO_4 + 2FeS \rightarrow Cu_2S + 2FeO + 3SO_2$
Everything is molten
$Cu_2O + FeS \rightarrow Cu_2S + FeO$
$10Fe_2O_3 + FeS \rightarrow 7Fe_3O_4 + SO_2$
$3Fe_3O_4 + FeS \rightarrow 10FeO + SO_2$

So, what are the reactions? We first have a roasting reaction. See the copper sulphide is mineral, is Cu Fe S 2. It forms; it tends to form Cu O and Fe 2 O 3. It tends to form sulphates. It can decompose to give Cu 2 S and Fe S also. It can give Fe 2 O 3. It can give Cu O. Cu S O 4 and Fe S O 4 and this compound (reaction is not balanced). Like the roasting of sulphides, all kinds of phases can come about.

Our aim will be to control the partial pressure of oxygen, partial pressure of S O 2 in such a manner that we will essentially have Cu 2 S, Fe S and Fe O and that Fe O during the smelting reactions, which will take place at 1250 degrees with fluxes. It will produce two layers; a slag layer which will remove the iron part and we will have a matte; metallic sulphides mixture of iron sulphide and copper sulphide.

Then during smelting in a smelter will continue with oxidation. Many reactions can take place. If any Cu O is there, it will convert itself to Cu 2 S forms Fe O. It will slagged off. If sulphate is there, it will form Cu 2 S, it will be slagged off. Everything is molten and many reactions take place.

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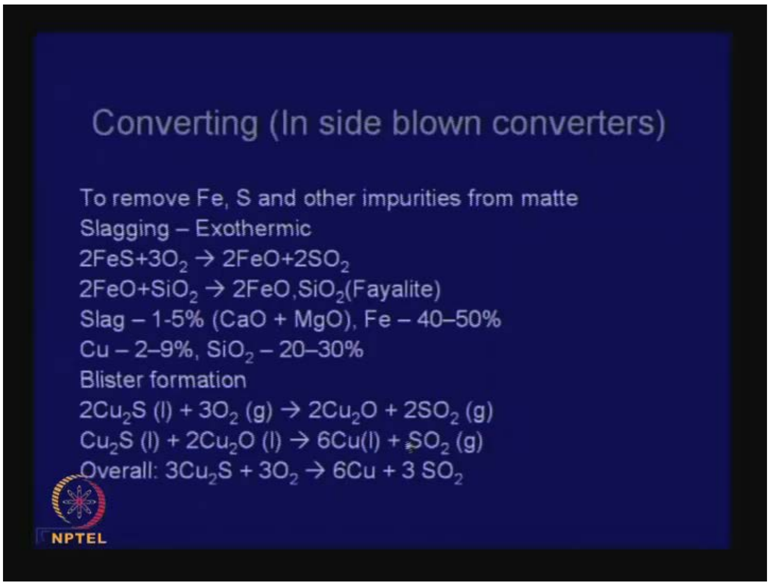

Converting (In side blown converters)

To remove Fe, S and other impurities from matte
Slagging – Exothermic
$2FeS+3O_2 \rightarrow 2FeO+2SO_2$
$2FeO+SiO_2 \rightarrow 2FeO.SiO_2$(Fayalite)
Slag – 1-5% (CaO + MgO), Fe – 40–50%
Cu – 2–9%, SiO_2 – 20–30%
Blister formation
$2Cu_2S\ (l) + 3O_2\ (g) \rightarrow 2Cu_2O + 2SO_2\ (g)$
$Cu_2S\ (l) + 2Cu_2O\ (l) \rightarrow 6Cu(l) + SO_2\ (g)$
Overall: $3Cu_2S + 3O_2 \rightarrow 6Cu + 3\ SO_2$

And then finally, by smelting, we will have iron sulphide and copper sulphide. Now, we have to remove iron, and sulphur, and other impurities from their matte and we will do that by slagging. We will continue in the converter. We blow oxygen to oxidize Fe S to Fe O stage, then Fe O will form react with Si O 2 to form fayalite slag. It will go into the slag phase. The slag will contain 1 to 5 percent calcium oxide, magnesium oxide. Iron will be mostly 40 to 50 percent. There will be some slag losses will be there; it would have silicon.

So, in the converter where the molten matte is being oxidized by blowing oxygen, these reactions take place. How we blow oxygen? We will see that at one time attempts were made to blow oxygen from their bottom; like it was done in the Bessemer converter, the air was blown. But, in copper converter things, oxygen comes from the side. Why it is from the side, I will discuss little later. And once we start doing that we automatically will produce blister copper. Blister copper means because once that copper is formed and then solidified and it is broken, it has a structure like blisters, there is lots of a holds. So, that is why it is called blister copper.

And the reactions are that in the matte there is copper sulphide. It reacts with the oxygen coming in produces Cu 2 O. Gradually Cu 2 S starts converting into Cu 2 O. At one stage, once you have twice as much Cu 2 O as Cu 2 S, and then these two react very quickly with each other to produce copper liquid and S O 2 gas. The overall reaction is Cu 2 S, being oxidized by oxygen to produce copper and S O 2. So, the entire process lot of S O 2 will be coming out. The whole thing is exothermic; all the reactions. The only energy required is to make sure it compensates for the heat losses that go from the high temperature reactors.

