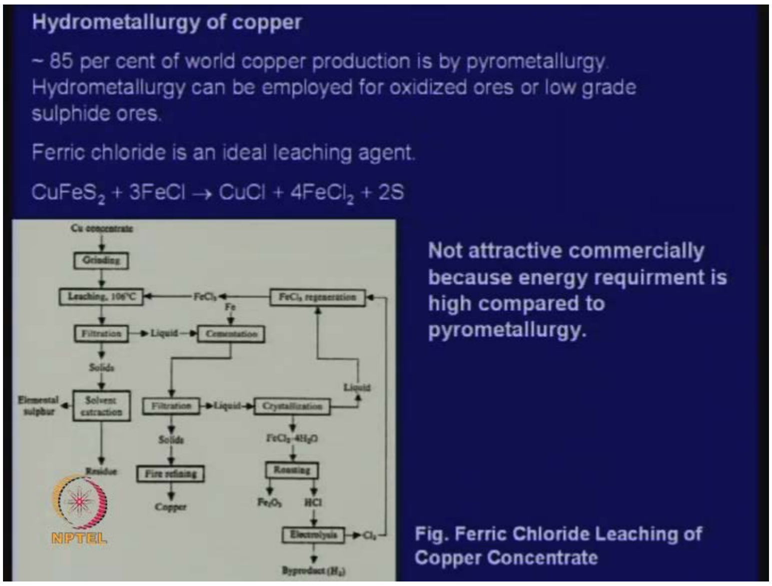
Non-ferrous Extractive Metallurgy

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

Module No. # 01
Lecture No. # 23
Hydrometallurgy of Copper

Friends, I will in this lecture discuss hydrometallurgy of copper.

(Refer Slide Time: 00:29)



Hydrometallurgy of copper

~ 85 per cent of world copper production is by pyrometallurgy. Hydrometallurgy can be employed for oxidized ores or low grade sulphide ores.

Ferric chloride is an ideal leaching agent.

$CuFeS_2 + 3FeCl \rightarrow CuCl + 4FeCl_2 + 2S$

Not attractive commercially because energy requirment is high compared to pyrometallurgy.

Fig. Ferric Chloride Leaching of Copper Concentrate

Now, you have known by now, that 85 percent of the copper is produced industrially by pyrometallurgical operations and we have discussed them in detail. In hydrometallurgical operations, no high temperatures are involved, things happen in eco solutions, which means you have to bring copper from the mineral into eco solutions.

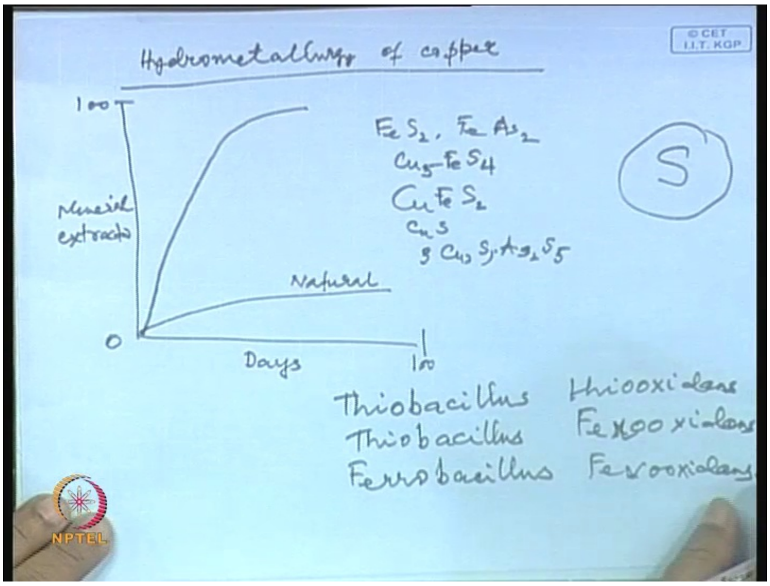
Now, for centuries people have found that in copper mines where water accumulates, there is copper in a mine waters. In other words, in natural conditions also, from from the copper in the mines where there are pools of water, copper comes into solution. And actually such solutions were used centuries ago, to produce copper by cementation using iron powder or iron finings.

You know, if you have copper sulphate and you put iron in that, copper precipitates, iron dissolves. So, in the mine waters where the copper was in solution and the solution could be tell, you know if you put copper sulphate, you know it is blue, people recovered copper that way.

Now, this was known, but it takes months, if not years to produce a soluble solution suitable for commercial exploitation. You cannot put copper concentrates in a pond and think that, it will dissolve and give you a solution of copper, because this sulphide; copper sulphate that does not happen; it will happen it will take years.

But in the early part of 20th century, it was accidentally discovered the certain types of bacteria considerably accelerated this process of natural conversion of copper into soluble soluble sulphates. Schematically, we can show it like this.

(Refer Slide Time: 03:08)



Say, suppose approximately if took, if it took 100 days for the natural process to recover 100 percent mineral extracted from the mines with bacteria, it will be far more rapid. And they were surprised that they were certain mines where very quickly, that in mine waters soluble copper was appearing.

Then, they found this is true in natural conversion of many kinds of sulphides, such as not only iron sulphide or some other arsenopyrite. It will be for other copper minerals, of course for chalcopyrite, there are other minerals of sulphur, of copper, various minerals.

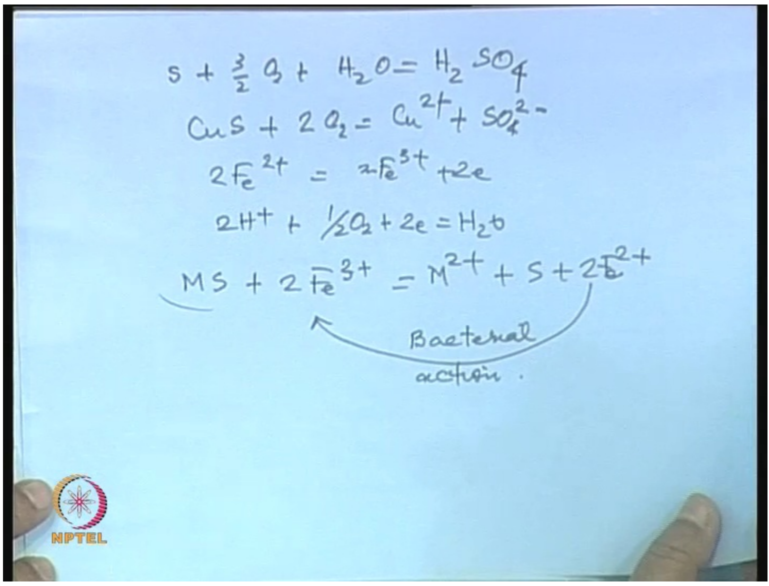
They found they were all sensitive to the bacterial a leaching phenomenon, there are many others, you can consider more book.

