

Materials and Energy Balance in Metallurgical Processes

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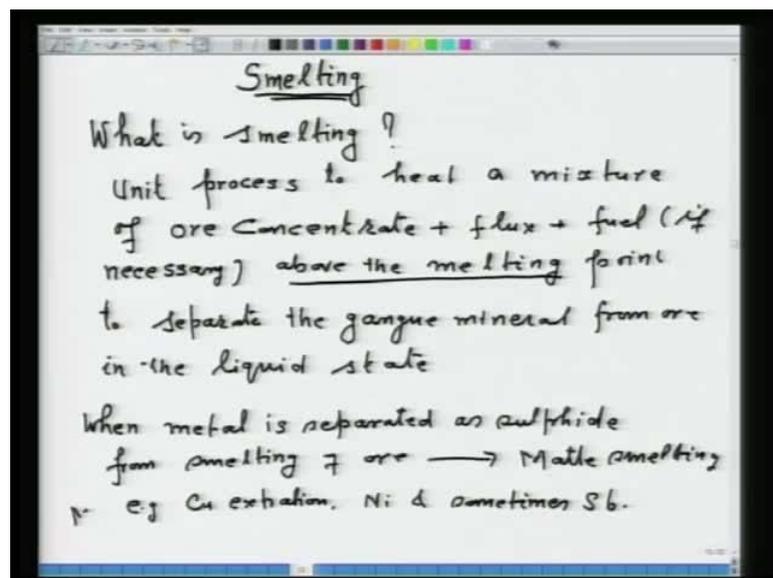
Module No. # 01

Lecture No. # 20

Smelting Matte Smelting

Today, I am going to take the next unique process for pyrometallurgical extraction of metals from ores. The next process is smelting.

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Let us see, what is smelting? Now, mind you, there is a difference between melting and smelting. The smelting - the definition is what I am going to give now. Melting means, you are melting; for example, pure metal or alloy or whatever, so that is melting. But, smelting - it is different. So, there is a difference between smelting and melting.

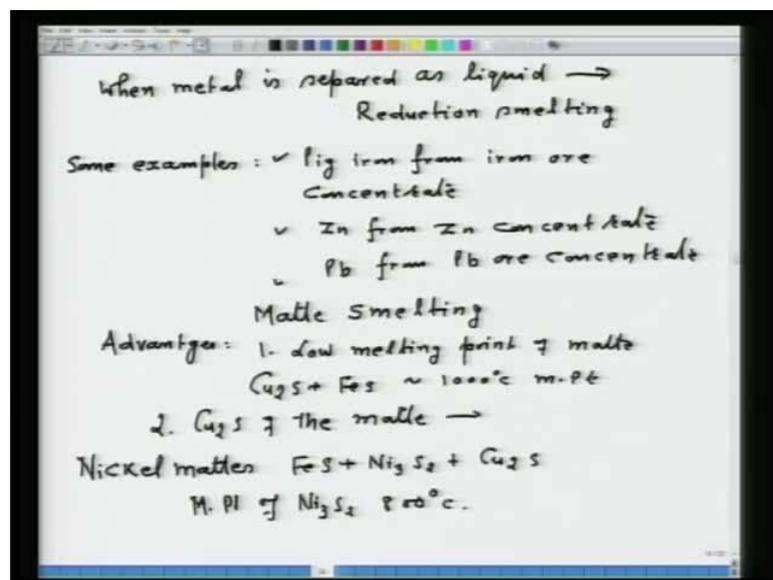
What is smelting? It is a unit process to heat a mixture of ore concentrate plus flux plus fuel, if necessary, above the melting point. This above the melting point is different than what was in the roasting. In the roasting, we were carrying out the process below the melting point, so that the initial state of the raw material was solid and final state is also

solid. In case of smelting, the initial state of the raw material is solid, but the final state is the liquid and gases. So that is very important difference between the two.

Above the melting point to separate the gangue mineral from ore in the liquid state, this is a general definition of smelting. The whole objective is to separate the gangue mineral, but remember, the state of the gangue mineral in case of smelting is the liquid. It is a difference between roasting and smelting. Again, I will like to point out, in the roasting both the states - initial and final were solid, but in case of smelting, initial state is solid and the final state is that of liquid.