You do not need any heat supply during the converting reactions because they are very highly exothermic. Like today's steel converters where in pig iron the oxygen is injected into pig iron to produce steel, you do not need any external heat supply; the same thing is also in the copper converter. But, in the smelting stage, which is done in a reverberatory furnace or electric arc furnace. Although you have exothermic reaction, you will need heat supply.

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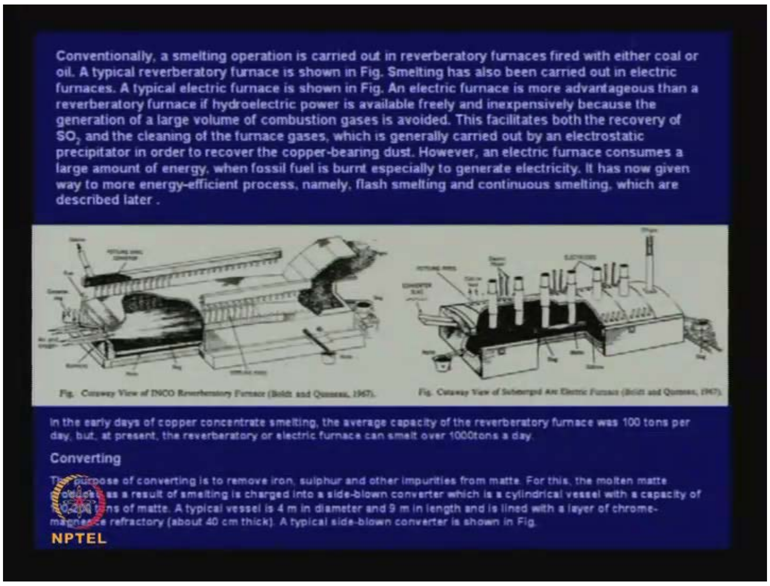

Conventionally, a smelting operation is carried out in reverberatory furnaces fired with either coal or oil. A typical reverberatory furnace is shown in Fig. Smelting has also been carried out in electric furnaces. A typical electric furnace is shown in Fig. An electric furnace is more advantageous than a reverberatory furnace if hydroelectric power is available freely and inexpensively because the generation of a large volume of combustion gases is avoided. This facilitates both the recovery of SO_2 and the cleaning of the furnace gases, which is generally carried out by an electrostatic precipitator in order to recover the copper-bearing dust. However, an electric furnace consumes a large amount of energy, when fossil fuel is burnt especially to generate electricity. It has now given way to more energy-efficient process, namely, flash smelting and continuous smelting, which are described later .

Fig. Cutaway View of INCO Reverberatory Furnace (Boldt and Queneau, 1967).

Fig. Cutaway View of Submerged Arc Electric Furnace (Boldt and Queneau, 1967).

In the early days of copper concentrate smelting, the average capacity of the reverberatory furnace was 100 tons per day, but, at present, the reverberatory or electric furnace can smelt over 1000tons a day.

Converting

The purpose of converting is to remove iron, sulphur and other impurities from matte. For this, the molten matte produced as a result of smelting is charged into a side-blown converter which is a cylindrical vessel with a capacity of [illegible] tons of matte. A typical vessel is 4 m in diameter and 9 m in length and is lined with a layer of chrome-magnesite refractory (about 40 cm thick). A typical side-blown converter is shown in Fig.

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Now, this is these are the two kinds of reverberatory furnaces used for smelting. This is the conventional reverberatory furnace, which uses liquid fuel or gaseous fuel. You have air and oxygen coming in. There is fuel coming from this side. The converter slag will be taken out this way, matte will come out this way, and outgoing gases will go out this way. Now, there are many complications of this design and we are not going into that. But, you see the flame is thrown from this side, and this is the feeding drag converter, and things are happening inside a long converter.

There are also submerged arc electric furnaces, where energy is not supplied by oxidation of a fuel, but by electrodes that stick into the molten charge. So, this is a cutaway view of submerged arc electric furnace, and this is a cutaway view of submerged electric arc furnace and this is a cutaway view of a reverberatory furnace. Now, let me read out what is written here. Conventionally a smelting operation is carried out in a reverberatory furnace filled with either coal fired with either coal or oil. A typical reverberatory furnace is shown.

Smelting has also being carried out in electric furnaces; that is also shown. And electric furnace is more advantageous than a reverberatory furnace, if the highly electric power is available freely. If we have the highly electric power supplying, then you will go for a submerged arc electric furnaces.

And it is also done inexpensively because the generation of large volume of combustion gases is avoided. When you are using coal or liquid fuel then, as it is lot of S O 2 is coming out from the system, but you would also generate C O, C O 2. The amount of gases, combustion gases coming out to be much larger. In the arc furnace, you are only getting S O 2. You are not getting C O, C O 2 that will come from combustion of oil or coal. So, that will be an advantage of electric arc furnace; however, the electric arc furnaces can only the operated where electricity is available.