So, actually it was not copper that was responsible, it was the sulphur that was critical in bacterial leaching. And finally, the bacteria bacteria that were studied and identified were found to be of families of which are known as thiobacillus thiooxidans or thiobacillus ferooxidans ferooxidans and ferrobacillus, these are the three most important types.

What do these bacteria do, the role of these bacteria is to grow in purely inorganic media, this bacteria do not need oxygen air to grow. They they obtain their energy by oxidizing inorganic substances such as sulphur and thiosulphate, the oxidation of these inorganic constituents give them the energy, and oxidation of ferrous iron to ferric iron that conversion give the energy to survive and grow.

A biological catalyst called enzyme is also synthesized by the bacteria that helps in acceleration of the rate of oxidation reactions. Forget about what the bacteria do, I will not go into the details of that, but the essentially these bacteria speed up the processes of oxidation of sulphur.

(Refer Slide Time: 07:09)



$$S + \frac{3}{2}O_2 + H_2O = H_2SO_4$$

$$CuS + 2O_2 = Cu^{2+} + SO_4^{2-}$$

$$2Fe^{2+} = 2Fe^{3+} + 2e$$

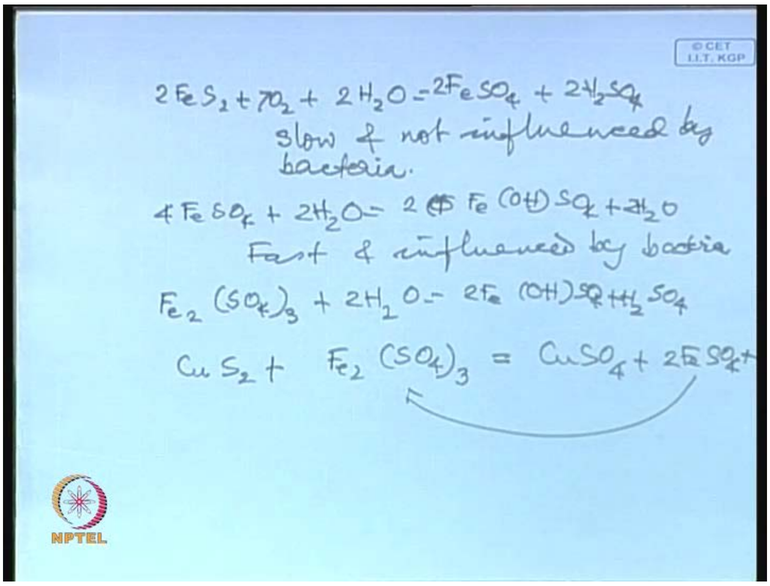
$$2H^+ + \frac{1}{2}O_2 + 2e = H_2O$$

$$MS + 2Fe^{3+} = M^{2+} + S + 2Fe^{2+}$$

Bacterial action.

Then dissolution of copper, conversion of ferrous iron to ferric iron, other reactions for oxidation of iron, essentially what happens is that, if we write the metal sulphide oxidation by ferric iron to be this. One of the functions of the bacteria is to reoxidize ferrous iron to ferric iron so that we are constantly getting ferric iron that will dissolve the metal sulphide to produce metal ions in solution; this is what the bacterial oxidation does.

(Refer Slide Time: 08:49)



© CET I.I.T. KGP

$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$

slow & not influenced by bacteria.

$4FeSO_4 + 2H_2O = 2Fe(OH)SO_4 + 2H_2O$

Fast & influenced by bacteria

$Fe_2(SO_4)_3 + 2H_2O = 2Fe(OH)SO_4 + H_2SO_4$

$CuS_2 + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 +$

And in the case of copper, it is generally believed that in the case of iron, this reaction is what brings soluble F e S O 4; this is slow and not influenced by bacteria. But under slightly alkaline or acidic condition, this ferrous sulphate is reacts to produce this, this is fast and influenced by bacteria. And then the ferric sulphate, this will hydrolyses and sulphuric acid is liberated by reaction like this, then we have many other reactions, essentially the dissolution of copper sulphide, we can write as reaction with ferric sulphate to produce copper sulphate 2 F e S O 4 plus 2 S and constantly the ferrous iron is converted to ferric iron by bacterial action.

So, if there are bacteria, then this goes on and on and the leaching reaction is speeded up. Similar things happen in the case of uranium ores also, and uranium ores also have been found to come into solution through the reaction of not these bacteria, there are other kinds of bacteria.

Now, this bacteria are sometimes there already or they can be introduced, they can be first grown in the laboratory and then introduced in the environment. For these bacteria, there are also some conditions for survival and growth. I mean in the temperature should be right, they operate well in medium temperatures, in very cold climates, they will not to work, you get temperatures very very become very high, they will not survive, there are some conditions of p h etcetera etcetera etcetera.

Now, it was found where it happened, naturally the conditions were very right, but we can create those conditions if we know how bacteria leaching will be very effective. Now, very large scale r and d work on such bacteria leaching of some sulphide ores are being carried out in our country, but still not a commercial process. For a commercial process, for hydrometallurgy, we have to use chemicals to take copper into solution.

So, I will not discuss the effects, the bacteria leaching for too much. I did not mention the conditions, let me mention that, and then you will appreciate why bacteria leaching can be ideal for our condition. First of all, temperature has a marked effect on conversion of ferrous to ferric iron through bacterial action and this is the most critical step. Maximum bacterial activity is between 30 to 35 degree centigrade, these are the ideal temperatures available in our climate, 30 to 35 degrees the bacteria are most effective.

If the temperature is above this, bacterial activity would come down; beyond 50, it will almost stop and at a temperature higher than 70 degrees, of course micro organisms become sterile and they are destroyed. Of course, in nature there are no temperatures like 70 degrees, but you know people have done to find out what happens to the bacteria, they becomes sterile and then they will die.

If the temperature decreases below 30 degrees, the activity also decreases and at a temperature below 18 degree centigrade, there is hardly any bacterial activity. So, in cold climate bacterial activity cannot be exploited, our country has a ideal climate, 30 to 35 degrees.

Of course, they are living organisms. So, they have to be fed with nutrients some food to grow and some obvious nutrients would be where there is ferrous iron like F e S O 4, F e S 2, ammonium sulphate, ferrous sulphate, these are the nutrients to the leaching solution. If they are added, then the increase the ferrous iron concentration increases and therefore, conversion from ferrous to ferric which is the, which on which the bacteria thrive, that also is there. And bacteria become more active, and rate and extent of conversion both will increase. There are other factors like, it is a surface phenomenon, after all bacteria will reside on the surface of the mineral particle and react there.

