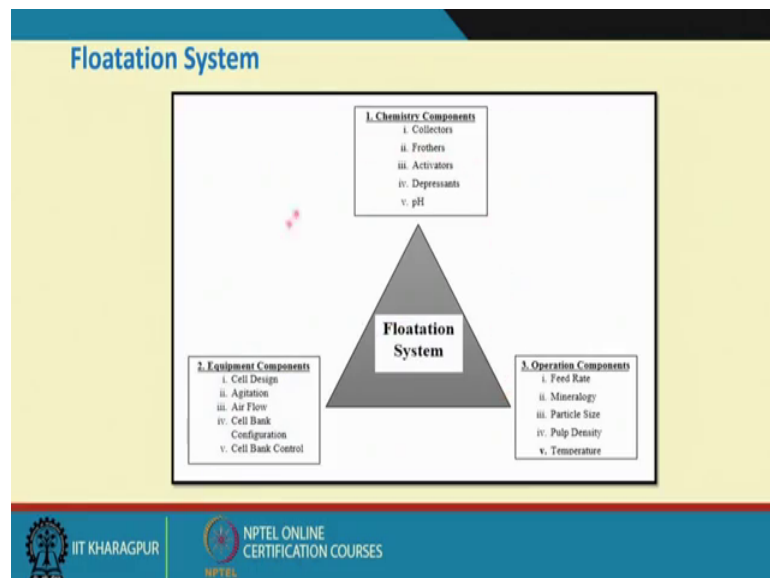


Introduction to Mineral Processing
Prof. Arun Kumar Majumder
Department of Mining Engineering
Indian Institute of Technology, Kharagpur

Lecture – 56
Flotation Chemicals

Hello, welcome. So, we are discussing about the floatation.

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So, we have discussed about the floatation system that is mainly the floatation has got three main components one is the chemistry component that is where we talk about the collectors frothers activators depressions and pH, then another part is the equipment components where what type of cell it is how we will agitate, then why what will be the air flow how many numbers of cells we require all this thing are dealt with this topic that is called equipment components and there is another one that is called operation components at the feed rate that is what is that material; at what rate you are feeding what are the mineralogy? What is the characteristic of that ore? What are the particle size distributions, what is the percentage solids you will be using? What are the effects of temperature?

So, normally these three components that is the chemistry equipment and operation they has to be synergize at an optimum level to have my optimum performances of the floatation system as I told you at the beginning; that it is a very fast subject. So, my so, it

is impossible to cover the entire topics that is each component in detail. So, what I will do? I will try to discuss about some of them briefly which are very important.

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Chemicals of Floatation

Chemicals are required,

1. To control the relative Hydrophobicities between the particles.
2. To maintain proper froth characteristics.

The different types of chemicals involved are,

1. COLLECTORS
2. FROTHERS
3. REGULATORS,
 - i. Activators
 - ii. Depressants
 - iii. pH MODIFIERS

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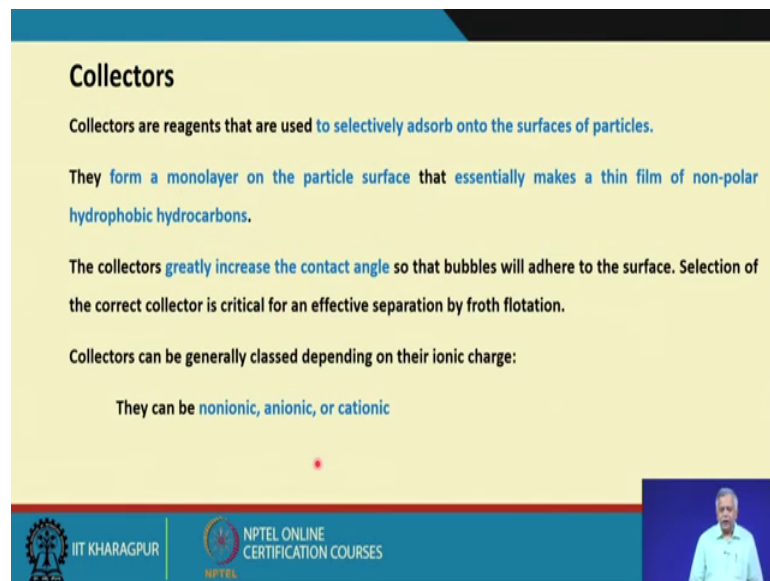
So, we start with this there is a chemistry component and where basically we call it the chemicals of floatation; why do we require chemicals that is the first thing, we have to understand, it is basically we said that the separation is made between the two particles depending on their water repellent or water say liking type of your say behavior you know we call it hydrophobic and hydrophilicity; hydrophobicity and hydrophilicity of the particles, but many times we have to have a minimum difference during the in between the degree of hydrophobicity.