When metal is separated as sulphide from smelting of ore, then we call it Matte smelting. In fact, in matte smelting, we have ore concentrate plus flux plus air plus fuel; if necessary, then we have matte slag and gases. The typical example of application of this matte smelting technology in case of copper extraction, rather in case of extraction of copper from sulphide, sometimes nickel from sulphide and sometimes antimony.

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Say, when metal is separated as liquid, then it is called reduction smelting; so that means, we have matte smelting and we have reduction smelting. In matte smelting, we separate gangue mineral and produce a matte. In reduction smelting, we also separate gangue mineral, but mind you here we produce liquid metal.

Some examples of reduction smelting; the famous example all of you know, is the production of pig iron from iron ore concentrate, is one such example. Another example is zinc from zinc concentrate. Here, slightly there is a way, because here zinc is produced in the form of vapor, then they are condensed and ultimately you get the liquid. Another example of reduction smelting is lead from lead ore concentrate. So, each one I will take in detail, we will go, we will solve the material in heat balance and so on.

First, I will be concentrating on matte smelting. Obviously, there are certain advantages of extraction of metal through matte smelting route, because what we are doing in matte smelting, we are separating gangue mineral and producing a matte from the copper ore concentrate.

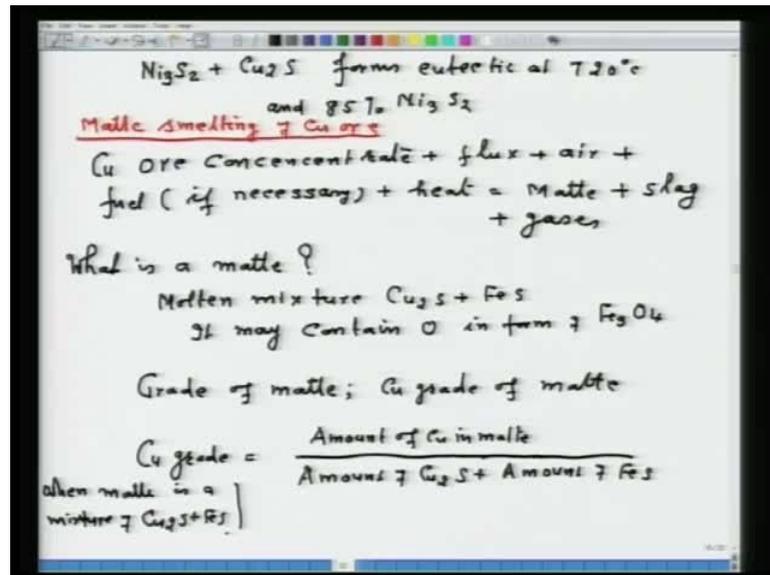
Now, what are the advantages of it? Advantages of matte smelting are first of all low melting point of matte; for example, Cu_2S plus FeS , it has around 1000 degree Celsius is its melting point. That means you do not require a very high amount of energy to produce the matte. This is the one such advantage; that means you will require less amount of thermal energy by converting the metal of the ore in the form of sulphide and then extract the metal.

However, it will vary from reserve to reserve or metal to metal, particularly for sulphide ore where direct reduction of sulphide to metal is rather relatively difficult. In some cases, the matte smelting route is technologically feasible and also energy efficient, you are seeing; for example, in copper extraction, the matte consists of Cu_2S and FeS , it has a melting point of around 1000 degree Celsius.

Also another advantage is that the Cu_2S , which is contained in the matte, it does not require any reducing agent. That means Cu_2S of the matte, it does not require any reducing agent in the sense of a carbon or those reducing agents; they are not required. It is said, by blowing oxygen you convert to oxide and then it is a sulphide oxide reaction that leads to the production of copper. So that is another advantage of having the matte smelting; this is for example of copper.

Similarly, if you take the nickel mattes; this is for the copper mattes. Similarly, nickel mattes, they typically contain FeS plus Ni_3S_2 plus Cu_2S ; this is typically the nickel matte.