Unfortunately, an electric arc furnace consumes a large amount of energy, when fossil fuel is burnt especially to generate electricity. Because, it is a roundabout way of getting energy, if you are using a fossil fuel into the furnace, either furnace oil, or coal, and you are generating heat directly, the process of heat generation will be much better. But, when if you are getting electricity that has been generated in the thermal power plant again by combustion of fossil fuels then, you have a two step thing that you are generating at some point from there it is giving electricity, which electricity is being consumed here.

So, if this electricity for the submerged arc is coming from a thermal power plant then you are not generating C O, C O 2 here, but you are generating C O, C O 2 elsewhere where the thermal power plant is located. If it is hydro electricity this problem is not there, otherwise you have to remember that you have only displaced the problem of combustion gases, in this case, if thermal power plant is giving with the electricity.

But then in this process, in the plant, you are generating less amount of combustion gases, because you are only generating what is coming from the reactions which do not include a combustion reaction. Now, there are both of these have now given away to flash smelting and continuous smelting operations, which I will discuss little later. Now, in the early days of copper concentrate smelting the average capacity of the reverberatory furnace was only 100 tons per day, but at present it has gone to almost ten times that much, 1000 tons per day.

Now, when your reactor becomes bigger then relatively energy losses would be lower. So, it will be give more energy efficient. When reactors are smaller, imagine ten small reactors with ten times as much as surface area, as compare to a something with capacity ten times larger. This will have lesser surface area and surface to volume ratio. Therefore, heat losses will be less.

So, the tendency is to make the reverberatory furnace as big as possible. But, then trying to operate with the bigger furnace also has operational problems. There will be other kinds of problem. So, the industry has to decide what it can do. So, this is the step where you produce from the roasted material, a matte. A matte, as I said, is a mixture of sulphide. This matte will go for converting and the purpose of converting is to remove iron. Part of that iron, you have removed earlier, by making Fe O, and removing partly, but again lot of that iron that is left there as Fe S, will be removed in the converting step. Sulphur and other impurities from matte will also be removed. For this the molten matte is produced as a result of smelting.

The molten matte produced from the smelting step is charged into a side blown converter which is a cylindrical vessel; I will show you a picture of that. With a capacity of 100 to

120 tons per of matte; it is not a continuous process, because you will charge the matte, it is like steel making, you will produce blister copper, pour it out and then take fresh amount of matte and again do converting.

So, at a time you will produce 100 to 120 tons of matte. A typical vessel will be 4 meters in diameter, 9 meters in length, so it is a big cylinder, and its line with a layer of chrome-magnesite refractory about 40 centimeter thick.

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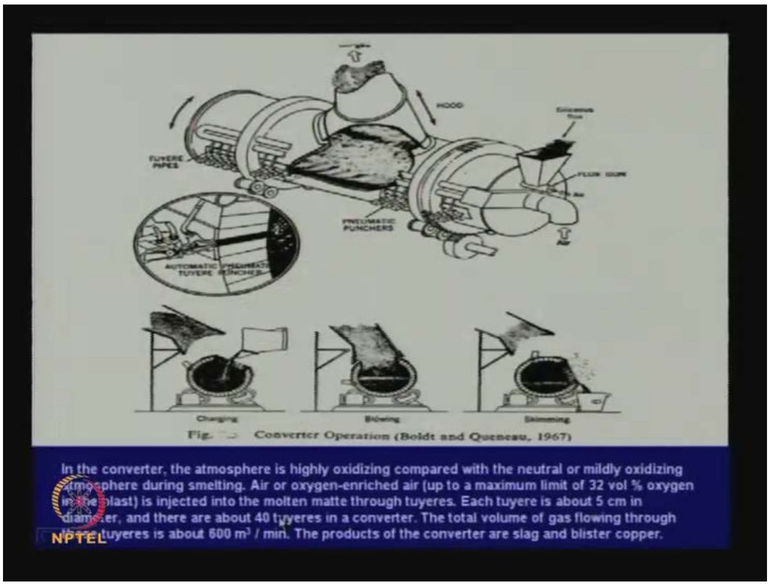

Fig. Converter Operation (Boldt and Queneau, 1967)

In the converter, the atmosphere is highly oxidizing compared with the neutral or mildly oxidizing atmosphere during smelting. Air or oxygen-enriched air (up to a maximum limit of 32 vol % oxygen in the blast) is injected into the molten matte through tuyeres. Each tuyere is about 5 cm in diameter, and there are about 40 tuyeres in a converter. The total volume of gas flowing through these tuyeres is about 600 m³ / min. The products of the converter are slag and blister copper.

Now, next figure shows you a typical side blown converter. This is the steel cylindrical vessel. There are pneumatic punchers, so that it can be rotated if necessary. This is the hood from which… This is necessary because you will have to pour out blister copper. So, that thing has to rotate. Tuyeres pipes, through which, the oxygen will blown in. There is intake of cerealicious flux because you have to create a slag. This is flux gun, how the gun it will be thrown into that etcetera. Gases will come out of here. All the details are there.

