Introduction to Mineral Processing
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Lecture – 58
Flotation Chemicals (Contd.)

Hello welcome. So, we are discussing about frothers in the last lecture and I have already mentioned that there are two types of frothers, one is natural, another one is synthetic and I have also discussed that the synthetic frothers are much stable in their composition and thus advantages over the natural, but the cost may be an hindrance in using these synthetic frothers always.

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Initially natural oils such as pine oil were used as frothers, but their use diminished over the years.

Some collecting properties of the natural oils also interfered with process selectivity.

Having collecting and frothing properties in the same reagent can make selective flotation difficult.

The major commercial frothers today are alcohols and polyglycols with a third type, alkoxy substituted paraffins, for example, triethoxy butane, in some use.

So, initially natural oils, such as pine oil were used as frothers, but their use diminished over the years other reasons as I said that the purity of the pine oil may be a question, then the when the purity differs then the effectiveness also disappears.

And this natural oils, they may have certain amount of collecting properties also and that is why these collecting properties of the natural oils also interfered with process selectivity; that means, it may be collecting some of the unwanted minerals along with your wanted minerals. So, their selectivity is basically getting lost, having collecting and frothing properties in the same reagent can make selective flotation difficult. So, I do not want my frother to be have a collecting property. The major commercial frothers today are alcohols and polyglycols, with a third type that is alkoxy substituted paraffins for example, triethoxy butane in some use.

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Alcohol frothers ($C_nH_{2n+1}OH$) usually contain a single hydroxyl (OH) group and are restricted to 5 - 7 carbons either straight or branch-chained.

Shorter chain alcohols are not surface active enough and longer chain alcohols are increasingly insoluble.

Availability and cost are still major considerations in selection of a frother, but many operations look toward new frothers or frother blends that are tailored to the operation.

Alcohol frothers usually contain a single hydroxyl group as it is shown here and, are restricted to 5 to 7 carbons either straight or branch chained.

It could be straight chain, or it could be branch chained. Shorter chain alcohols are not surface active enough and longer chain alcohols are increasingly insoluble, these are the two problems, these are the two contradictory properties. So, availability and cost are still major considerations in selection of a frother, but many operations look toward new frothers, or frother blends that are tailored to the operation lot of research is going on and so, many reputed chemical or say your flotation chemical manufacturing companies are there, who invest lot of money in research, in designing a particular frother or a collector appropriate for a certain variety of minerals.

The still research is going on and I think the large proportion of mineral community in research, they are engaged only in this flotation chemical related research. So, it is a very active area of research and, these are the research part.

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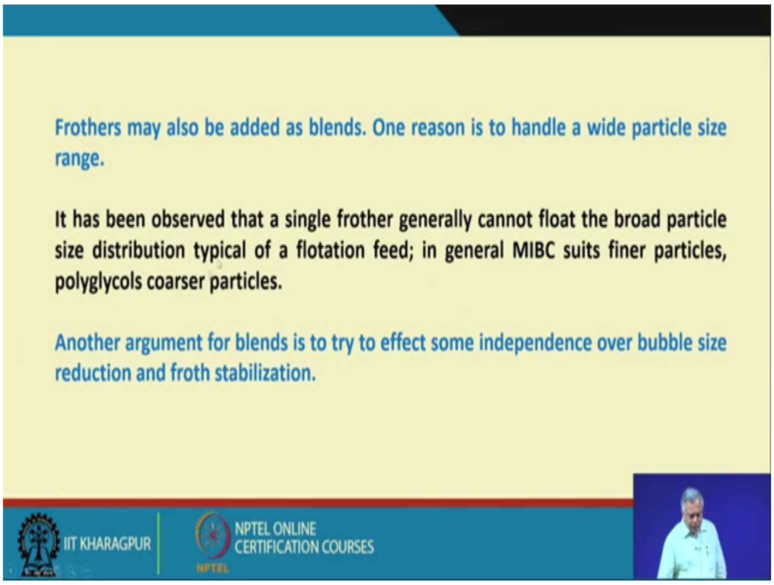

Frothers may also be added as blends. One reason is to handle a wide particle size range.

It has been observed that a single frother generally cannot float the broad particle size distribution typical of a flotation feed; in general MIBC suits finer particles, polyglycols coarser particles.

Another argument for blends is to try to effect some independence over bubble size reduction and froth stabilization.

Frothers may also be added as blends like, I can have mixture of two frothers one reason is to handle a wide particle size range, the reason is that is when you have a wide particle size range that different particle sizes because, it will have different mass. So, I need different amount of stability of the frothers of the bubbles and, then I need a different amount different amount of say different rising velocity of my bubbles because, if my bubble rising velocity is too less. So, what will happen if it is less than the settling velocity of my coarser particles, the particle will never be floated.

So, in that case also so, when I have used long huge size distribution, a single frother may not have all these properties that is your every size needs a different rising velocity, of my bubble and it needs to have a different sizes of the bubble. So, it is very difficult to control this with a single frother. So, many times the blend of different frothers they are being used.