So, natural e occurring minerals may not have that degree of hydrophobicity or even though they have the difference it may not be that significant. So, we have to control the relative hydrophobicity between the particles and for that we have to add some chemicals what chemicals that we will discuss and they number two is that we said that the bubble has to carry upward the my hydrophobic materials and there has to be a foam formation, but this froth should have certain characteristics that is after reaching the top of the my vessel if the bubble is vast then what will happen again the particle will come back to the cell.

So, because you have to collect the froth at a certain rate to take out the mind some materials which are already floated; so, for that the bubble stability is required to some

extent. So, for that also we add some chemicals. So, the different types of chemicals involved based on their purpose that is for what purposes; they are used; we have you we normally use the different names for them first one; we call it collector we will discuss; it in detail; what is that collector means then the name of the another group of your chemicals what to use we call them frother, then there are regulators the regulators also have got different varieties like we call them activators depressions pH modifiers like that.

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Collectors

Collectors are reagents that are used to selectively adsorb onto the surfaces of particles.

They form a monolayer on the particle surface that essentially makes a thin film of non-polar hydrophobic hydrocarbons.

The collectors greatly increase the contact angle so that bubbles will adhere to the surface. Selection of the correct collector is critical for an effective separation by froth flotation.

Collectors can be generally classed depending on their ionic charge:

They can be nonionic, anionic, or cationic

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So, let us start about the collectors; let us discuss about the collectors what they are. So, collectors are reagents that are used to selectively adsorb onto the surfaces of particles; that means, it is a basically a specific group of chemical which selectively gets adsorbed onto the surfaces of those particles which I want to be floated it may be your wanted material it may be your unwanted material.

So, when we try to float the wanted material we have already said we call it direct floatation and when we try to float only the unwanted material we call them the indirect floatation or the reverse floatation now they form now why should they be observed onto the surfaces of the particles what is their role. So, the collectors they form or they suit for a mono layer on the particle surface that essentially makes a thin film of nonpolar hydrophobic hydrocarbons.

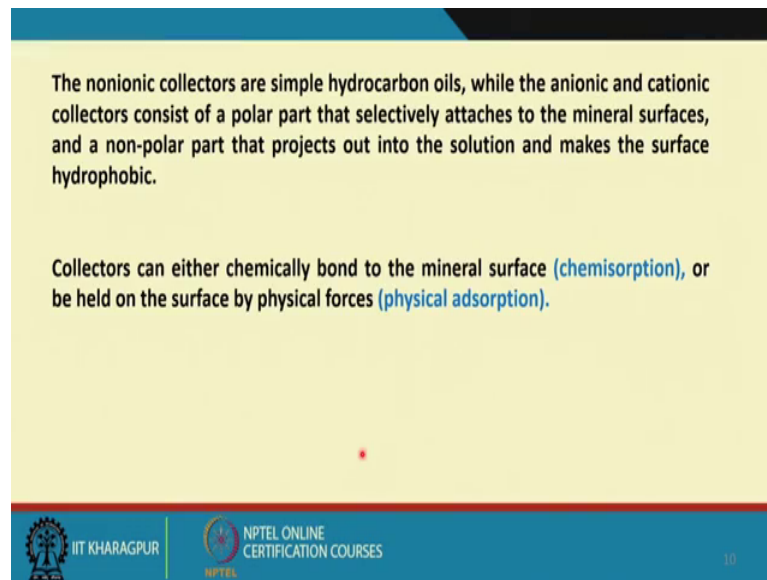
So; that means, the party this chemical should attack selectively my particles what I want; it is to be adsorbed onto the surfaces of those particles and then once they are adsorbed they should form a mono layer on the particle surfaces in such a manner that a thin film of nonpolar hydrophobic hydrocarbon is found; that means, I want to increase the degree of hydrophobicity of those particles by this mechanism.

Now, how they increase my hydrophobicity that the essential properties or essential purpose of these chemicals should be to increase the contact angle that is the Young Dupra equation we have discussed in the last class. So, the collectors they greatly increase the contact angle. So, that bubbles will adhere to the surface; that means, the bubbles when the contact angle increases. So, the surface becomes more hydrophobic and the bubble should be adhered to the surfaces of these particles.