This is more important. See, this is the converter. I am looking at here from the sectional point of view. It is charged. This is the hood, at every stage; whatever the gases are coming will go out to this hood. Then this is straightened up, put straight under the hood. We start blowing oxygen from this side. And after it is blown, we can tilt it the other way; pour out the product which is blister copper. So, charge, blow, tilt the other way, and fully take out the blister copper, this is the converter operation.

Now, in the converter, the atmosphere is highly oxidizing, compared with the neutral or mildly oxidizing atmosphere during smelting. Air or oxygen enriched here up to a maximum limit of 32 volume percent of oxygen in the blast is injected into the molten matte through tuyeres. Each tuyeres is about five centimeter in diameter and there are about forty tuyeres in a converter. The total volume of gas flowing through these tuyeres is about 600 meter cube per minute. The products of the converter are slag and blister copper.

So, you have three steps. You have roasting; converting, smelting and then converting. Now, let us come to what is happening during converting. So, during converting you have starting with a mixture of sulphides; copper sulphide and iron sulphide. Then iron sulphide is converted to Fe O. It is taken out as a slag. You are left now with a metal, very often it is called a white metal, because it looks white, it is copper sulphide. Now it is copper sulphide turn to start getting oxidized.

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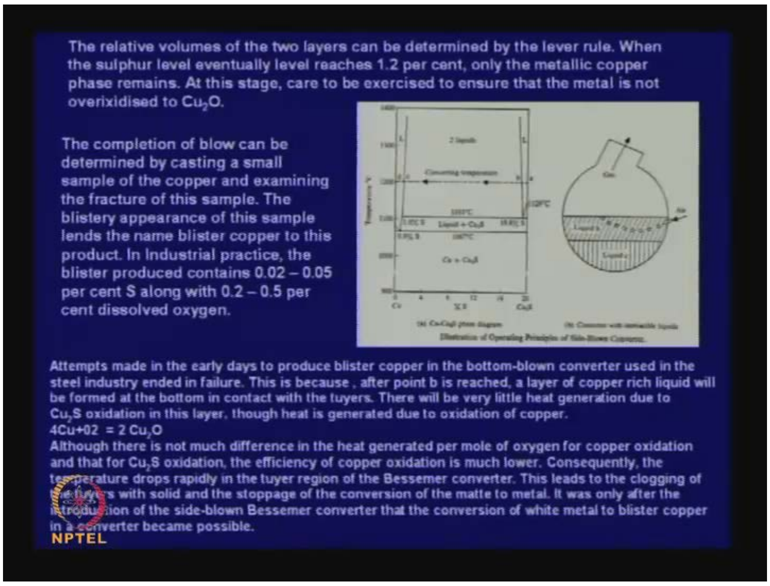

The relative volumes of the two layers can be determined by the lever rule. When the sulphur level eventually level reaches 1.2 per cent, only the metallic copper phase remains. At this stage, care to be exercised to ensure that the metal is not overixidised to Cu_2O.

The completion of blow can be determined by casting a small sample of the copper and examining the fracture of this sample. The blistery appearance of this sample lends the name blister copper to this product. In Industrial practice, the blister produced contains 0.02 – 0.05 per cent S along with 0.2 – 0.5 per cent dissolved oxygen.

Attempts made in the early days to produce blister copper in the bottom-blown converter used in the steel industry ended in failure. This is because , after point b is reached, a layer of copper rich liquid will be formed at the bottom in contact with the tuyers. There will be very little heat generation due to Cu_2S oxidation in this layer, though heat is generated due to oxidation of copper.

$4Cu+02 = 2 Cu_2O$

Although there is not much difference in the heat generated per mole of oxygen for copper oxidation and that for Cu_2S oxidation, the efficiency of copper oxidation is much lower. Consequently, the temperature drops rapidly in the tuyer region of the Bessemer converter. This leads to the clogging of the tuyers with solid and the stoppage of the conversion of the matte to metal. It was only after the introduction of the side-blown Bessemer converter that the conversion of white metal to blister copper in a converter became possible.

You gradually begin to build up Cu 2 O and then you create two layers. What are these layers and that you come to know if you look at the phase diagram here, let me go through this first. The reality volumes are the two layers and can be determined by the lever rule. When the sulphur level eventually drops to 1.2 percent, only the metallic copper phase remains and at this stage, care to be exercise to ensure the metal is not over oxidized to Cu 2 O.

Now, as I said, there is a stage comes when Cu 2 S reacts with 2 Cu 2 O to produce copper and you are left it copper and copper sulphide. And in that case, you will get two layers. Air is coming through this layer and this is the phase diagram of copper and copper sulphide. You see there is a complete separation here. This is the melting point of copper; this is the melting point of copper sulphide.

Now, if the converting operation is taking place here, you are going from copper sulphide towards this direction. You go from a to b to c to d and there is a clear separation between here and here. There is a copper layer with very small amounts of sulphur and you have copper sulphide here. This is the two layers you are getting. And we are injecting here continuously into the copper sulphide layer, copper is at the bottom. The completion of blow can be examining the fracture of the sample. The blistery appearance of this sample lends to the name blister copper to this product.