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Here, the melting point of Ni_3S_2 is around 800 degree celsius, whereas Ni_3S_2 plus Cu_2S it forms eutectic if you see the phase diagram; forms eutectic at 720 degree celsius, 85 percent Ni_3S_2 . So, what I wanted to tell you is that the matte smelting technology is sometimes suitable for extraction of metal from sulphide ore, particularly when sulphide ore is associated with iron also. For your information, most of the sulphide ore are associated with iron, in that case this matte smelting technology for sulphide ore is good because of the advantages.

Now, what is again matte smelting? If I want to represent in the form of the reaction I will put it; say copper ore concentrate plus flux plus air plus fuel, if necessary, then plus heat. Externally if it is sufficient, otherwise you have to supply it by combustion of the fuel that will give you matte plus slag plus gasses; this is what I am referring now to matte smelting of copper ore. That is the subject matter of the following lecture.

Here, what is a matte? Already I have said what a matte is. In connection with the copper melting, say matte is a molten mixture essentially of Cu_2S plus FeS . Sometime, it may contain oxygen in the form of Fe_3O_4 . I am talking the industrial matte; it is very difficult to control their dissolution of oxygen in the matte during the smelting state.

Sometimes you may get - industrial may consist of Cu_2S plus FeS plus Fe_3O_4 , but in the problems, which you will solve unless and otherwise it is given, you will be considering matte is a molten mixture of Cu_2S plus FeS . If it had something, then it

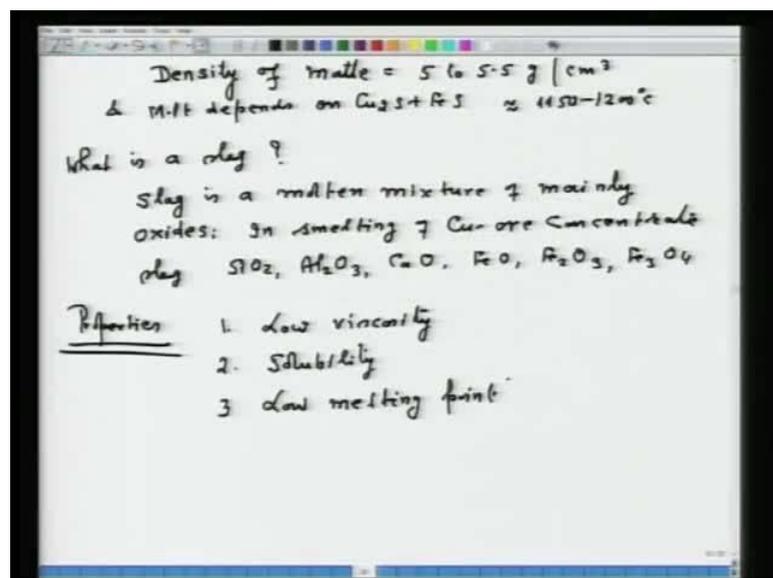
will be given in the problem, but for your information, the industrial matte will may contain Cu_2S , FeS is there, but in addition to - because of the dissolved oxygen, it may form to Fe_3O_4 also.

Now, important thing in case of matte is to define the grade of the matte; grade – matte grade or you can also call copper grade of matte; you can call grade of matte or sometimes you can also call copper grade of matte. It is useless to call iron grade of the matte, because you are not concerned with the iron that is why you call copper grade; that means, how much amount of copper is over there.

This is defined, a copper grade or you say matte grade; you are producing a matte of 40 percent that means, it is having its copper grade as 40 percent. So, matte is always given in terms of copper, because it is used to produce copper not iron, remember. The problem may have 40 percent matte or the grade of matte is 40 percent or copper grade of the matte is 40 percent; all have the same meaning.

For example, if you write copper grade, it can be defined as amount of copper in matte upon amount of Cu_2S plus amount of FeS . This is copper grade when matte is a mixture of Cu_2S plus FeS only. If it has Fe_3O_4 also, then amount of copper in the matte upon amount of Cu_2S for the amount of FeS plus amount to Fe_3O_4 into 100; that is how you will define the density of matte, it is given in percent.