Now, once the bubble they get adhered to the surfaces of these particles that the bubble for his natural tendency it will try to go up and then it should carry my particle that is the very purpose of this froth floatation process. Now question is what type of collector, I will select; how do I know that what chemical I have to use? So, therefore, the selection of the correct collector is critical for an effective separation by froth floatation not a single chemical can be used as a collector irrespective of the particle surface properties.

So, that is a critical issue that is for a particular type of mineral or a ore to be floated what type of chemicals or what type of collector I should use. So, therefore, depending on the mineral surfaces there are various categories of collectors. So, it can be generally classed depending on their ionic charges like they can be non ionic they can be anionic or they can be cationic. So, there are three broad groups of this that is it can be non ionic it does not have any surface charge; it can be anionic or it can be cationic.

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The nonionic collectors are simple hydrocarbon oils, while the anionic and cationic collectors consist of a polar part that selectively attaches to the mineral surfaces, and a non-polar part that projects out into the solution and makes the surface hydrophobic.

Collectors can either chemically bond to the mineral surface (chemisorption), or be held on the surface by physical forces (physical adsorption).

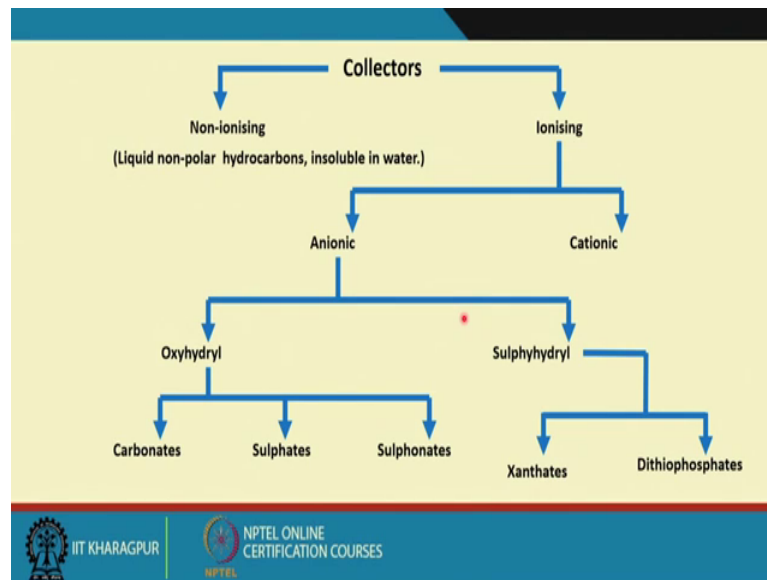
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Now, in this case the non ionic collectors are simple hydrocarbon oils these are basically a simple hydrocarbon oils while the anionic and cationic collectors consist of a polar part that selectively attaches to the mineral surfaces and a non-polar part that projects out into the solution and makes the surface hydrophobic; that means, what is happening.

Now, the non ionic collectors they are basically a simple hydrocarbon oils they just sit on the surfaces of the particles and they make the your surface a hydrophobic, but the anionic and cationic collectors they have got two parts that is a polar part and a non-polar part. So, the polar part; it should selectively get attached to the mineral surfaces and the projected part of the act chemical is the non-polar part which makes the particle surface hydrophobic I will show you some examples later on.

So, collectors can either chemically bond to the mineral surface now how the chemicals will adhere to the surfaces of the my minerals, there can be two broad methods of or say a broad mechanism of absorption. So, one is called chemisorption or be held by the surface by physical forces that is when the collectors can either chemically bond to the mineral surface when it is chemically bonded; do we call it chemisorption or be held on the surface by physical forces, they will call it physical adsorption.