In industrial practice, the blister produced contains 0.02 to 0.05 percent sulphur; along with 0.2 to 0.5 percent dissolved oxygen. So, the blister copper, we are producing here, you will find that there is always a bit of sulphur and it will also contain some oxygen, because after all you are injecting oxygen. Now, attempts made in the early days to produce blister copper in the bottom blown converter used in this steel industry ended in a failure. Now, of course, the there is top blown converters, but in Bessemer converters had oxygen coming from the bottom. So, same thing was tried in the case of copper.

It ended up in a failure because after point b is reached, and once you have reached this point b, you are coming from copper sulphide part to the copper part. Once you reach this point (Refer Slide Time: 37:08), means after you have removed certain amount copper sulphide and produce certain amount of copper, the relative amounts you will know from the lever rule. A layer of copper rich liquid will be formed at the bottom. So, once you start producing copper, you have gone this way, a copper rich liquid will be formed at the bottom in contact with the tuyers. And there will be very little heat generation due to Cu 2 S oxidation in this layer. There is no more Cu 2 S left. Cu 2 S oxidation is generating heat. Once it produced copper and the copper would sink and cover the tuyers and because there is no heat being generated you have a problem there.

There will be very little heat generation due to Cu 2 S oxidation, though this heat is generated due to oxidation of copper. But, there is not much difference in the heat generated per mole of oxygen for copper oxidation and that for Cu 2 S oxidation. The efficiency of copper oxidation is much lower. Consequently, the temperature drops rapidly in the tuyers region of the Bessemer converter. This leads to the clogging of the tuyers with solid and stoppage of the conversion of the matte to the metal.

So, if we are trying to inject from the bottom, after sometime the process will have to be discontinue, because as copper sulphide begins to produce copper metal. That metal will come down to the bottom, and then it will get frozen, and then it will stop will interfere with the incoming oxygen. So, the tuyers will be clogged with the solid and the conversion of the metal matte to metal will stop.

So, then the industry have to come up with the invention that have a side blown converter and the conversion of white metal to blister copper in a converter becomes possible. So, from the side oxygen will be blown into the Cu 2 S layer. Copper goes on forming; it goes to the bottom as almost pure copper and copper. So, this layer gradually becomes thinner and thinner and this layer becomes thicker and thicker. When it is all over, this entire converter will be turned and the blister copper will be taken out. This is how the converter operates.

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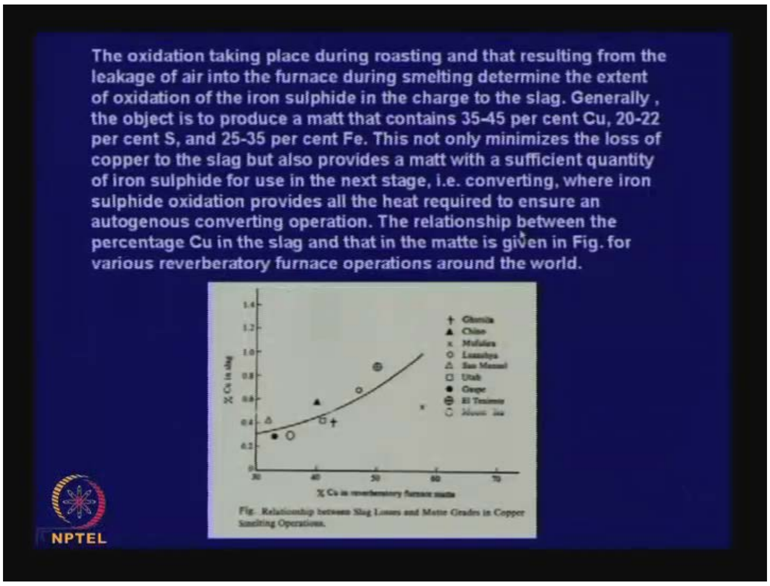

The oxidation taking place during roasting and that resulting from the leakage of air into the furnace during smelting determine the extent of oxidation of the iron sulphide in the charge to the slag. Generally, the object is to produce a matt that contains 35-45 per cent Cu, 20-22 per cent S, and 25-35 per cent Fe. This not only minimizes the loss of copper to the slag but also provides a matt with a sufficient quantity of iron sulphide for use in the next stage, i.e. converting, where iron sulphide oxidation provides all the heat required to ensure an autogenous converting operation. The relationship between the percentage Cu in the slag and that in the matte is given in Fig. for various reverberatory furnace operations around the world.

Fig. Relationship between Slag Losses and Matte Grades in Copper Smelting Operations.

Now, again I am repeating what I have said earlier that,” the oxidation taking place during roasting and that resulting from the leakage of air into the furnace during smelting determine the extent of oxidation of the iron sulphide in the charge to the slag”. During roasting it is an oxidation process. There is some leakage of air also into the furnace during smelting. All these tend to oxidize iron sulphide to iron oxide and it goes into the slag. Generally, the object is to produce a matte. There should be any that contains 35 to 45 percent copper, 20 to 22 percent sulphur and 25 to 35 percent iron in the matte. This iron is as sulphide; that copper also is a sulphide.