Therefore, the particle size of the solids which are undergoing bacterial leaching are important, fine as solids will be more amenable to bacteria leaching. And once it ground the ore, surface area available is lot more leaching rate will be high, because surface area for bacteria too come and grow is more. There are some problems always, you must understand, if you make the deposit very fine, then the bacterial action may begin to draw because the permeability you drop. Because in all these, air needs to be supplied you will find in all reactions air is required.

So, if the particles have very fine, the permeability is low and air cannot get access to all the sides where bacterial action is taking place. It will also help if you have a shallow bed, means if you have a very deep bed with lot of water level, then the bacterial action is very effective, it should be a shallow bed, you know wide area with fine concentrates lying around ideal for bacterial action.

What about direct sunlight? In our country there is a lot of sunlight, it is been found that if there is too much of direct sunlight, then the bacterial action is not destroyed, but it is very much adversely effected, like you know all humans also. You know, if if we are put in the sun in a desert, we really cannot be very active, we need hot humid conditions. But not too much of light, bacteria will not die, but they will not be so active.

It is very sensitive to ultraviolet light; even a short exposure will completely stabilize bacteria. So, preferably some kind of a shade would be ideal for bacterial action, then it needs aeration also and they are active only in acid media. So, the acidity will have to be controlled p h will have to be controlled, they have to be aeration and ideally a p h value of 2 to 3.5 should be maintained, that kind of a p h value is ideal both above and below this bacterial action will drop, at p h value around 6 when it is almost becoming neutral oxidation is inhibited.

And if it becomes alkaline, means if it is goes well beyond 7 bacteria die. So, the bacteria lived in acid conditions, not in alkaline conditions. Supply of oxygen is vital and there has to be aeration in a portion of the bacterial solution and subsequently the aerative solution will have to be supplied to this side.

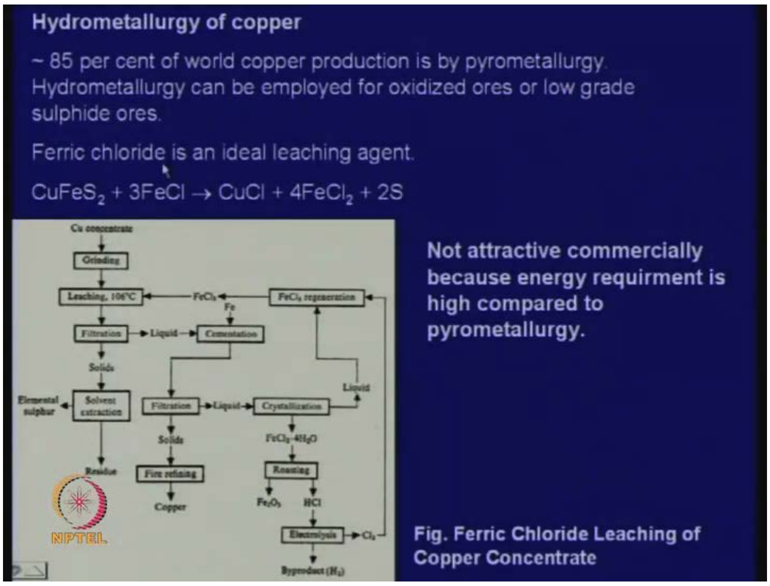
So, from a central aerated solution it is sprinkled on to the rest of it. So, there are this conditions, but the scope is very good in India for bacterial leaching operations where the sulphide ores are often lean and they must be exploited by hydrometallurgical methods. The climate often hot and humid is ideally suited for bacterial activity, but then strangely most r and d work in bacterial leaching has been done in the west. In our country, it is only last 15 or 20 years that we have started this work and there are some fields where bacterial leaching is being tried out.

There is also a question of finding the right kind of bacteria. I think in the west, they have experimented with different kinds of bacteria that are highly effective. People say that, if a bacteria is found to be very effective in one climate, it may not be so in another climate, but then you know like all living organisms, bacteria can also acclimatize themselves in climate changes.

So, even if initially some bacteria may not be so effective, when you try it out given time they might start becoming active. So, these are various studies that are being carried out in our country to find the right kind of bacteria, the right kind of conditions. And at least in the case of sulphide minerals, there are now tries being carried out in some fields and this is, this from the Ghatsila based Copper Corporation that these studies are happening in somewhere in Madhya Pradesh.

But as I said, these are still in not in; you know in the r and d stage, this is not found an industrial application. For industrial application, we need a process where chemically we will convert in the copper minerals into a solution.

(Refer Slide Time: 21:06)



Hydrometallurgy of copper

~ 85 per cent of world copper production is by pyrometallurgy. Hydrometallurgy can be employed for oxidized ores or low grade sulphide ores.

Ferric chloride is an ideal leaching agent.

$CuFeS_2 + 3FeCl \rightarrow CuCl + 4FeCl_2 + 2S$

Not attractive commercially because energy requirment is high compared to pyrometallurgy.

Fig. Ferric Chloride Leaching of Copper Concentrate

Now, let see how we do that. Now, there are two ways, two things that are become common that get soluble copper chloride or produce soluble copper sulphate. Both chloride in solution and sulphate in solution can be electrolyzed to produce copper through electrolysis of eco solutions.

Now, for copper chloride rod, the copper concentrate has to be ground always. Whenever we are going for leaching, we have to go for fine ores leaching at about 106 degrees which means you need again an auto claim, why above 100 degrees? Because, we accelerate the process of leaching.

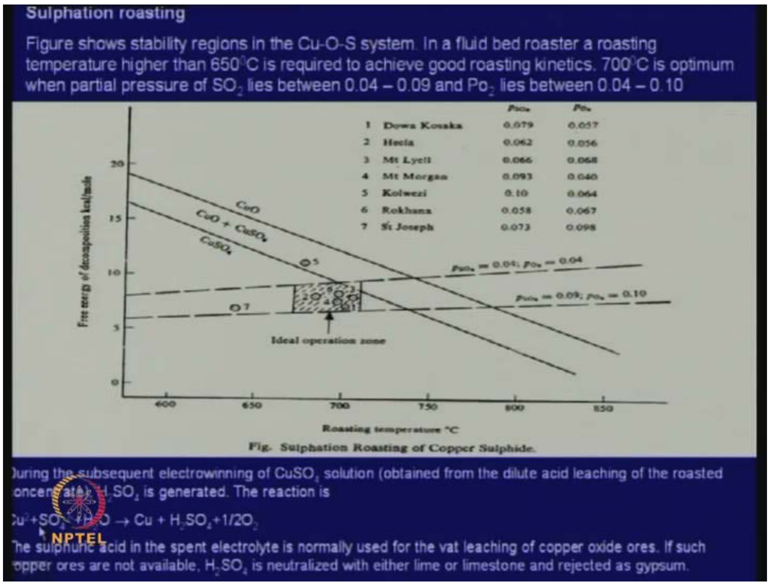
Leaching will be by a ferric chloride solution, it is called ferric chloride leaching process. Copper will be taken into solution, you filter, this solids will go for solvent extraction to get elemental sulphur, the liquid will go to the cementation route, that you put iron filings, copper will precipitate, the filtration will give a liquid from which through crystallization we can be recover F e C l 2, by roasting we produce hydrochloric acid gas. And then after electrolysis, we can get hydrogen and this chlorine which will go for ferric chloride regeneration, because from here it is coming here and so, we will get copper.