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Now, another important feature is the density of matte. Density of matte that is equal to 5 to 5.5 gram per centimeter cube and the melting point depends on proportions of Cu_2S plus FeS . But, normally in the industrial grade matte the melting point is in-between 1150 to 1200 degree celsius. You can imagine this matte smelting is usually carried out anywhere between 1200 to 1250 or 1300 degree celsius; not higher than this temperature. This is what a matte is.

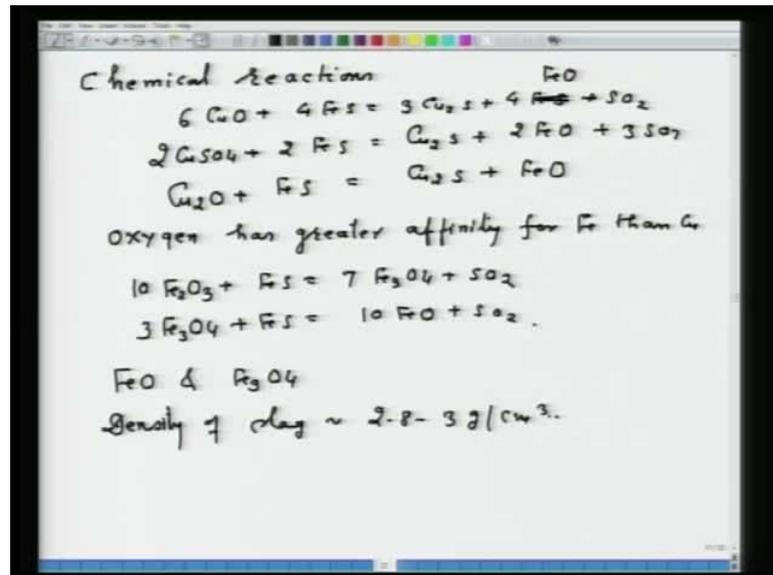
Now, another product is slag, what is slag? Remember, slag is a molten mixture, I am talking in connection with the copper smelting, is a molten mixture of mainly oxides. It may contain sulphide, it depends, but mainly is a mixture of oxides in smelting of copper ore concentrate. For example, in smelting of copper ore concentrate the slag may contain SiO_2 , Al_2O_3 , calcium oxide, FeO , Fe_2O_3 , Fe_3O_4 . It may contain sometimes unreacted sulphide that depends on the process of smelting, but in ideal condition, it will contain SiO_2 , all oxides are there, but some un reacted sulphide is there, it will also be there.

Some of the properties which are required for a slag, because slag is normally highly viscous; at the end of the process, you have to drain out the slag at desire metal. Some of the desirable properties are; one, low viscosity; second, the solubility is important. That means slag should be able to dissolve the oxides, which are being separated during smelting of ore concentrate; that is an important thing.

That is you have to make slag of composition such so that the oxides present in the ore concentrate they are dissolved. You have to form the liquid; it is a homogeneous liquid solution, rather molten solution.

Third important property, it should have a low melting point, because you will not go more than 1200 or 1300 degree celsius. At that particular temperature, the oxides which are being separated from the ore concentrate, they should be able to dissolve and they should be liquid. Here, we should also think that slag normally here does not act as a refining agent in contrast to the iron making, so that part we separated at the moment here. In case of this melt smelting copper slag, these are the important properties that the slag should possess.