So, I have written that frothers may also be added as blends one reason is to handle a wide particle size range, it has been observed that a single frother generally cannot float the broad particle size distribution typical of a floatation field, in general MIBC methyl isobutyl carbinol suites finer particles, polyglycols coarser particles these are the general observations and that is why when we study the kinetics of floatation, the kinetics has to be based on the particle sizes also. That the kinetics that is the different particle sizes may have different kinetics, now how do I control the kinetics of the entire particle size distribution, they are the selectivity of a frother or the selection of a particular frother may be difficult.

So, may have do you the blend of to frothers as the example, I am giving there is a MIBC it has been observed that, if we consider only the size ranges the relatively finer particles whereas, polyglycols they may be used for coarser particle floatation. Another argument for blends is to try to effect some independence over bubble size reduction and froth stabilization, that is different particle sizes size group, they need different bubble sizes and it requires different amount of froth stability. So, the blend can actually engineer it in a much better way.

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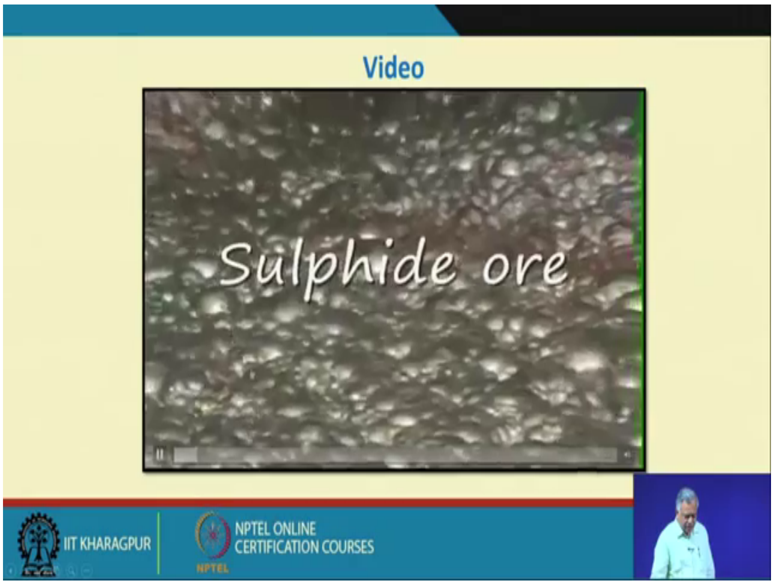

There is a video what I would like to show you that what is this froth and what is this froth stability I am talking about. So, there is a general picture of a froth, now with this video you see that how this froth is formed that is for a sulfide ore and, it is the example I have taken from open sources and, you see the how the forth is being collected, that is it like your overflow mode and if the forth becomes viscous. So, I will have difficulty in collecting them and, if the bubbles they bursts before they are collected through this mechanism. So, the particle also will go back to my suspension. So, my entire effort is lost.

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Video

This is ultra fine ore floatation and see, that if I have a very low air flow rate. So, what will happen? It takes a lot of time to come out as a basically overflow. So, what will happen the very less air flow rate and even the bubbles may be rising up and they are basically getting burst and the particles are going back and the process goes on, but there is no flotation because you are not able to collect it.

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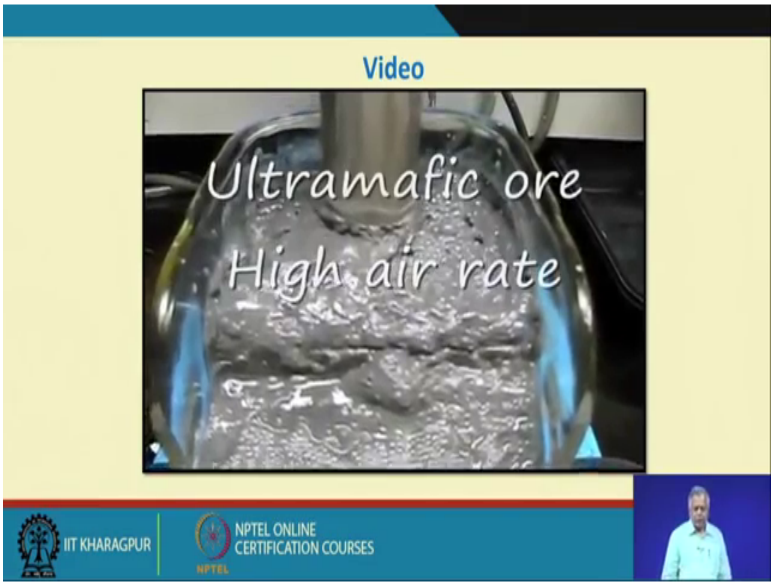

Video

If it is too high flow rate, even you see that what happens the bubbles may break and then you may have you may not be able to collect the, your material selectively. So, you have to maintain an adequate flow rate and one of the role of frother, that can be easily understood that it has to control the it has to give you an optimum air flow rate, your bubble sizes the stability all these are required to be done selecting an appropriate frother.