Unfortunately, this process always sound in theory is not very attractive from the energy point of view. Surprisingly, although it is a room temperature process, on the whole we needs more energy than compared to a pyrometallurgical process.

You might think it is ironical, but in this case it is not. Because, you have seen that in copper metallurgy reactions are exothermic, you are not supplying heat from outside to carry out the reactions here, essentially supplying heat to take care of the heat losses in some reactors. Otherwise if you do things well, you do not need any supply.

So, the bigger the reactor, the more continuous the process, the heat requirements become lower, whereas in a process like this, of course grinding is there also in pyrometallurgy. But in all this leaching, you need an auto clay evaporation, you need electricity to operate autoclaves at higher temperatures, you need lot of this pumping of fluid from here to there, you need solvents which are expensive, you need filtration, the operational steps are there, there is a fire refining here finally to get copper, all this actually adds up to the energy requirements. So, it has not been found very attractive, commercially, but the next one is more attractive.

(Refer Slide Time: 24:33)



Sulphation roasting

Figure shows stability regions in the Cu-O-S system. In a fluid bed roaster a roasting temperature higher than 650°C is required to achieve good roasting kinetics. 700°C is optimum when partial pressure of SO_2 lies between 0.04 – 0.09 and Po_2 lies between 0.04 – 0.10

		p_{SO_2}	p_{O_2}
1	Dowa Kosaka	0.079	0.057
2	Hecla	0.062	0.056
3	Mt Lyell	0.066	0.068
4	Mt Morgan	0.093	0.040
5	Kolwezi	0.10	0.064
6	Rokhana	0.058	0.067
7	St Joseph	0.073	0.098

Fig. Sulphation Roasting of Copper Sulphide.

During the subsequent electrowinning of $CuSO_4$ solution (obtained from the dilute acid leaching of the roasted oncentrate) H_2SO_4 is generated. The reaction is

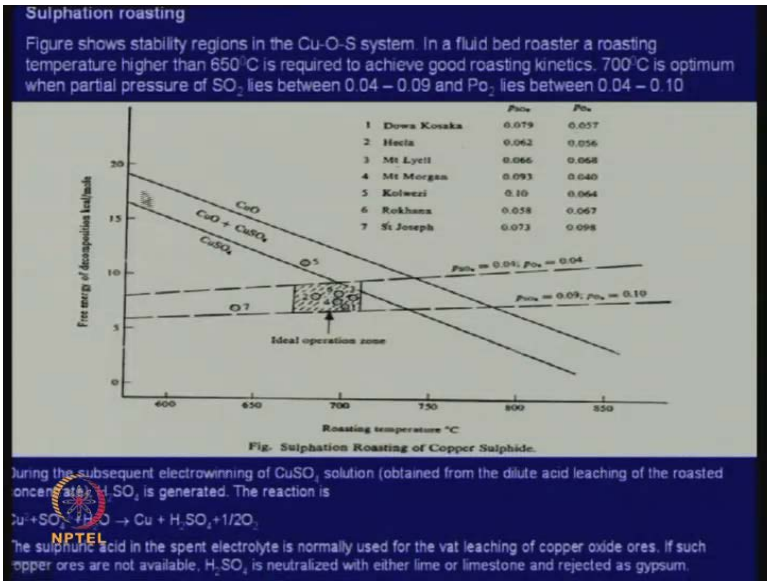
$Cu^{2+} + SO_4^{2-} + H_2O \rightarrow Cu + H_2SO_4 + 1/2O_2$

The sulphuric acid in the spent electrolyte is normally used for the vat leaching of copper oxide ores. If such opper ores are not available, H_2SO_4 is neutralized with either lime or limestone and rejected as gypsum.

It is to get copper sulphate into solution, now one’s obvious way will be that, you take copper pyrites concentrate and you roast to produce copper oxide and that dissolve by sulphuric acid to get copper sulphate, but no, there is a simpler way of doing that. If you go back to my lectures general lectures on roasting, we have seen that if you take a metal oxide and if you oxidize metal sulphide and oxidize, you can generate a whole whole range of products, could be a lower oxide, could be a sulphate, could be a compound which both has some oxides, some sulphate etcetera etcetera.

It all depends on how you control a partial pressure of sulphur and partial pressure of oxygen. So, the copper sulphide can be converted straight to copper sulphate by roasting operation. And then that copper sulphate would simply dissolve in water, you do not have to bring in acid, as a matter of fact in that process, you generate S O 2 which you go for sulphuric acid generation.

(Refer Slide Time: 26:17)



Sulphation roasting

Figure shows stability regions in the Cu-O-S system. In a fluid bed roaster a roasting temperature higher than 650°C is required to achieve good roasting kinetics. 700°C is optimum when partial pressure of SO_2 lies between 0.04 – 0.09 and Po_2 lies between 0.04 – 0.10

		P_{SO_2}	P_{O_2}
1	Dowa Kosaka	0.079	0.057
2	Hecla	0.062	0.056
3	Mt Lyell	0.066	0.068
4	Mt Morgan	0.093	0.040
5	Kolwezi	0.10	0.064
6	Rokhana	0.058	0.067
7	St Joseph	0.073	0.098

Fig. Sulphation Roasting of Copper Sulphide.

uring the subsequent electrowinning of $CuSO_4$ solution (obtained from the dilute acid leaching of the roasted oncentrate), H_2SO_4 is generated. The reaction is

$u^{2+} + SO_4^{2-} + H_2O \rightarrow Cu + H_2SO_4 + 1/2O_2$

he sulphuric acid in the spent electrolyte is normally used for the vat leaching of copper oxide ores. If such opper ores are not available, H_2SO_4 is neutralized with either lime or limestone and rejected as gypsum.

Now, look at this diagram, this figure shows the stability regions in the C u O S system in a fluid bed roaster. A roasting temperature higher than 650 is required to achieve good roasting kinetics, 700 degree centigrade is optimum when partial pressure of S O 2 lies between this and this and P o 2 lies between this and this.

Let see what is that we are plotting here, we are plotting free energies of decomposition of the whatever is written here as a function of temperatures, free energies of decomposition, mind you. This is the line for C u O, this is the line for C u O, C u O S O 4, and this is the line of C u S O 4. We have also plotted here the line for P S O 2 and P o

2 combination of 0.4 and 0.4 and P S O 2 and P o 2 combination of 0.9 and 0.1, more or less 0.1 0.1.