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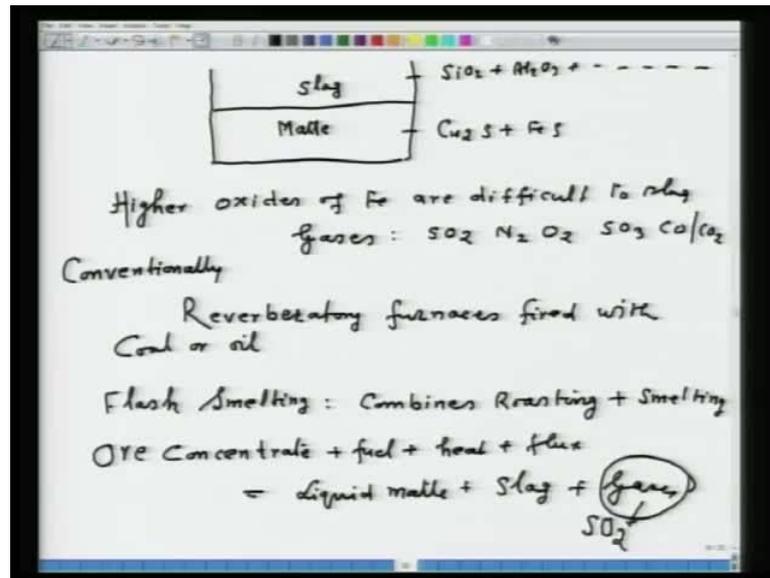


Next, let us consider some of the chemical reactions, which can occur. For example, 6 Cu O plus 4 Fe S equal to 3 Cu 2 S plus 4 Fe S plus S O 2 or 2 Cu S O 4 plus 2 Fe S. The Cu S O 4 may form during roasting, you might have roasted it a little higher P O 2 pressure, so Cu S O 4 might form. This also has to reduce to Cu 2 S because, you have to reduce otherwise you will be losing copper here.

You have Cu 2 S plus 2 Fe O plus 3 S O 2; here this should be Fe O. Then, you have Cu 2 O plus Fe S that is equal to Cu 2 S plus Fe O that is what some of the reaction. Sometimes the oxygen has greater affinity for iron than copper, so the unreduced Fe S may react with Fe 2 O 3 or Fe 3 O 4. Accordingly 10 Fe 2 O 3, it may reduce with Fe S that may form 7 Fe 3 O 4 plus S O 2 or 3 Fe 3 O 4 may react with Fe S and it forms 10 Fe O plus S O 2.

So, Fe O and Fe 3 O 4 they are dissolved in the slag, mind you Fe 3 O 4 is difficult to dissolve as compared to Fe O. Density of slag that is equal to 2.8 to 3 gram per centimeter cube, so you are seeing there is a difference in density of matte and slag. By virtue of this difference in density we are able to separate a matte and slag.

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You have this, is sort of interface, somewhere here you have the matte and somewhere here you have the slag. So, you can see now the matte smelting is able to separate the metal in the form of sulphide from rest of the ore. This matte, it only contains an ideal condition Cu_2S plus FeS and nothing else; plus little amount of Fe_3O_4 , if oxygen is been dissolved, but normally it has Cu_2S plus FeS ; all impurities are eliminated. Here you have the slag; it may contain all SiO_2 Al_2O_3 plus all other impurities which you have in the ore concentrate; that is what this matte smelting process is.

Now, it should also be remembered that higher oxides of iron are difficult to slag. Slag means, it is difficult to remove, this precaution must be taken during roasting. During roasting you have to see that the iron **I mean** should not be converted to Fe_2O_3 or Fe_3O_4 , it will have a lot of problems in the smelting and further stages. Therefore, a controlled amount of roasting is needed; this is what the thing you should know.

Now, conventionally the technology of smelting, before I say about the technology smelting, the third component that was coming was the gases; the gases were also forming. So, gases essentially consists of SO_2 normally, sometimes SO_3 may be there, but it depends on the oxygen content to SO_2 , nitrogen; if excess amount of air is used then you have oxygen also. Sometimes SO_3 could be there, depends upon the technology or depend on the process, depend upon the reaction, so on and so forth, these

are the mainly the gases which you will find in the smelting. If fuel is used, then you may get CO or CO₂ depend upon the state of combustion. So, these are the gases.

Now, conventionally the roasting is carried out, sorry, conventionally smelting is carried out in reverberatory furnaces, fired with coal or oil; they are very long furnaces. Traditionally, the smelting of copper ore is carried out in reverberatory furnaces, still reverberatory furnaces are used, but now these reverberatory furnaces are replaced in recent years by so called flash smelting.

The advantages of flash smelting is that it combines both roasting and smelting, whereas in the reverberatory furnace the ore has to be roasted first and then it is transferred to reverberatory furnace for smelting purposes. Then, the new technology came that is the flash smelting; here roasting and smelting both are combined. The reason for this you must have seen in case of roasting, a large amount of sulphur dioxide is created.