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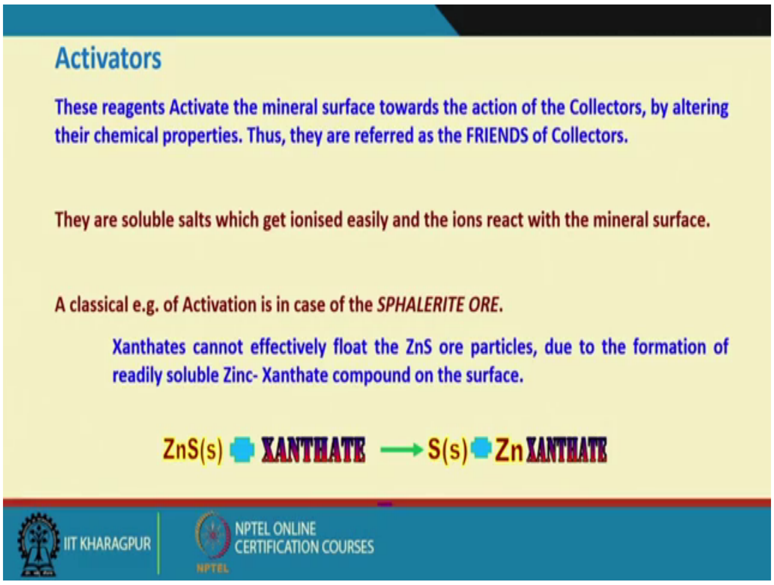

Activators

These reagents Activate the mineral surface towards the action of the Collectors, by altering their chemical properties. Thus, they are referred as the FRIENDS of Collectors.

They are soluble salts which get ionised easily and the ions react with the mineral surface.

A classical e.g. of Activation is in case of the *SPHALERITE ORE.*

Xanthates cannot effectively float the ZnS ore particles, due to the formation of readily soluble Zinc- Xanthate compound on the surface.

$ZnS(s) + XANTHATE \longrightarrow S(s) + Zn\,XANTHATE$

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Now, there are other chemicals like the collectors and frothers, essentially they are there 2 chemicals required for any froth floatation process, but as we have studied in chemistry that a chemical kinetics it depends essentially on the reaction, that is whether a chemical reaction will occur, or not and then how fast is the reaction that basically controls the reaction kinetics. But many times when I want to accelerate this kinetics process, we add some other chemical that is called a catalyst.

So, it catalyzes the process; that means, the reactions become much more faster. So, that by kinetics is faster. So, like that in flotation process also it is ultimately a physical chemical process, but it involves the also the your mechanics part that is how fast we are carrying and all this and, then you need to control the flow of the air and the bubbles and all these you are trying to basically negotiate.

And then how effectively my chemicals will work, that is they will get absorbed onto the surfaces of my material, how the father's will be more effective is the pH of my water to be controlled at a particular level many times the effectiveness of the collectors and the frothers, they are pH dependent. So, how do I alter by pH how do I control that pH. So, for that some other chemicals we use that is called the one group is called the activators.

So, these reagents activate the mineral surface towards the action of the collectors; that means, they prepares the mineral surface. So, that the my collectors they get adsorbed onto the surfaces of those particles, how by altering their chemical properties that is your surface chemical properties thus, they are referred as friends of collectors. So, the activators are those reagents, which activate the mineral surface towards the action of the collectors by altering their chemical properties and, thus they are referred as the friends of collectors.

They are basically the soluble salts which get ionized easily and the ions react with the mineral surface a classical example of activation is in case of the color right, or that is your ZnS here, the xanthates cannot effectively that is your xanthates you have used it, but the xanthates cannot effectively float the ZnS ore particles, although it is being termed as a collector, but the effective, but the effectiveness of this very poor because of the formation of readily soluble zinc xanthate compound on the surface based on this reaction, where as ZnS plus xanthate it give you a zinc xanthate like this. So, because of this zinc xanthate compound the floatability of the xanthate ore gets reduced. Now what happens?

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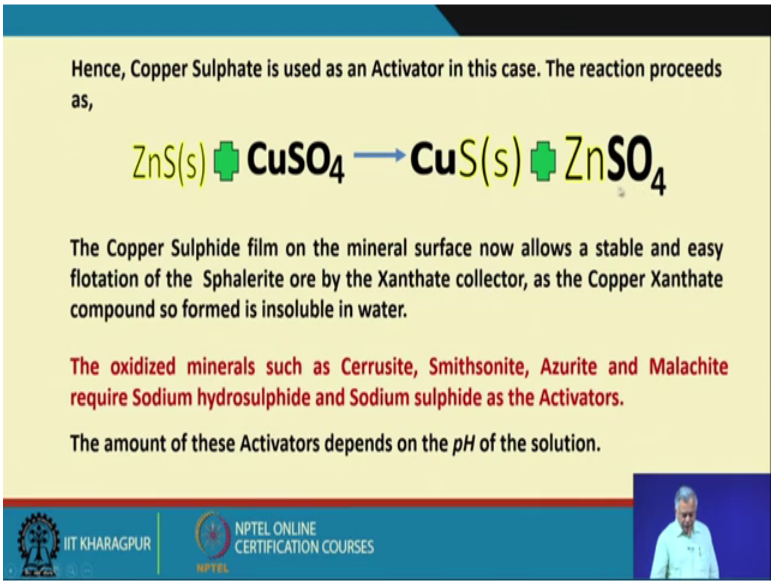

Hence, Copper Sulphate is used as an Activator in this case. The reaction proceeds as,

$$ZnS(s) + CuSO_4 \rightarrow CuS(s) + ZnSO_4$$

The Copper Sulphide film on the mineral surface now allows a stable and easy flotation of the Sphalerite ore by the Xanthate collector, as the Copper Xanthate compound so formed is insoluble in water.