Now, if we had somewhere here, we will always produce copper sulphate. If you go into this region, will produce C u C u S O 4, if you go beyond this, will produce C u O. Going beyond this means, going to a very high temperatures and it is more easily done, if you have the S O 2 or P o 2 things high.

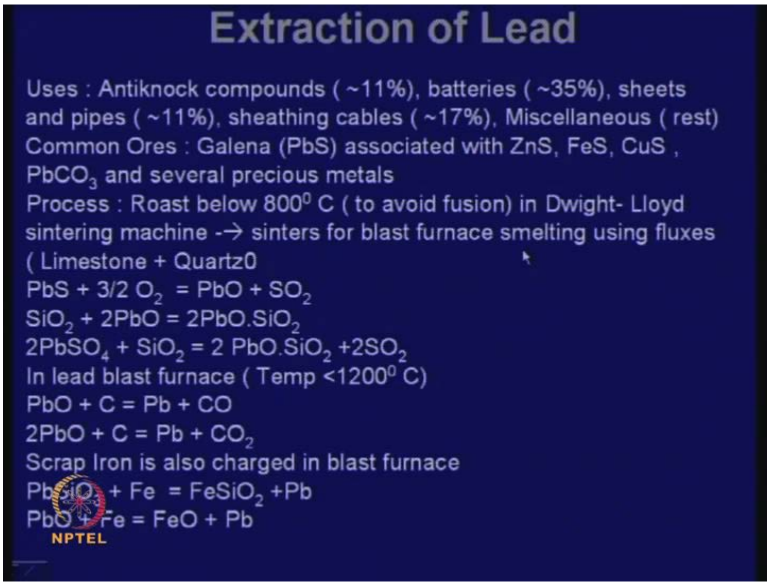
Now, the ideal operational zone is here. In this zone, we produce copper sulphate that is ideally suited for going into solution. And these are the names of the various processes, how they operate, see these are a processes from different countries are named here in different, there are many plants operating, these are the names, who and they use this combination of S O 2 and O 2 to get directly from copper sulphide copper sulphate.

And this copper sulphate would be taken into solution, and then during subsequent electro winning of copper sulphate solution obtained from the dilute acid leaching of the roasted concentrate C u H 2 S O 4 is generated.

The reaction is C u S O 4 H 2 O C u half O 2, the sulphuric acid in the spent electrolyte used for the vat leaching of copper oxides ores. If such copper oxide ores are not available, H 2 S O 4 is utilized with either lime or limestone and rejected as gypsum.

So, some amount of H 2 s o 4 will be used to dissolve some C u O into solution or into we are also getting soluble sulphate by a control roasting operation.

(Refer Slide Time: 29:38)



Extraction of Lead

Uses : Antiknock compounds (~11%), batteries (~35%), sheets and pipes (~11%), sheathing cables (~17%), Miscellaneous (rest)
Common Ores : Galena (PbS) associated with ZnS, FeS, CuS , $PbCO_3$ and several precious metals
Process : Roast below 800^0 C (to avoid fusion) in Dwight- Lloyd sintering machine -→ sinters for blast furnace smelting using fluxes (Limestone + Quartz0
$PbS + 3/2\ O_2 = PbO + SO_2$
$SiO_2 + 2PbO = 2PbO.SiO_2$
$2PbSO_4 + SiO_2 = 2\ PbO.SiO_2 + 2SO_2$
In lead blast furnace (Temp $<1200^0$ C)
$PbO + C = Pb + CO$
$2PbO + C = Pb + CO_2$
Scrap Iron is also charged in blast furnace
$PbSiO_3 + Fe = FeSiO_2 + Pb$
$PbO + Fe = FeO + Pb$

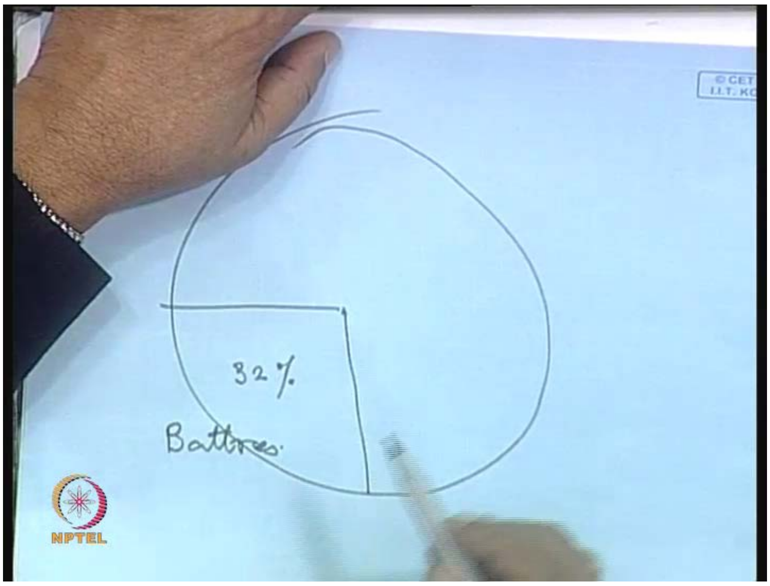
I would stop this subject here, and now I would like to move into another a metal and that is lead.

Now, let me mention here that there are experts who work on copper metallurgy, there are experts who who who work only in one segment of copper metallurgy, one can discuss in detail either roasting or smelting or converting, one can discuss with theory of all this, we can talk about the plant design, the process design, the equipment design.

But basically, I think in this course, what we need to do is to get an over view of the entire subject of production of non ferrous metals. So, I am going to some basic concepts and at the end, I would like to come back to one or two extraction of processes.

I will look at them little more critically, taking as a specific example, how you analyze for energy, how you analyze for process steps. But at this moment, let me rush through all this metals without going in to too much of detail. So, I move on to lead, now the lead finds many many uses.

(Refer Slide Time: 31:20)



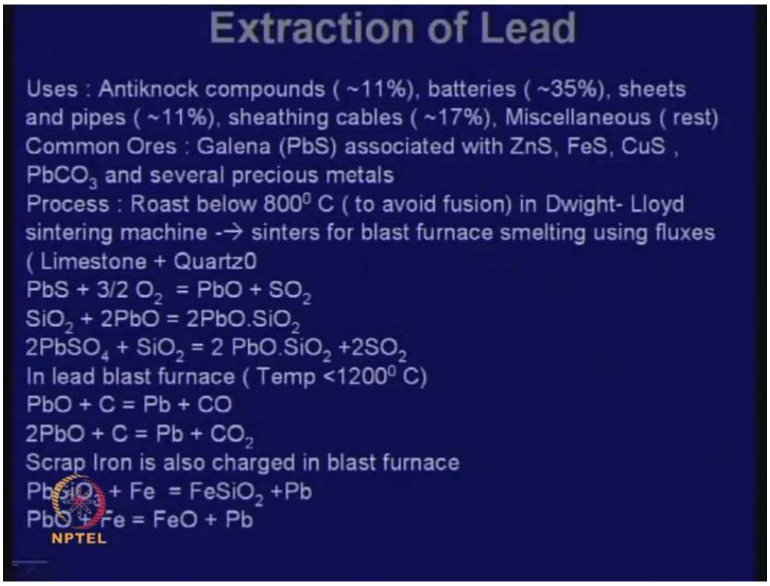
And maybe I can draw a diagram for you to make it simpler, you know that batteries constitutes almost a third of that, 32 percent going to batteries, this is the more important.