This byproduct sulphur dioxide can be very easily used to form sulphuric acid. There is very substantial amount of SO₂ is being produced. Imagine you have at one stage roasting, take the roast product and then smelt it. So, you have SO₂ in the roasting state and then you have SO₂ in the smelting state. Both you have to collect and then send it for the H₂SO₄ plant; this is little bit uneconomical as compared to a process.

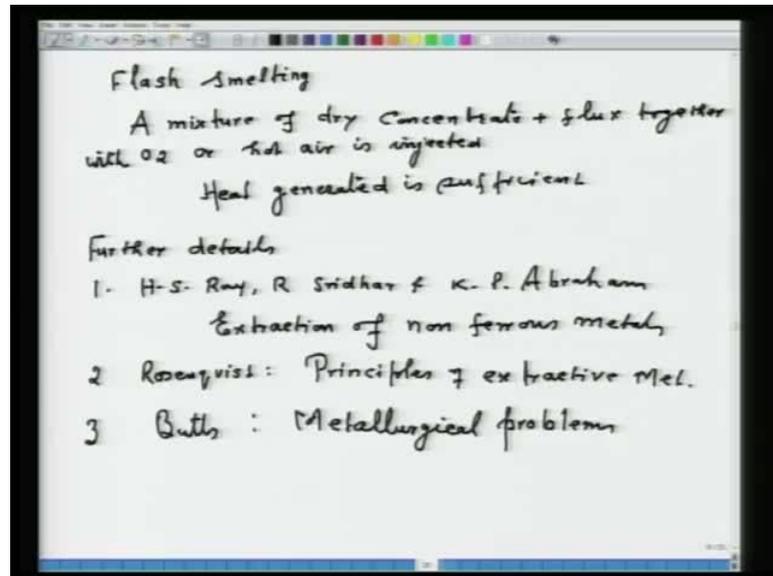
This can do both these functions simultaneously; that means, you start with the ore concentrate and get a product which is liquid matte, liquid slag and gases. What will be the advantage of this? Here, you will get a concentrated amount of SO₂ only from one reactor in contrast to a technology which has roasting first, followed by smelting as it was done in reverberatory furnaces.

So, the advantage of flash smelting is that you have ore concentrate; mind you, it is not roast ore, it is ore concentrate which is coming from the mineral beneficiation plant. This ore concentrate plus fuel plus heat plus flux, you get here liquid matte plus slag of course liquid slag and plus gases. Here, the main interest in sulfide ore is in the SO₂-sulphur dioxide and some proportion of sulphur trioxide is also formed.

But, the main reason for the development of this technology called flash smelting, which combine both of them together is to see that how SO₂ can be produced in a concentrated way, so that a large amount of byproduct can be converted into a salable

product like for example H_2SO_4 . So, in most of the copper extraction plant this reverberatory furnace is being replaced by the modern technology, which is called flash smelting.

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In flash smelting what is being done is that a mixture of dry concentrate plus flux together with oxygen or hot air is injected into a reactor. Remember - **if you are exposed** - I think you are exposed to the course of kinetics, you are injecting very fine particles of ore concentrates, so the reaction will be extremely rapid and very high temperatures are created in the flash smelting, accordingly control of temperatures is required. Now, this is a well-developed technology, so what I wanted to say that because of the reaction rate it is very fast in case of flash smelting.

Here, heat generated is sufficient to carry out the smelting. This flash smelting could be so called autogenous in nature also, where you may not be requiring any heat from outside. This is what about the brief idea of what is smelting and I hope with this brief introduction on smelting or on matte smelting, we are able to solve the problems concerning material and heat balance in matte smelting.

So, I will suggest that for further details you may consult the reference for example, H. S. Ray, R. Sridhar and K. P. Abraham, Extraction of non ferrous metals. You can also see a book which is Rosenqvist, Principles of extraction metallurgy plus you can also see by Butt's Metallurgical problems.