The oxidized minerals such as Cerrusite, Smithsonite, Azurite and Malachite require Sodium hydrosulphide and Sodium sulphide as the Activators.

The amount of these Activators depends on the *pH* of the solution.

Now, how do I improve on this now the copper sulfate is therefore, used as an activated in this case and the reaction now proceeds as, ZnS plus CuSO 4 you get a ZnSO 4 plus

CuS. Now, this copper sulphide film on the mineral surface now allows a stable and easy flotation of the sphalerite ore by the xanthate collector as the copper xanthate compound. So, formed is insoluble in water.

Now, what is happening now these ZnS plus CuSO 4 gives you CuS a copper sulphide film and on the mineral surface it makes, these allows you a stable and easy flotation of this sphalerite ore maybe ZnS surface is only you are getting it coated with a CuS and that helps you in the flotation process. And it by making a copper xanthate and with the original material surface you have changed it. So, that its affinity towards your collector is much more, the oxidized minerals such as cerrusite, smithsonite, azurite and malachite, they require sodium hydrosulphide and sodium sulphide as the activators. The amount of these activators depends on the pH of the solution. Now, the effectiveness of these activators again depends on the pH of the solution.

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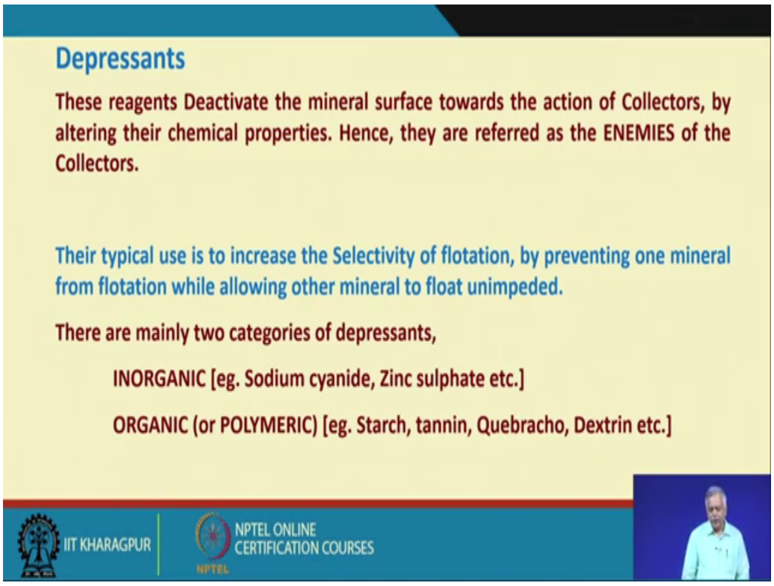

Depressants

These reagents Deactivate the mineral surface towards the action of Collectors, by altering their chemical properties. Hence, they are referred as the ENEMIES of the Collectors.

Their typical use is to increase the Selectivity of flotation, by preventing one mineral from flotation while allowing other mineral to float unimpeded.

There are mainly two categories of depressants,

- INORGANIC [eg. Sodium cyanide, Zinc sulphate etc.]
- ORGANIC (or POLYMERIC) [eg. Starch, tannin, Quebracho, Dextrin etc.]

There is another group of chemical; they termed as depressants what is the depressants do. Now, these reagents deactivate the mineral surface towards the action of collectors, by altering their chemical properties, as they are referred as the enemies of the collectors, like many times now why do you need enemies of the collectors, collector is to is supposed to float your mineral.

But many times you may have 2 minerals and you have used a collector, but both the minerals they like that collector. So, both the minerals will become hydrophobic and, they will all be both of them will be collected. Now, how do I separate them I do not want the mineral a to be floated, I want only the mineral b to be floated. So, in that case before you use a collector, you use a depressant which deactivate that mineral surface, which I do not want that is the mineral a I to float.

So, that the affinity towards the collector is gone and that is why it is called and thus you bring the selectivity towards the of the collected towards the mineral B and therefore, they are called Enemies of the collectors. They typically used to increase the selectivity of flotation by preventing 1 mineral from flotation while allowing other mineral to float unimpeded, there are mainly two categories of depressants one could be inorganic, another could be organic. Inorganic depressants for example, sodium cyanide, zinc sulphate etcetera organics or polymeric like your starch, tannin quebracho, dextrin etcetera.