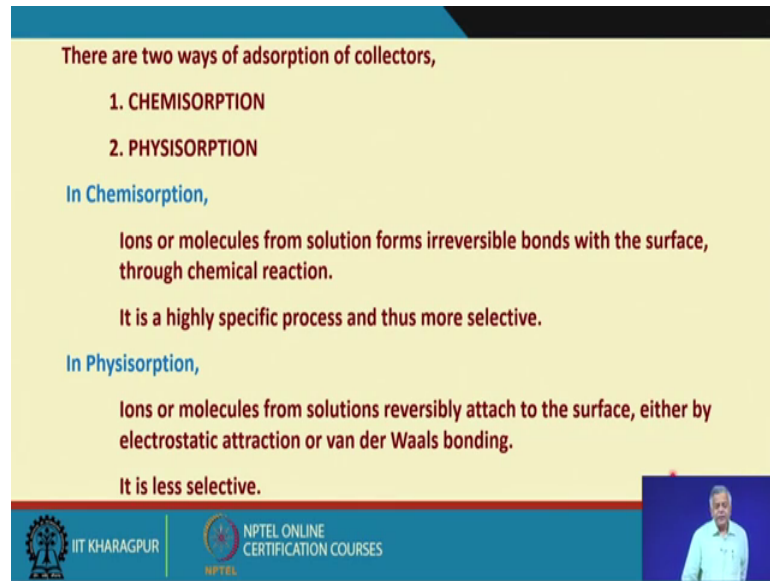
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Now if I group them in the collectors in terms of a flow chart, I can represent the group of broad categories of collectors can be grouped like this, it is as I said that it can be non ionizing that is your liquid non-polar hydrocarbons they are in soluble on water like your hydrocarbon oils ok

Now, another category is ionizing that is what we have discussed these ionizing collectors could be anionic and cationic typic and ionic collectors could be oxy hydril or sulphy hydril type, again oxy hydrils could be your more applicable or say actually, it has got a various as types like it could be carbonates, it could be sulphates, it could be sulphonates. Similarly, sulphy hydril collectors also can be grouped into that is one is called xanthates, another is called dithiophosphates.

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The slide is titled "There are two ways of adsorption of collectors," and lists two types: 1. CHEMISORPTION and 2. PHYSISORPTION. It then provides detailed descriptions for each. Under "In Chemisorption," it states that ions or molecules from solution form irreversible bonds with the surface through chemical reactions, and that this process is highly specific and more selective. Under "In Physisorption," it states that ions or molecules from solutions reversibly attach to the surface through electrostatic attraction or van der Waals bonding, and that this process is less selective. The slide footer includes the IIT Kharagpur logo and the NPTEL Online Certification Courses logo. A small video inset of a presenter is visible in the bottom right corner.

There are two ways of adsorption of collectors,

1. CHEMISORPTION
2. PHYSISORPTION

In Chemisorption,

Ions or molecules from solution forms irreversible bonds with the surface, through chemical reaction.

It is a highly specific process and thus more selective.

In Physisorption,

Ions or molecules from solutions reversibly attach to the surface, either by electrostatic attraction or van der Waals bonding.

It is less selective.

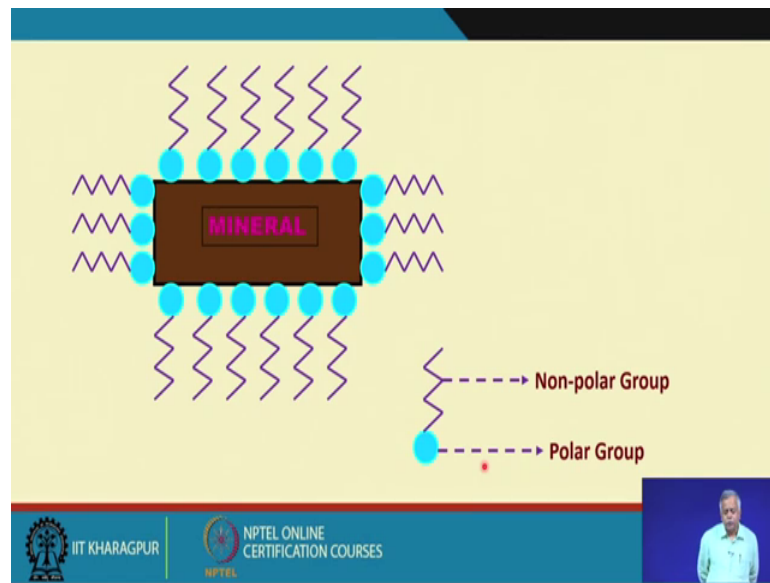
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Now, as I said that there are two broad mechanism that how the particles gets adsorbed that is the collectors they get adsorbed onto the particle surfaces, one is called chemisorption that is based on your chemical your say mechanism or another one is the by the physical forces. So, any chemisorptions; what happens? The ions or molecules from solution that is the collector has to be dissolved first and then when it is in solution it forms irreversible bonds with the surface through chemical reactions chemical surface reaction ok.

It is a highly specific process and thus more selective; that means, this process is highly selective because it depends on the weather my that targeted material surface likes that chemical or not it depends on that and there has to be a rea surface reaction between this two otherwise this bond will not be stronger and they will not be say getting adsorbed onto the surfaces of those ores or the minerals.