This is about so called brief introduction and to prepare you for carrying out the material and heat balance in the matte smelting. Now, what I have planned, let me go for a very simple problem and then, we will go for the further problem.

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In a copper ore Chalcopyrite is 34%,
pyrite 30% and SiO₂ 36%. Determine %
Cu, % Fe and % S

$$\% \text{Cu} = \frac{34}{184} \times 64 = 11.83\%$$

$$\% \text{Fe} = \frac{34}{184} \times 56 + \frac{30}{120} \times 56 = 24.35\%$$

$$\% \text{S} = \frac{34}{184} \times 32 + \frac{30}{120} \times 64 = 27.83\%$$

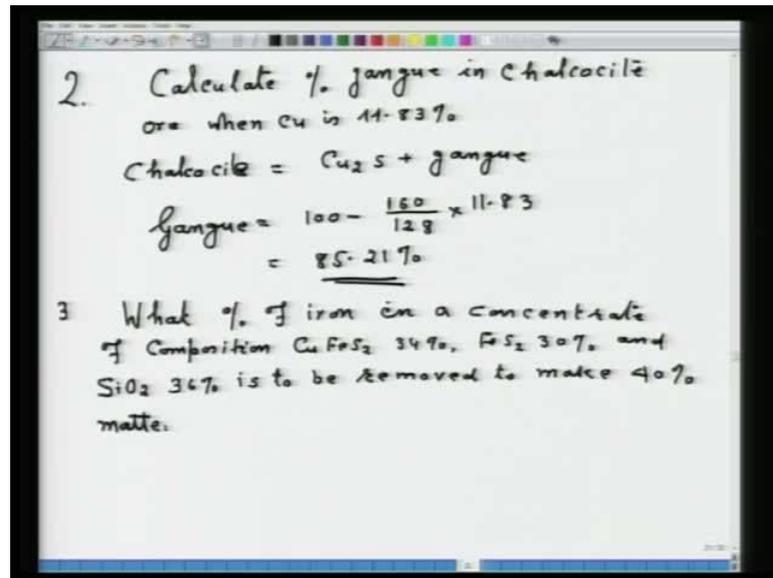
Cu = 64
 Fe = 56
 S = 32

Chalcopyrite CuFeS₂ - Pyrite FeS₂

Let us take in a copper ore chalcopyrite is 34 percent, pyrite 30 percent and Si O 2 36 percent. Now it is very simple, determine percent copper, percent iron and percent sulphur. Here you have to take atomic weights of copper 64, iron 56, sulphur 32. It is a straight forward, you can find out percent copper that will be equal to 34 upon 184 into 64. By the way chalcopyrite is - I will tell you what chalcopyrite is - that is equal to 11.83 percent.

By the way, chalcopyrite represents a mineral which is Cu Fe S 2 - I think you know because, in several lectures I have said it. Similarly, percent iron pyrite is Fe S 2, so percent iron is coming from two sources 34 upon 184 into 56 plus 30 upon 120 into 56. I hope you can add both of them and that will be 24.35 percent, this is the percent iron. Similarly, percentage of sulphur that will be equal to 34 upon 184 into 64 plus 30 upon 120 into 64 that will be equal to 27.83 percent. The answers for this, just starting with a very easy **problem** so that you can also solve the problem.

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Let us see the next - second - problem, calculate percent gangue in chalcocite ore when copper is 11.83 percent. Do you know what chalcocite ore is? Chalcocite ore is a sulfide ore, which contains Cu_2S , so chalcocite that is equal to Cu_2S plus gangue. So, 11.83 percent copper is given, the gangue would be 100 minus 160 upon 128.

Next is what percent of iron in a concentrate of composition given CuFeS_2 34 percent, FeS_2 30 percent and SiO_2 36 percent is to be removed to make 40 percent matte. As I said in the lecture, when I say to make 40 percent matte that means what? That means the copper grade of the matte is 40 percent and rest nothing is defined, except when we say 40 percent matte that means, the only means of this, it has a copper grade of the matte is 40 percent that is what I have to say.