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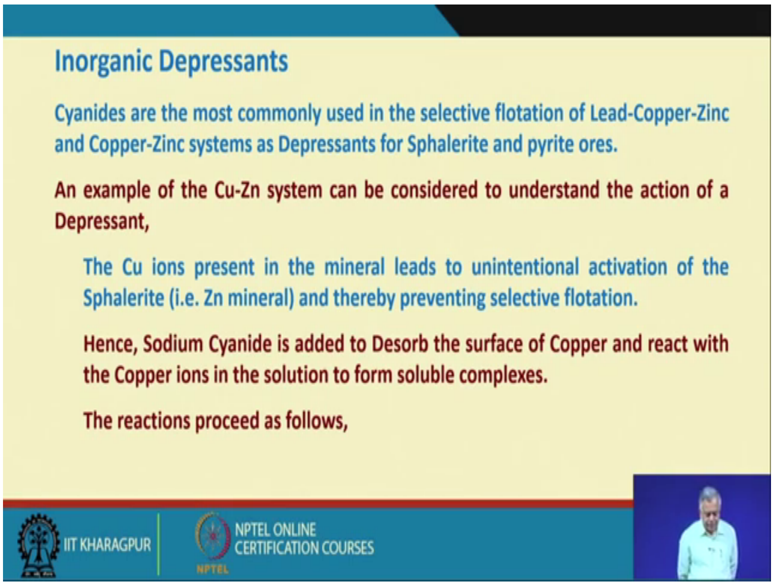

Inorganic Depressants

Cyanides are the most commonly used in the selective flotation of Lead-Copper-Zinc and Copper-Zinc systems as Depressants for Sphalerite and pyrite ores.

An example of the Cu-Zn system can be considered to understand the action of a Depressant,

The Cu ions present in the mineral leads to unintentional activation of the Sphalerite (i.e. Zn mineral) and thereby preventing selective flotation.

Hence, Sodium Cyanide is added to Desorb the surface of Copper and react with the Copper ions in the solution to form soluble complexes.

The reactions proceed as follows,

Inorganic depressants like cyanides are the most commonly used in the selective flotation of lead copper zinc and copper zinc systems as depressants for sphalerite and pyrite ores. An example of the copper zinc system can be considered to understand the action of a depressant, I tried to explain you this. The copper ions present in the mineral leads to unintentional activation of the sphalerite that is the zinc mineral. And thereby preventing selective flotation hence, sodium cyanide is added to dissolve the surface of copper and react with the copper ions in the solution to form soluble complexes.

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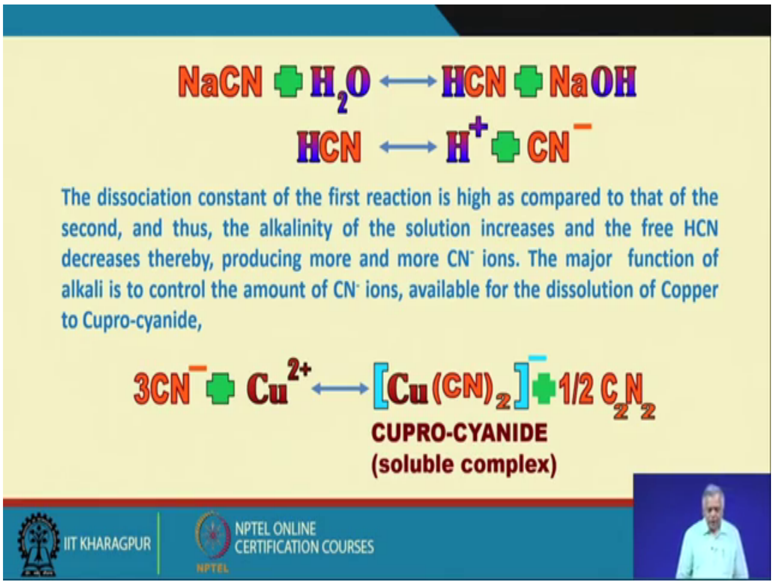

$NaCN + H_2O \longleftrightarrow HCN + NaOH$

$HCN \longleftrightarrow H^+ + CN^-$

The dissociation constant of the first reaction is high as compared to that of the second, and thus, the alkalinity of the solution increases and the free HCN decreases thereby, producing more and more CN^- ions. The major function of alkali is to control the amount of CN^- ions, available for the dissolution of Copper to Cupro-cyanide,

$3CN^- + Cu^{2+} \longleftrightarrow [Cu(CN)_2]^- + 1/2\ C_2N_2$

CUPRO-CYANIDE
(soluble complex)

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So, the reactions are like this, like you have got sodium cyanide plus H 2 O, this gives you HCN plus NaOH and these HCN can get dissociated with the hydrogen ion and cyanide ion. The dissociation constant of the first reaction is high as compared to that of the second and, thus the alkalinity of the solution increases because, of this part and the free HCN decreases thereby, producing more and more cyanide ions. The major function of alkali is to control the amount of cyanide ions, available for the dissolution of copper to cupro cyanide and this is the reaction three CN plus Cu 2 plus gives you Cu CN whole twice cupro cyanide soluble complex plus half C 2 N 2, this is a very complex 1, I do not want to take you to that complexity of this world because this is only an introductory course of mineral processing.

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Also, cyanide ions can react with the Metal Xanthates to form soluble complexes, thereby preventing the adsorption of Xanthates on the mineral surface (in the above case Zn mineral), although this cannot occur until the metal ions (in the above case Copper) have been complexed.

In the above example, unless the ratio of CN^- to Cu^{2+} is greater than 3:1, the prevention of Xanthate adsorption cannot occur.

The more soluble a Metal Xanthate is in cyanide, less is the attachment of Xanthate to that mineral.