This not only minimizes the loss of copper to the slag, but also provides a matte; again there should be a need, with a sufficient quantity of iron sulphide for use in the next stage. Now, in the next stage where there is converting, the iron sulphide oxidation will provide all the heat required to ensure an autogenously converting operation. You need to have certain amount of iron sulphide because that will oxidize and begin to give you lot of heat so that you do not need any extra heat in the converter. Now, the relationship between the percentage copper in the slag and that in the matte is given in the figure (Refer Slide Time: 41:52).

Lot of experiments has been done in the industry to find out how to cut down copper losses in the slag. What has been found is something you should expect from common sense that if you have a very rich matte with a lot more copper then copper losses in the slag perhaps will also be more. That is what it says. The relationship between the percentage copper in the slag and that in the matte is shown in the figure for various reverberatory furnace operations around the world.

So, wherever we are producing matte in the smelting step; data have been taken and you have been found that percentage copper in the reverberatory furnace made the higher it is; the higher will be the copper losses in the slag. But you know it is never more than one percent. The copper losses are not that alarming.

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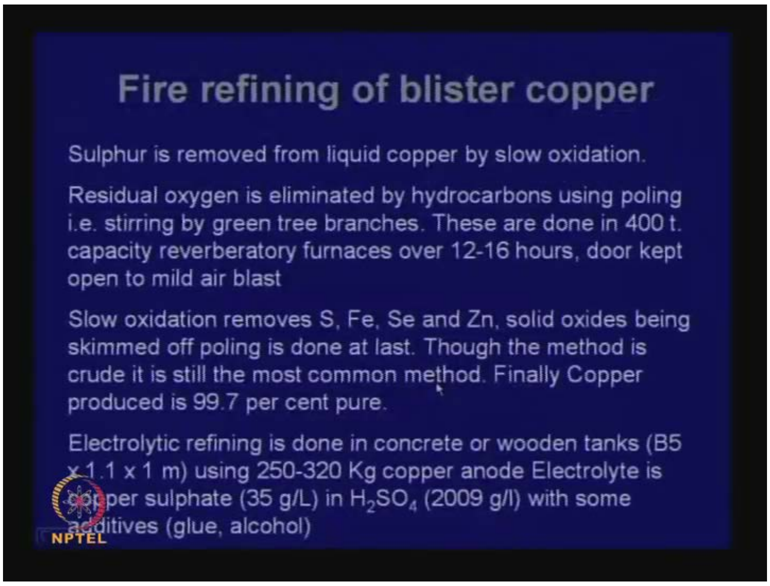

Fire refining of blister copper

Sulphur is removed from liquid copper by slow oxidation.

Residual oxygen is eliminated by hydrocarbons using poling i.e. stirring by green tree branches. These are done in 400 t. capacity reverberatory furnaces over 12-16 hours, door kept open to mild air blast

Slow oxidation removes S, Fe, Se and Zn, solid oxides being skimmed off poling is done at last. Though the method is crude it is still the most common method. Finally Copper produced is 99.7 per cent pure.

Electrolytic refining is done in concrete or wooden tanks (B5 x 1.1 x 1 m) using 250-320 Kg copper anode Electrolyte is copper sulphate (35 g/L) in H_2SO_4 (2009 g/l) with some additives (glue, alcohol)

Now, once we have produced a blister copper, we have produced an impure copper. That copper will now have to be refined and refining of copper is a very elaborate process. In the sense that it will give whole lot of products, let us see how. One is first of all there is some sulphur. The sulphur can be removed from the liquid copper by slow oxidation. If we have the copper pool, the blister copper in the molten state and it is slowly oxidized then all the sulphur will be removed as S O 2.

Some copper might get oxidized also, and in the process some oxygen may go into the copper. So, to eliminate that oxygen now, the industry years ago, have found a very simple process, which is still applied in industry. There is a pool of copper which has to be refined; it has impurities, it had sulphur. That sulphur is removed by keeping it through a slow oxidation that can be done in a reverberatory furnace. Just keep the door open and the air leakage itself to gradually remove all the sulphur. But, the air also then goes into copper. We want to remove that and that is done by a process called Poling.

Poling is stirring the bath with green branches taken from trees. It is a very crude process, but very effective process, and industry even today apply the technique. When green branches are taken from trees and those branches are use to stir the bath, those branches generate reducing gases like methane, and the methane will reduce the oxygen. People have tried in modern industry to remove that oxygen by hydrogen injection, but that is too elaborate and too complicated, hence industry still uses poling and it is done by stirring green branch trees.

This is done in 400 ton capacity reverberatory furnace where 12 to 16 hours door kept open to mild air blast. This is the technique. Now, during this slow oxidation many other things are also removed such as sulphur, iron, selenium and zinc. Solid oxides being skimmed off and poling is done at the end. So, initially we allow lot of oxidation of the bath for many hours and oxides keep on floating to the surface and they are skimmed off. We allow all the impurities mentioned to get oxidized and get removed. When we are sure that all those have been gone, we know there is lot of oxygen has gone in now, so it will be poled using green branches. So, poling is done at the end. Though the method is crude it is still the most common method.