Then comes antiknock compounds we use in cables, 17 percent sheets and pipes, there are miscellaneous uses in many things. So, lead is a very very important metal not one time, lead because it is it can be found very easily, use to be, use to use, were used in piping. Even in our childhood, in our wash basins, it was connected to the water supply through lead pipes. And you will be surprised to know that the Romans used lead pipes for their water supply, because there was no other material easily available at that time, they did not have those quantities of iron pipes. And lead was also very easy to lay down, it could be it was flexible, it could be given any shape they wanted, it could be bent, it it could be also may be diameter could be may increased or decreased in case they wanted to have connections, those lead pipes are still there in Roman Ruins.

And they have stayed like this intact, but these days we cannot use lead in piping, because people know about the toxic effects of lead, there can be lead poisoning. If you were drinking that water which is coming through a lead pipes day in and day out, then there are problems, so lead is no longer used in pipes.

Besides, there are now cheaper materials more effective, we have steel, we have plastics, and we have polymers and all kinds of things. But at one time, lead was used, but lead is still used in cable sheathing, may be you want the flexible cable, you can have a sheathing of lead, very effective.

(Refer Slide Time: 33:46)



Extraction of Lead

Uses : Antiknock compounds (~11%), batteries (~35%), sheets and pipes (~11%), sheathing cables (~17%), Miscellaneous (rest)

Common Ores : Galena (PbS) associated with ZnS, FeS, CuS , $PbCO_3$ and several precious metals

Process : Roast below 800⁰ C (to avoid fusion) in Dwight- Lloyd sintering machine -→ sinters for blast furnace smelting using fluxes (Limestone + Quartz0

$PbS + 3/2\ O_2 = PbO + SO_2$

$SiO_2 + 2PbO = 2PbO.SiO_2$

$2PbSO_4 + SiO_2 = 2\ PbO.SiO_2 + 2SO_2$

In lead blast furnace (Temp <1200⁰ C)

$PbO + C = Pb + CO$

$2PbO + C = Pb + CO_2$

Scrap Iron is also charged in blast furnace

$PbSiO_3 + Fe = FeSiO_2 + Pb$

$PbO + Fe = FeO + Pb$

But then, the maximum use is in batteries and advantage there is where a battery is thrown out, that lead can be taken out and reused very easily. So, it can be re circulated, in our country most lead is for re circulation is coming from batteries.

Unfortunately, it is done in an unorganized sector, in Calcutta there are not dozens, but hundreds of units where lead batteries, lead from batteries are being re processed to produce lead for the market.

Now, when there is a some raids on that, they simply close down, they go to another place and start operation. The problem there is, they do not worry about pollution problems, because whenever you are melting lead, lead fumes are generated. It creates high vapour pressure fumes, those fumes are lither, it causes all kinds of problems but, you know the labourers either do not know or they do not have (audio not clear from 35:00 to 35:13) from all over the country. Besides if there are people who are doing it locally, people find it very easy to select of to them and so, anywhere you you buy this battery, they are very very willing to give you some price for the whole batteries and they reprocessed that, they goes to those who reprocess lead.

Anyway, so all I wanted to mention is, in the batteries which uses maximum and as as the automating industry expense in our country, more lead is required that the more secondary lead, let us leave it there. The common ore of lead is galena which is written as P b S and because it is a sulphide, it is always associated with zinc sulphide, iron sulphide, copper sulphide, several precious metals can be there, and some carbonate is also there.

But then, extraction of lead from galena seems to be a very straight forward, you see what we need is simply blast furnace reduction of lead oxide by carbon, the in theory, the it can be done at a temperature below 1200 degrees. In blast furnace operation, we need 7, for iron production we need 1700 degrees.

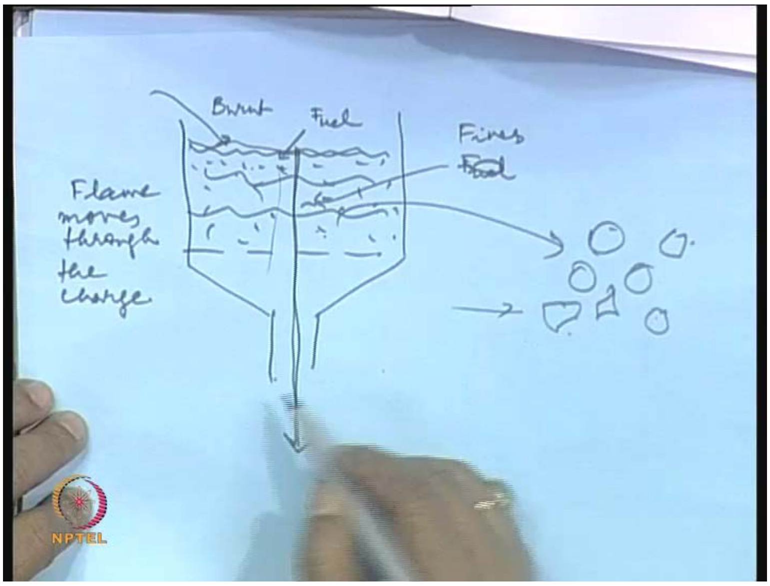
In lead blast furnace, one operates just about 1200 degree centigrade, blast furnace is also a shorter in height, but one problem here is that, lead sulphide is coming from a floatation process. You know from a sulphide ore which has copper sulphide, lead sulphide, zinc sulphide. Lead sulphide concentrate is obtained by a differentials floatation process that requires very fine ore to start with. So, what one obtains is also in very fine form, the concentrate will be very fine. When that lead sulphide is roasted to produce lead oxide, it will also be fine, that fines cannot be charged in blast furnace, because you know how blast furnace operates.

It is a vertical reactor in which the oxide charge is reduced by carbon, there are Tuyere's from with oxygen is coming, air is coming to oxidize the coke to produce C O, that C O will have to permit through the bed for reduction, so if if their finds they they simply cannot go through. In the case of iron blast furnace also, one needs particles of iron ore, initially they use to have iron ore particles from the mines of a certain size.