The cyanide ions can react with the metal xanthates to form soluble complexes, thereby preventing the adsorption of xanthates on the mineral surface, in the above case zinc mineral although this cannot occur until the metal ions in the above case copper have been complexed, there is a very complex chemistry involved and you have to understand a lot of basic chemistry related to this to understand all this, but just for your information I am I wanted to tell you that how this depressants work just for example, ok.

So, in the above example it is necessary that to maintain a ratio of cyanide to copper ions, unless the ratio of these 2 is greater than 3 is to 1, the prevention of xanthate adsorption cannot occur. So, we have to maintain that ratio or maybe higher. The more soluble a metal xanthate is in cyanide less is the attachment of xanthates to that mineral that is how you bring the selectivity.

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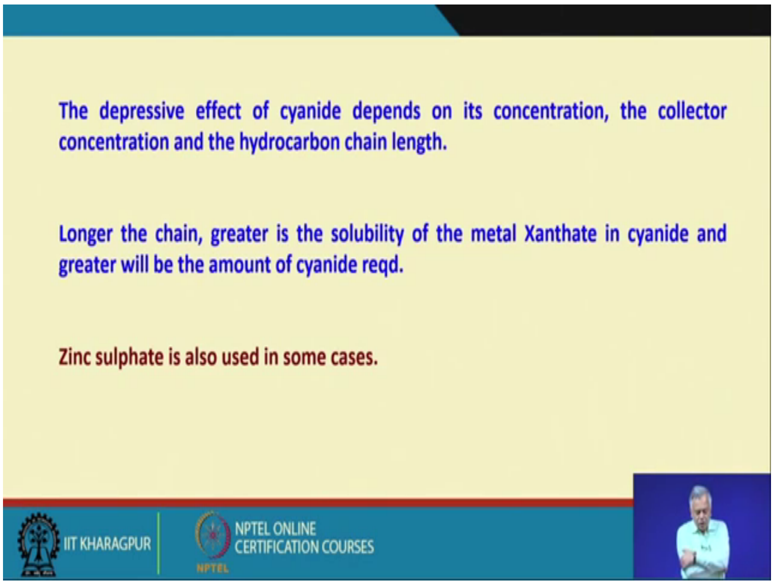

The depressive effect of cyanide depends on its concentration, the collector concentration and the hydrocarbon chain length.

Longer the chain, greater is the solubility of the metal Xanthate in cyanide and greater will be the amount of cyanide reqd.

Zinc sulphate is also used in some cases.

The depressive effect of a cyanide depends on it is concentration, the collector concentration and the hydrocarbon chain length, all these will decide that how effective this depressants are. Longer the chain what will happen greater is the solubility of the metal xanthate in cyanide and greater will be the amount of cyanide required. So, the cost will go up and you know the cyanide is very poisonous highly poisonous. So, handling of cyanide also requires lot of cost zinc sulphate is also used in some cases.

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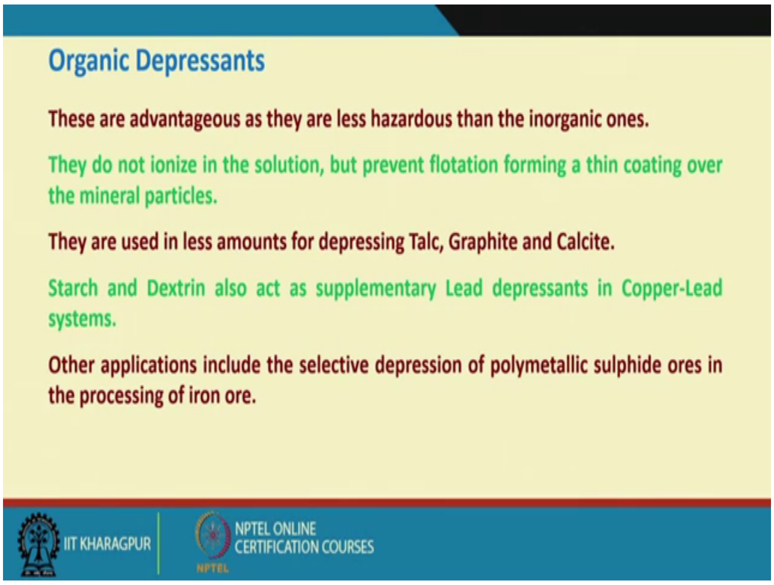

Organic Depressants

These are advantageous as they are less hazardous than the inorganic ones.

They do not ionize in the solution, but prevent flotation forming a thin coating over the mineral particles.

They are used in less amounts for depressing Talc, Graphite and Calcite.

Starch and Dextrin also act as supplementary Lead depressants in Copper-Lead systems.

Other applications include the selective depression of polymetallic sulphide ores in the processing of iron ore.

Now, these are inorganic type and there are some organic depressants also, these are advantageous as they are less hazardous than the inorganic ones as I said the cyanide a very hazardous. So, handling the hazardous chemicals is always very difficult. So, and many times you may not get the required clearances from the concerned ministries because, they were using hazardous chemicals.