Now, finally, after we have removed all these impurities by slow oxidation we get a copper which is 99.7 percent pure. Now this copper has to be refined further. And it will be done by electrolytic refining, which is done in concrete or wooden tanks of dimensions are roughly given, using 250 to 320 kg copper anode, a thick anode, which is that impure copper in a copper sulphate solution, 35 gram per liter in sulphuric acid. This in this is not nine.

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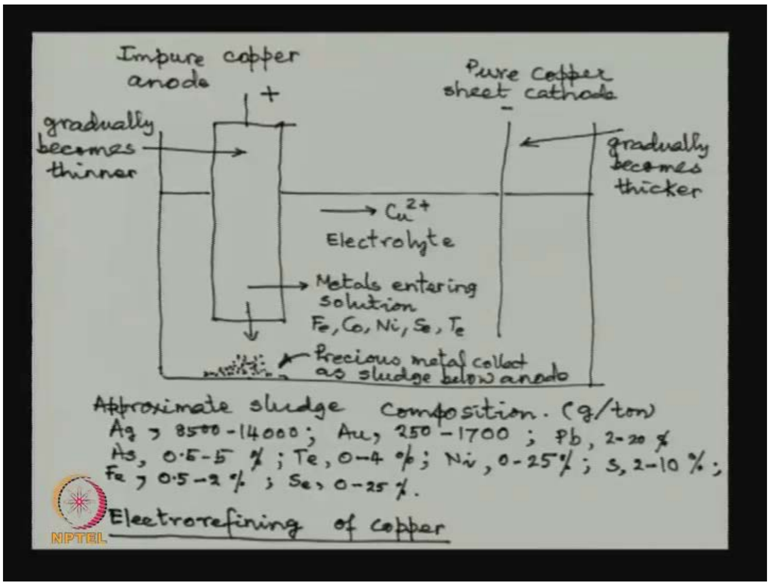

Approximate sludge composition. (g/ton)
Ag, 8500 - 14000; Au, 250 - 1700; Pb, 2-20 %
As, 0.5-5 %; Te, 0-4 %; Ni, 0-25%; S, 2-10 %;
Fe, 0.5-2 %; Se, 0-25 %.

Electrorefining of copper

It should be zero with some additives like glue and alcohol. Why glue and alcohol, because, we get a nice cathode deposits. Now, the scheme is simple. The impure copper will be made into a thick anode and there is a pure copper sheet cathode. We have the electrolyte with copper ions in that. As electro refining starts copper will dissolve from anode and it will get deposited on the cathode. Using glue and other additives is to make sure that the deposit is very coherent. So, this gradually becomes thinner and this gradually becomes thicker.

Now, what happens when copper is coming from here to here, what happens with the impurities that are beginning, this. Now there two things can happen. There are some metals here which enter the solution because they can dissolve in the solution. Like, if you have impurities like iron, cobalt, nickel, selenium, tellurium, we have sulphuric acid electrolyte, they will go into the solution. But, there are in this impure anode are precious metals. As copper leaves this anode while these impurities go into the solution, the precious metals simply drop below the anode to form sludge.

Below the anode there will be some insolubles which you call the sludge and that contain all the precious metals. So, all the precious metals that were in the original concentrate, they will come all through, because there will always been in copper sulphide and it will end up in the copper finally. And only here it will get separated, because other impurities can dissolve, copper will go through electrolytic refining to the other electrode. And the sludge that comes, the approximate composition is this, which are grams per ton.

Silver, gold, lead, arsenic, tellurium, nickel etcetera, depending on the amount of sludge, considerable amount of this precious metals are collected and there price actually can account for the cost of electro refining and many other things.

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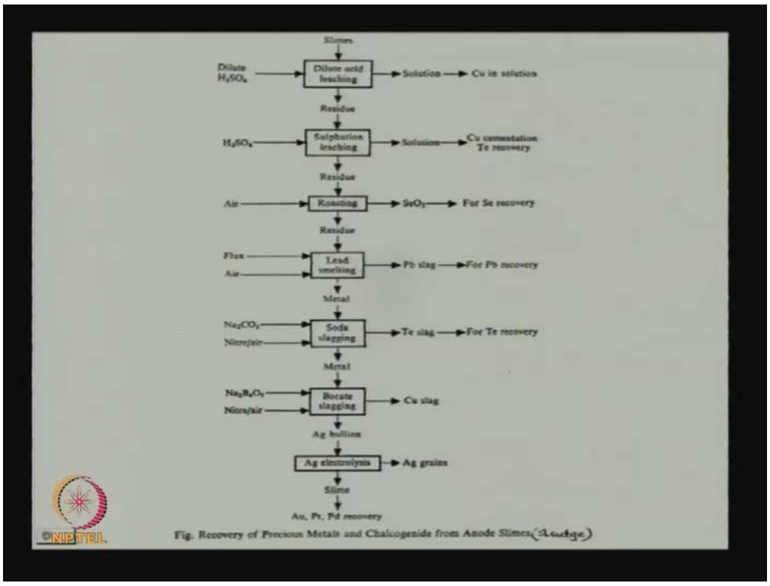