In physisorption ions or molecules from solutions reverse reversibly attach to the surface. So, the first one is the irreversible bond there is a reversible bond attached to the surface either by electrostatic attraction or Vander Waals bonding; that means, you can detach this you can dislodge this bond by applying some other physical forces and that is why it is less selective.

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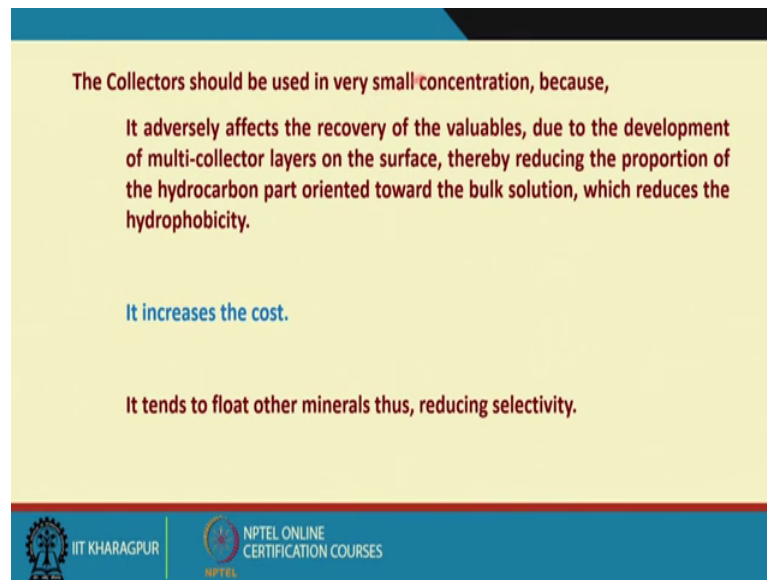
This is what I was talking about that is how a collector basically works. So, this part of the chemical that is the collector so that is the polar group suppose this is the mineral surface. So, this polar group they get adsorbed onto the surface of these minerals either by the two mechanisms it could be chemisorption or by physisorption processes and this part we call it non-polar group and this gives you the hydrophobicity of that mineral surfaces.

So, this is an idealistic view because what happens now that if the particle surface is not prepared well for this polar group to be attached or they are not susceptible to this mechanism either by chemisorption processes or by physisorption processes, then these chemicals will not be effective.

So, the selection of that collector is very much dependent on what is the surface property of your material. Now, it is also evident from the previous figure that the collectors, it should be optimally added; that means, the doses how much of that collector that is you may have chosen a right kind of your chemical to be used as a collector for a particular ore to be to make the surfaces hydrophobic, but what will happen now you see that if I am adding.

Now, these surfaces are almost coated with the your collector, but if I have excessive of this. So, what will happen? They again starts getting your adhered to these say polar and nonpolar groups?

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The Collectors should be used in very small concentration, because,

It adversely affects the recovery of the valuables, due to the development of multi-collector layers on the surface, thereby reducing the proportion of the hydrocarbon part oriented toward the bulk solution, which reduces the hydrophobicity.

It increases the cost.

It tends to float other minerals thus, reducing selectivity.

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So, that is why I have written that the collectors should be used in very small concentration because it adversely affects the recovery of the valuables, why now because due to the development of multi collector layers on the surface that is quite evident from the previous picture that if I have a more amount of collected, we will have multi layers of these chemicals on to the surfaces of this material which is not required and therefore, it will reduce the proportion of the hydrocarbon part oriented toward the bulk solution which reduces the hydrophobicity because what will happen say when I am having more of this collector then this polar and non-polar group will be randomly distributed which is projected to my fluid phase.

So, the selectivity of the mineral surface towards the bubble will be lost and therefore, the recovery will be lost and unnecessarily you will be incorporating cash cost for excessive chemicals. So, it is not only important that what should be my ideal collector for a particle surfaces to be made hydrophobic selectively what is equally important also that how much of that collector or that chemical I have to add.

So, what is the optimum dose of that collector and what will happen if I have excessive collector; it tends to it; it may seat on the surfaces of other minerals which I did not want to float. So, what will happen? So, those mineral surfaces also will be hydrophobic and they will be also floated along with my wanted minerals which I want; which was supposed to be floated. So, my the selectivity will be reduced as well as my recovery of

my valuable minerals or I would say the material are the minerals which I wanted to float that will be reduced and it will add extra cost to the entire process additional problems which is not written here that is this chemicals excessive amount of chemicals may cause environment related problems because ultimately that water what is going out of the system, they will be carrying all these unused chemicals and that may be causing environmental hazards.