They do not ionize in the solution the organic ones, but prevent floatation forming floatation forming a thin coating over the mineral particles. So, how this works the organic your depressions. Now, they form a thin coating over the mineral particles which you want to depress, they are used in very less amounts for depressing less depressing talc graphite and calcite, that is your organic depressant starch and dextrin also act as supplementary lead depressants in copper lead systems. Other applications include the selective depression of polymetallic sulphide ores in the processing of iron ore. So, even you see that the depressions also is not very easy to select and is not very easy to handle.

So, you have to have a cost is one controlling factor, another one is the environment, another one is related to hazards and other is the effectiveness. Now, as I said that all these chemicals their effectiveness are at their best at a particular pH range. So, you may have to add something additionally to modify your pH, or to bring the pH back to your that optimum level than those the chemicals required.

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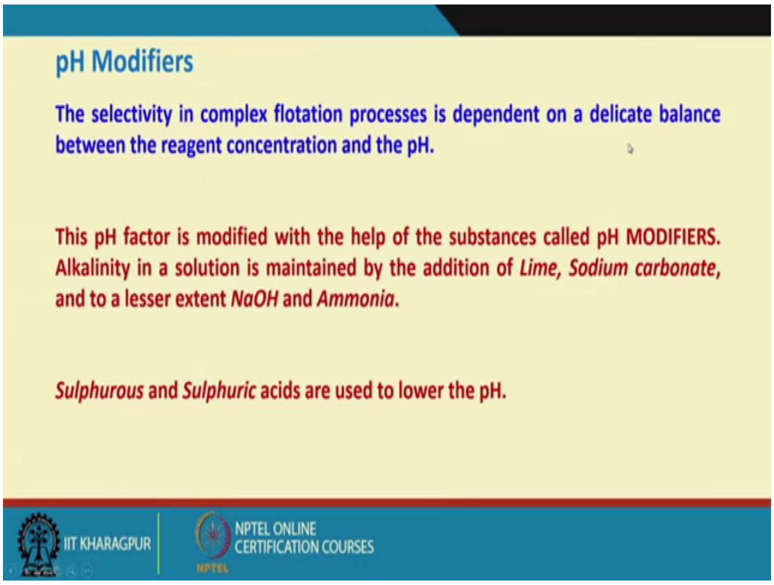

pH Modifiers

The selectivity in complex flotation processes is dependent on a delicate balance between the reagent concentration and the pH.

This pH factor is modified with the help of the substances called pH MODIFIERS. Alkalinity in a solution is maintained by the addition of *Lime, Sodium carbonate,* and to a lesser extent *NaOH* and *Ammonia*.

Sulphurous and *Sulphuric* acids are used to lower the pH.

So, the selectivity in complex floatation processes is dependent on a delicate balance between the reagent concentration and the pH. So, it is not only not only the reagent selection I am reiterating, it again and again it is not only your reagent selection, it is also their dosages and also how do you add them, how do you ensure that they are mixed properly and what is the best pH of that chemical to have his best effectiveness. These are all very important factors in controlling the, your floatation parameters.

This pH factor is modified with the help of the substances called pH modifiers, alkalinity in a solution is maintained by the addition of line sodium carbonate and to a lesser extent sodium hydroxide and ammonia like, I want to maintain an alkaline pH there I can use all this. Similarly if I want to lower the pH, then we can use sulphurous and sulfuric acids in dilute concentrations, they can use them as a to lowering the pH.

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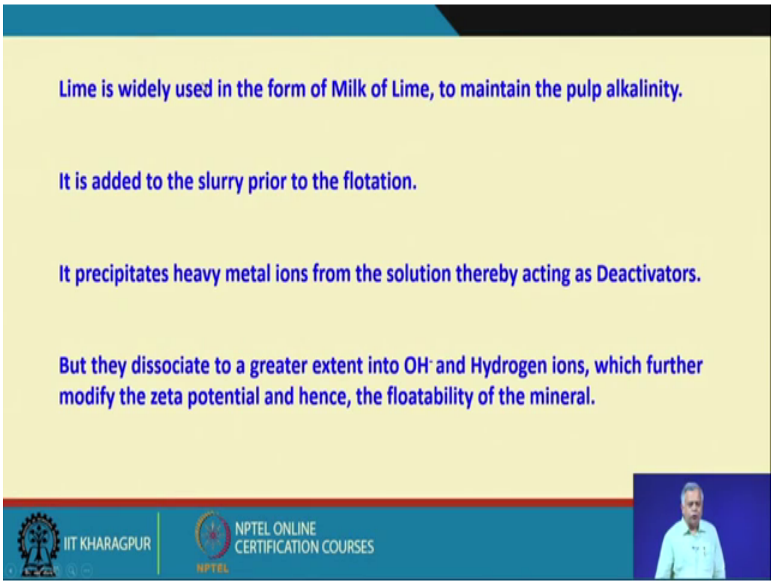

Lime is widely used in the form of Milk of Lime, to maintain the pulp alkalinity.

It is added to the slurry prior to the flotation.

It precipitates heavy metal ions from the solution thereby acting as Deactivators.

But they dissociate to a greater extent into OH^- and Hydrogen ions, which further modify the zeta potential and hence, the floatability of the mineral.