Now, sinter sulphate, sinters are made from finder particles by the process of sintering. Sintering means you take a lot of smaller particles, let them undergo incipient fusion. Incipient fusion means only fusion on the particle surfaces so that smaller particles agglomerate. So, from a fine we can produce agglomerates of the size we want, typically it will be several centimeters, so a kind of nodules. Once you have produced those agglomerates, that agglomerate will be charged in the blast furnace so that in the furnace, there will be sufficient permeability for the gases to go through.

You cannot charge the fine oxide you have obtained from roasting operation, you need sinters, and to repeat sinters are agglomerates of fines obtained through incipient fusion of particular matter which create bigger particles, which one packed will have enough permeability in them.

(Refer Slide Time: 40:04)

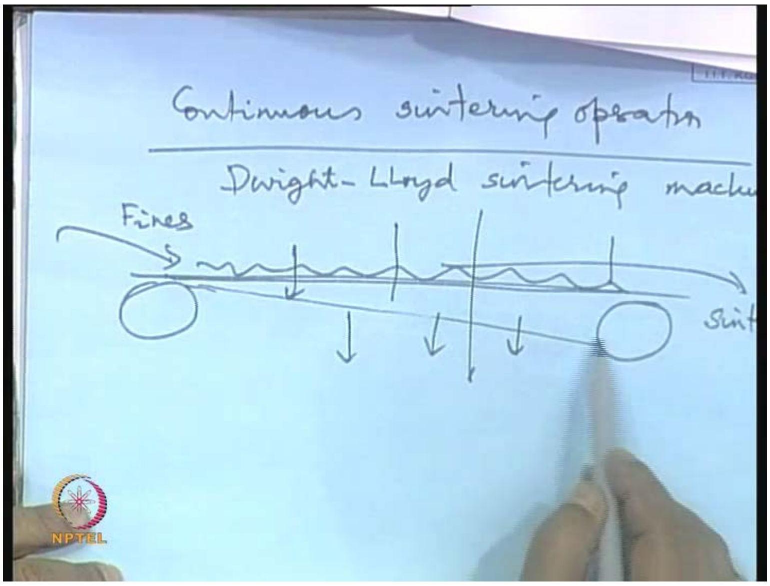


Now, there are different kinds of sintering machines, a simple sintering machine is a bag sintering, where in a sinter port the fines are charged along with some fuel, no sorry the fuel a small amount of combustible fuel is given here, this is burnt to make a flame and then a section is given from the top to the bottom. So, the flame front moves, flame moves through the charge, you might need little bit of fuel inside also.

So, basically we need that a flame will go through the whole charge not very slowly, the whole idea is not to melt anything, but as the flame goes to this this particles begin to stick to each other, because only the surfaces are melted. And from once we get we get particles, irregular shaped, the size can be controlled by the speed of movement of the flame front which is controlled by the vacuum, also the initial particles size of this and some other parameters.

So, the whole idea is from fines, we get particular matter but, this is a batch process and you fill it up, you you do sintering, then pour it out, and then start all of again.

(Refer Slide Time: 42:00)



But now, there are continuous operations, continuous sintering operation and the standard machine is called Dwight Lloyd sintering machine. There the basic scheme is that, fines are poured on to a moving belt somewhere here, as they come the sintering operation will take place and from here continuously sinters are discharged. So, on the bed as they move the, there is a vacuum the and there is a flame here, burning the flame flint is moving through and gradually, it starts sintering here, finally the whole bed get sintered and everything is poured out of it.

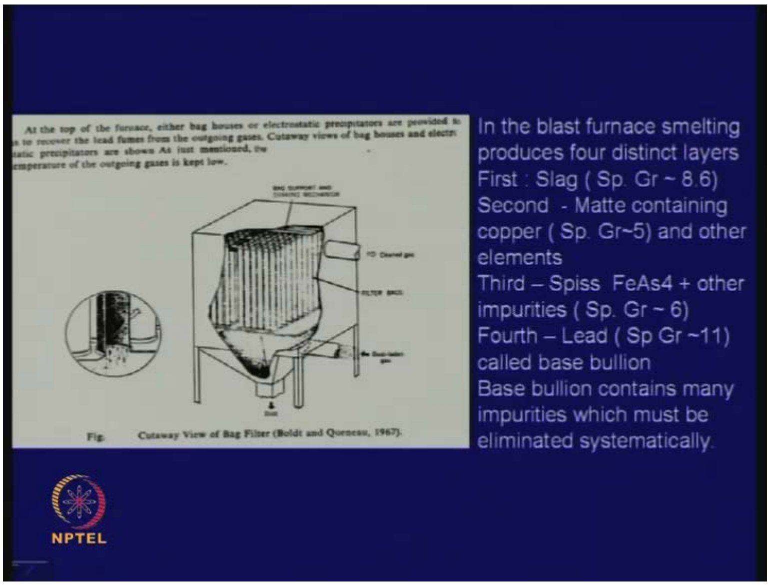
So, sintering begins here, some particles are sintered and as we go on and on bed, the whole thing particles will gets sintered, they will report that. So, this is a sintering machine and operates in a continuous manner, this is a must for lead blast furnace. Now, the requirement of strength of the sinter is not as critical in the case of iron blast furnace, because the blast furnace has smaller insides, but still, it is those sintered particles which have to stand the weight of the entire bed. In that, there will be, the coke will be there, so initially the whole bed is maintained by coke and this particle the porosity.

Now, in the sintering machine, roasting is below 800 degrees, because sintering is a process of oxidation below the fusion point. We do not want fusion, this is the machine name and sinters for blast furnace melting using fluxes, you also incorporate into the sinter some limestone and quartz.

So, they will create the slag in the blast furnace operation, so lead sulphide will become lead oxide in the sintering machine. There will be a certain amount of P b O, S i O 2 can also form, because we have introduced a little bit of quartz and you can also, if there is a lead sulphate, we can also form this.

In the lead blast furnace now, this oxide will be reduced by carbon to produce lead, we will also introduce some scrap iron in the charge, in the blast furnace charge to ensure that if there is a silicate in the charge or if it is in this slag, it will produce a liberate lead. So, the charge will have fluxes, sinters, coke and some scrap iron, that will be the charge for the lead blast furnace.

(Refer Slide Time: 45:56)



At the top of the furnace, either bag houses or electrostatic precipitators are provided s to recover the lead fumes from the outgoing gases. Cutaway views of bag houses and electr tatic precipitators are shown As just mentioned, the emperature of the outgoing gases is kept low.

Fig. Cutaway View of Bag Filter (Boldt and Queneau, 1967).

In the blast furnace smelting produces four distinct layers
First : Slag (Sp. Gr ~ 8.6)
Second - Matte containing copper (Sp. Gr~5) and other elements
Third – Spiss FeAs4 + other impurities (Sp. Gr ~ 6)
Fourth – Lead (Sp Gr ~11) called base bullion
Base bullion contains many impurities which must be eliminated systematically.