Fig. Recovery of Precious Metals and Chalcogenide from Anode Slimes (sludge)

Now, you got sludge. There, from the sludge again we have to recover all the precious metals one by one. And for that there is again an elaborate flow sheet. Let me look at that flow sheet. We use the word, ‘sludge’ and also sometimes the word, ‘slimes’. This is the anode sludge or slimes that collect below the anode. With dilute sulphuric acid leaching, any residual copper that may be in the sludge can be taken into solution. Then there will be the residue, the residue will be treated with slightly stronger H 2 S O 4.

And we will say that we will do what is called, ‘sulphation leaching’ in the solution. There will be copper and copper cementation can give you tellurium, means by adding copper it may get tellurium. The residue by roasting will give selenium oxide, if you go for selenium recovery. There will be a residue, which will go for lead smelting to get lead. You get a metal and it will go through some other process to get another metal; some other step and finally, we can recover silver grains etcetera and the slime will have gold, platinum, palladium. These are processing steps of chemistry that have been developed over many years. So, the sludge that has all these valuable impurities, it can be treated by chemical steps to recover them. And I need not go into the details of this. So, this is the basis of copper metallurgy.

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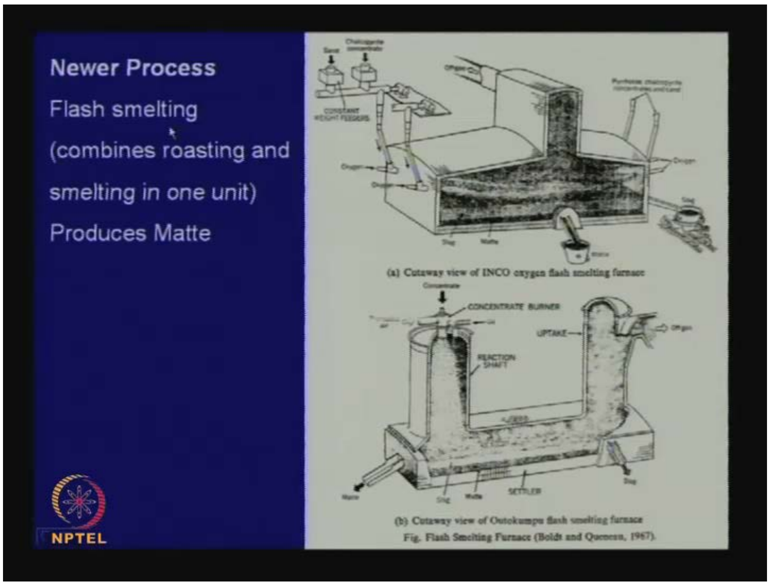

Newer Process

Flash smelting

(combines roasting and smelting in one unit)

Produces Matte

(a) Cutaway view of INCO oxygen flash smelting furnace

(b) Cutaway view of Outokumpu flash smelting furnace

Fig. Flash Smelting Furnace (Boldt and Queneau, 1967).

But, now there have been developments and remember once we have talked about flash roasting, flash smelting, etcetera. When roasting is done in an earth roaster, where there are rotating platforms and the calcine is going from one bed to another bed to another bed, so that things are exposed to the oxidizing atmosphere. People found that maximum an oxidation takes place during flight, not when they are sitting on a rotating platform; it is only when they are discharge from one to the other; maximum takes place. So, people argued why have these platforms, why not let the practical drop from the top straight down to the bottom and during flight they get oxidized the way you want to do that, in a furnace.

This is the basis of newer process of flash smelting, means smelting in a flash and that combines roasting and smelting in one unit. There are different kinds of flash roasters. Here is a cutaway view of Inco flash roaster. You see from here chalcopyrite concentrate is coming here; oxygen is creating an oxidizing environment. So, during the process of this flights, all the reaction that you want, would takes place. You produce a matte here and you produce a slag here. Now, of course, this means you need to control the oxidizing potential very accurately. So, from this side oxygen comes in, because from the end you have putting oxygen, the oxidation potential will be higher here, because you know as you go towards from matte generation of matte, you need higher and higher oxidation potential.

So, initially what is happening is the sulphides are getting roasted then by the time it is coming higher oxidation potential it forms a matte, and matte comes here, slag comes here. Similar process here is cutaway view of how to come to flash smelting furnace, I think it is there in Ghatshila. Here concentrate is coming from here. There is a concentrate burner. This is the reaction shaft and from here it is the off-gases are coming in the process of flight and the fuel air is all here, you produce like a matte. So, you have expedited the process of roasting or smelting. They have combined in one step in a flash roaster. We will find that there is a newer process where we will have one more step, the conversion of matte to blister copper is also combined in one step. Those are the ultimate, but the more you combine the steps, the more difficult it becomes to control things. You need higher technology. I will come to that in the next lecture.

Thank you very much.