Lime is widely used in the form of milk of lime, to maintain the pulp alkalinity it is added to the slurry prior to the flotation, there is a conditioning tank and is your slurry preparation tank, before you send it to the actual flotation plant where, you ensure the mixing of your collectors to the surfaces of the minerals effectively. And there these collectors, they are more effective at a particular pH range.

So, there you start maintaining that pH to ensure that my collectors are properly adsorbed to my targeted mineral surfaces, it precipitates heavy metal ions from the solution thereby acting as deactivators, but they dissociate to a greater extent into hydroxyl and hydrogen ions, which further modify the zeta potential and has the floatability of the mineral, these are all complex things I am not going into detail of this when mechanisms.

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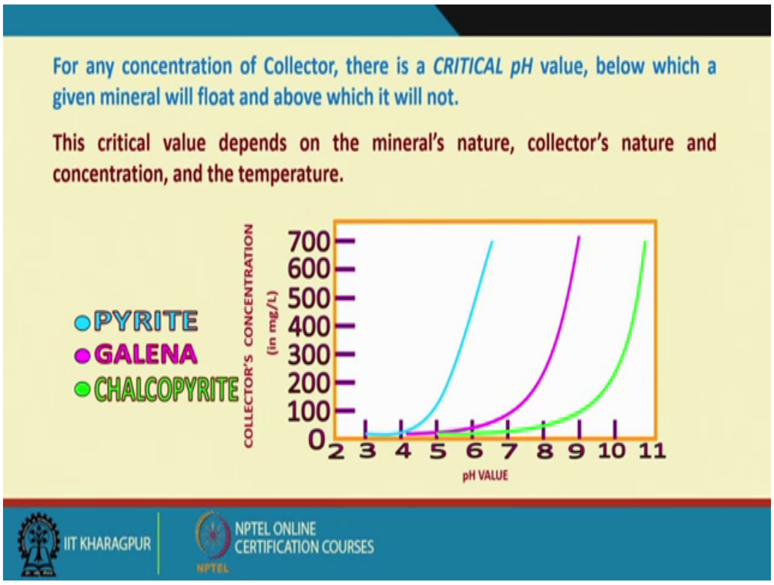

For any concentration of Collector, there is a *CRITICAL pH* value, below which a given mineral will float and above which it will not.

This critical value depends on the mineral's nature, collector's nature and concentration, and the temperature.

For any concentration of collector there is a critical pH value, below which a given mineral will float and above which it will not. Now, this critical value depends on the minerals nature, collectors nature and, concentration and the temperature as well.

Like as for example, I am showing it here, like your there is the pH value x-axis is the pH value and y-axis is the collectors concentration. And suppose I have got three minerals like your pyrite galena and chalcopyrite, you see that your pyrite with a particular your when it is too less the pH is too less and added collector concentration is at a very less amount as recovery is very less.

So, a defectiveness goes up as we increase the collectors concentration with these pH range, that is in between your 5.5 to 6. Similarly Galina has got a several other pH range for its optimum condition and the concentration and your chalcopyrite has got a different. So, you should make this type of graphs in a control environment test done at a control environment like in a laboratory process and, you should try to understand first that what are the best conditions for my effective froth flotation process that should be the guidelines for controlling them your parameters in a plant scale operation.

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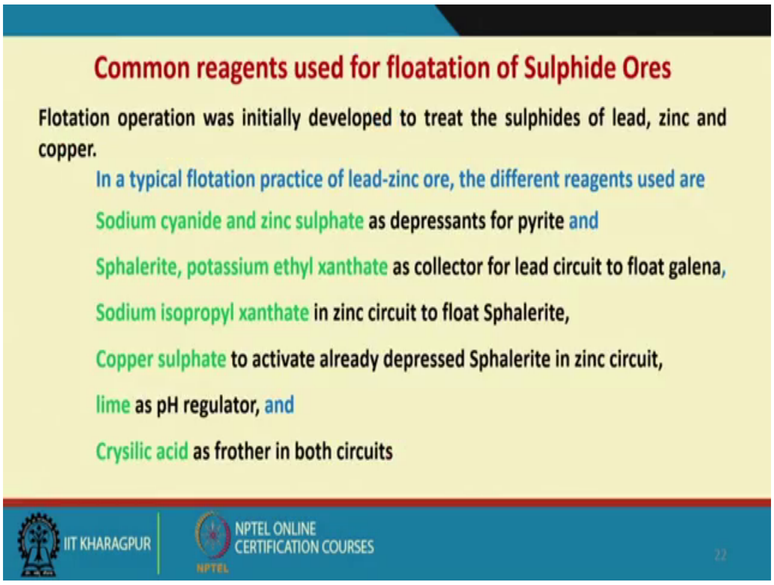

Common reagents used for floatation of Sulphide Ores

Flotation operation was initially developed to treat the sulphides of lead, zinc and copper.

In a typical flotation practice of lead-zinc ore, the different reagents used are

Sodium cyanide and zinc sulphate as depressants for pyrite and

Sphalerite, potassium ethyl xanthate as collector for lead circuit to float galena,

Sodium isopropyl xanthate in zinc circuit to float Sphalerite,

Copper sulphate to activate already depressed Sphalerite in zinc circuit,

lime as pH regulator, and

Crysilic acid as frother in both circuits

We will continue this discussion in next lecture till then.

Thank you very much.