Now, in the case of all lead blast furnaces, a very critical thing is a bag filter, everywhere you will find whenever they are talking about lead blast furnace. At the top of the furnace, there is a filter to trap all lead fumes or lead oxide fumes. Otherwise the entire plant would would not be environmentally safe and at the top of the furnace, either bag houses will be there or electrostatic precipitators can also be there, like we have for iron blast furnaces to recover the lead fumes from outgoing gases, and we show you one cutaway views of this.

Now, the blast furnace smelting in the case of iron ore smelting, we get two layers. We produce pig iron at the bottom and above that is a slag layer. In the case of lead, four distinct layers are produced in the blast furnace, and they have to be tapped separately. Incidentally, the lead blast furnaces are not circular, there kind of elliptical, there are some design requirement, they are slightly elliptical, the height is smaller. Otherwise, there are many similarities with the iron blast furnace, but obviously, the blast furnace for iron making is always far more sophisticated.

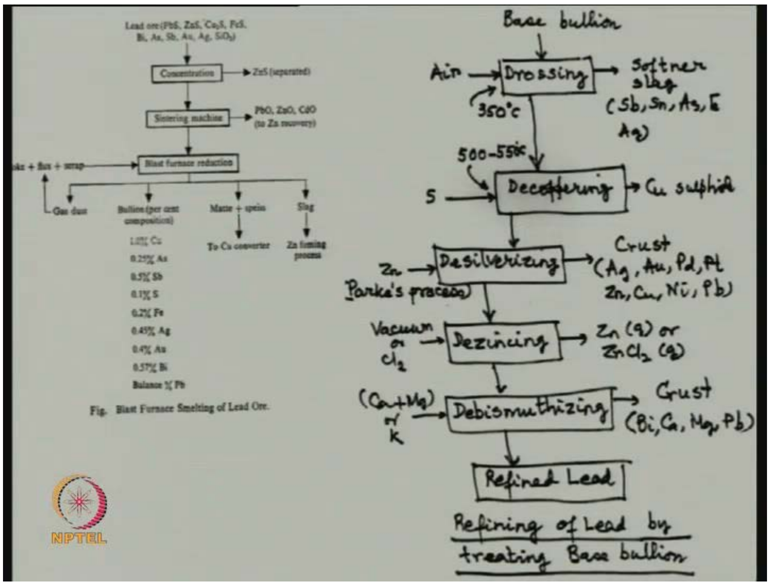
Now, what are the layers? Remember the lead is very heavy, so we have at the bottom lead; the specific gravity is 11, because the lead has many things also in it. And there is another distinct layer call spiss, there is an e missing spiss which is essentially an intermetallic compound F e A s 4 with some other impurities is about 6. And then there is a matte, because there is always some copper in lead, so there will be a matte with specific gravity is 5.

And above that, there is a slag and there there is a mistake there, I think the just a minute. This specific gravity, I think it is not 8.6, it will be 2.6, please check the book, because slags mostly silicates around 2.6 or so.

So, it floats on top of a matte, if there is no copper sulphide at all then there may not be any matte, but if there is any copper sulphide it will come out as matte which would have dissolve some other element, then there is a there is a lot of arsenic and iron that will form this F e A s 4 (()). And then at the bottom, there is a lead and it is called the base bullion, because it is at the bottom, it is called base bullion. So, this is the simple technique for making lead in the lead blast furnace, yes I have the figure now, this is actually 3.6 sorry, this 8 is 3.6 3.6 3 5 6 and 11.

Now, this is not the end of lead extraction process, actually this is the beginning, because producing the bullion in a blast furnace is straight forward. Then, we have the question of how you purify this lead and recover all that is there in solution is lead and there all kinds of things in this lead base bullion. So, we come to the treatment of base bullion now, how we are going to treat this base bullion.

(Refer Slide Time: 50:07)



Now, for that again we have to go into a flow sheet. Now, before that flow sheet, let us go back to what we have done in lead extraction, what we have done? We start with a lead ore which has lead sulphide, zinc sulphide, copper sulphide, and iron sulphide necessarily in varying amounts, it will also have some other elements, and it will also have silica necessarily. After concentration, zinc sulphide can be separated fairly easily in the sintering machine. We will produce a sinter, but it will also give you fumes of Z n O, C d O, P b O and it will go for zinc recovery, if there are such fumes.

Now, the blast furnace using the sinters will produce slag, the slag will have some zinc and therefore, zinc has to be recovered from lead slag and therefore, that we have what we call a fume in process, that I will discuss. Then we have a layer, below that which would be matte plus spice, it will have arsenic and iron. On top, there is now and then there is a in the bottom, we have the base bullion, of course the gas that is etcetera go out.

It is this bullion now, we have to think of pretty, this would necessarily have some copper, it will also have some arsenic, it will have other elements, it will also have precious elements like silver, gold etcetera, and balance would be lead. So, I will discuss the treatment of base bullion in the next lecture. So, now let me quickly recapitulate what we did today, we started with hydrometallurgy of copper and I mentioned that in hydrometallurgy, the idea is not to use high temperature reactors, you go list to have copper in solution, aqueous solutions. From there we want to get copper out, so electrolysis or whatever method.

Now, in nature in copper mines, copper dissolves naturally in water bodies, but it takes many many months, I mean years, it was accidently discovered that some bacteria can expedite this process.

These bacteria do not need for their life oxygen, they thrive on inorganic constituents and they derive energy from reaction such as ferrous oxide, ferrous iron, being oxidized to ferric iron. Many many things happen, but if there is a sulphur or sulphate, if there is a ferrous iron, then the bacteria can be effective and they for more rapidly than natural process can bring in into solution copper.

It is applicable a bacterial action in many many minerals, mostly suphide minerals, but also oxide minerals like uranium, the different kinds of bacteria people have are trying them out, bacteria leaching has been applicable for gold also in leaching, but we will not get into that now.

But then in the industry today, we cannot depend on bacteria leaching as of now. Because for that, you need very shallow beds, fast areas and you you have to wait for months, if you want to do it in an industrial scale, you have to use chemicals to build copper into solution. We can do it by ferric chloride leaching, but then, we have seen it is not very active commercially, what is active commercially is sulphate process.

We can roast copper minerals under control conditions to produce sulphate or we can also leach by hydrochloric hydrosulphuric acid to bring copper oxide into sulphate solution, this sulphate solution can go for cementation, electrolyze or whatever. Then we came to lead metallurgy, which look straight forward to start with excepting that for reduction in a blast furnace, the fine concentrate which becomes fine roasted oxide, they have to be agglomerated using a sintering process. So, the sinters are charge in the blast furnace, along with cock, along with fluxes and some scrap iron also for recovery of a lead.

And then, lead will come out at the base as a bullion and there are some other layers as I mentioned, that base bullion is in pure lead which contain some valuable impurities and we have to now treat that base bullion for recovery of those valuable, by products as well as to produce pure lead, this I will do in the next lecture. Thank you.