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The image shows a whiteboard with handwritten mathematical work. At the top, there is a fraction: $\frac{40}{100} = \frac{11.83\%}{14.78\% + \% \text{ Fe S}}$. Below this, the equation is rearranged: $0.4(14.78 + \% \text{ Fe S}) = 11.83$. This leads to $\% \text{ Fe S} = 14.795$ and $\% \text{ Fe} = 9.415$. The next line shows the calculation for iron to be removed: $\% \text{ Fe to be removed} = 24.35 - 9.415 = 14.935\%$. At the bottom, there is a question: "4. If the ore concentrate of problem 1 is fused down and only excess S is eliminated, what would be the composition of the resulting matte?"

Let us put the solution, say we put the definition that will be 40 upon 100 - that is the matte rate - that is equal to 11.83 percent is copper upon 14.78 percent plus percent Fe S. Now, if I solve this thing, I will be getting 0.4 into 14.78 plus percent Fe S that will be equal to 11.83. From here, I get percent Fe S that will be 14.795, so percent iron that will be 9.415. This percent iron or this percent Fe S should remain in the matte.

What has to be removed? Percent in iron has to be removed that will be equal to total 24.35 minus 9.415 that will be 14.935. That means, I have to remove 14.935 percent of iron in a mixture which has been given Cu Fe S to this Fe S to this (O) this if I want to get a matte of 40 percent grade.

Now another problem let us take it, you recall the problem 1 - the data refers to problem 1. So, if the ore concentrate of problem 1 is fused down and only excess sulphur is removed - eliminated. The question is what would be the composition of the resulting matte? Could you understand what this means; that is, you have to remove the excess sulphur from the ore concentrate of composition given in 1.

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$Cu_2FeS_2 = 34\%$
 $FeS_2 = 30\%$
 $SiO_2 = 36\%$

$FeS_2 \rightarrow FeS + S$

$\% Cu_2S = 14.78\%$ $\% FeS = 38.25\%$

Matte grade = $\frac{\% Cu}{\% Cu_2S + \% FeS} \times 100$
 $= 22.2\%$

A copper matte may be represented by $mCu_2S \cdot nFeS$ with no fixed values of m & n .
If the matte grade is 38%, what would be the entire composition of matte?

What was given over there? It was given that Cu_2FeS_2 34 percent, FeS_2 30 percent, and SiO_2 36 percent. So, the FeS_2 decomposes to FeS plus S that is the excess sulphur that you have to remove it in order to calculate the matte. So, percent Cu_2S that will be 14.78 percent and percent FeS , if you calculate that will come out to be 38.25 percent then, matte grade that will be equal to as defined percent is copper upon percent Cu_2S plus percent FeS into 100, if we substitute that will come 22.2 percent. So that is how you will be calculating this particular problem.

Now, another interesting problem is that let us consider, a copper matte may be represented by $mCu_2S \cdot nFeS$ with no fixed values of m and n .

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The whiteboard shows the following handwritten work:

$$0.38 = \frac{\text{Amount of Cu}}{\text{Amount of Cu}_2\text{S} + \text{Amount of FeS}}$$
$$= \frac{128m}{160m + 88n}$$
$$60.8m + 33.44n = 128m$$
$$\frac{m}{n} = \frac{33.44}{67.2} = \underline{\underline{0.5}}$$

Cu₂S · 2 FeS

If the matte grade is 38 percent, what would be the entire composition of matte? This is a very simple, you have to again write down say 0.38 that will be equal to amount of copper upon amount of Cu₂S plus amount of FeS, all that now we have to put it so that will be equal to 128 m upon 160 m plus 88 n. Here again, CuS molecular weight, atomic weight, everything I have given; so, all that you have solve.

If you solve this equation, you will be getting for example, 60.8 m plus 33.44 n that will be equal to 128 m. Here, all that you can calculate the ratio of m is to n that is equal to 33.44 upon 67.2 that is equal to 0.5 that means, you have the composition Cu₂S into 2 FeS that is what the composition of matte is. However, in the ratio of m into n say for example 2 Cu₂S, 4 FeS or 4 Cu₂S whatever the composition, in all the composition range where the ratio of m by n is 0.5 the grade of matte will be 0.38.