So, that doses selection is also very important and what is the most important thing about the selection of the collectors that it is not on this it is the it has to be specific to that mineral surfaces and then your doses how much I require and then whether these chemical is easily available and then can we regenerate these chemicals; these are all the issues related to that collectors in general.

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Non-ionic collectors

These are required to enhance the hydrophobicities of the partially hydrophobic minerals surfaces (e.g. coal), by selectively adsorbing on their surface.

Fuel and Kerosene oil are some of the non-ionic collectors.

Ionic collectors

These have complex molecules, which are asymmetric in nature and are Heteropolar, i.e., molecules have a non-polar hydrocarbon group (which is water repellent in nature) and a polar group (which reacts with water).

Ionic collectors are classed into:- Anionic and Cationic Collectors

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Now, let us discuss about the non ionic and ionic collectors. So, the non ionic collectors as I said that when do I require this now these are required to enhance the hydrophobicities of the partially hydrophobic mineral surfaces like take the example of coal is a naturally hydrophobic mineral; that means, it has got certain degree of hydrophobicity naturally, but many times that much of hydrophobicity is not enough to have an effective separation of the coal and shell particles.

So, there many times, we use the non ionic collectors by selectively adsorbing on their surfaces because they are very low cost materials and they are easily available and they

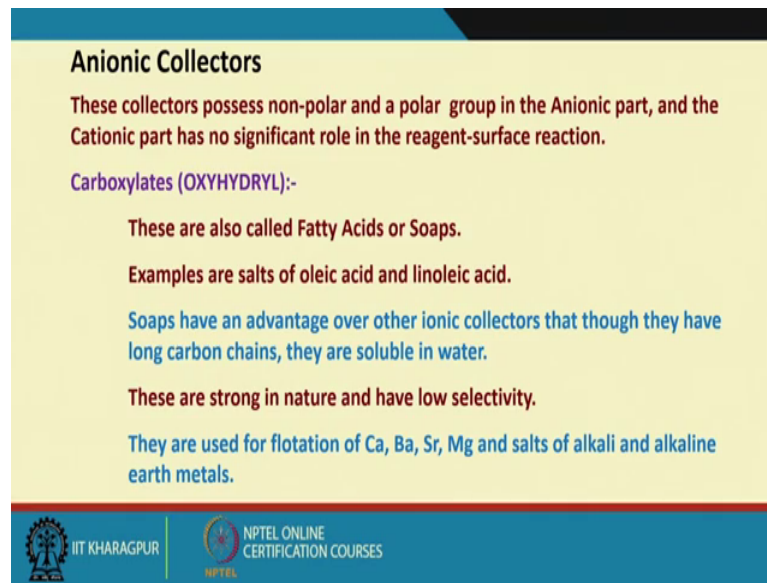
are many times can be recycled back also. So, that is the fuel and kerosene oil are some of the non ionic collectors which are used for coal floatation; that means, when we have a naturally hydrophobic mineral there you may require a little amount of non ionic collectors it is a something like your mineral oil or the is like your kerosene oil and then we can use them as non ionic collectors, but here the selectivity is less. So, except for certain minerals or say like your coal; it is not being used that your it does not have that widespread use.

Now, let us talk about ionic collectors; that means, the minerals which are very difficult to float for that we need some targeted chemical or targeted collectors these are complex molecules what are these ionic collectors are; they have a comp have complex molecules which are as symmetric in nature and are hetero polar what does it mean the molecules have a non polar hydrocarbon group which is water repellent in nature.

So, it should have a its must be a hetero polar; that means, or naturally they are hetero polar and it has got a non-polar and a polar group and non polar group is basically water repellent in nature and the polar group which reacts with water; that means, which likes water or which starts reacting with water and that is why I said that this polar group should selectively sit on the surfaces of my chemical and the non-polar part should be projected towards the my fluid that is the water.

So, as because it is water repellent the non polar group. So, my particle surface now coated with a thin film of collector will behave like hydrophobic mineral ionic collectors as I said that it can be having two types that is anionic and cationic collectors if I look at anionic collectors.

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Anionic Collectors

These collectors possess non-polar and a polar group in the Anionic part, and the Cationic part has no significant role in the reagent-surface reaction.

Carboxylates (OXYHYDRYL):-

- These are also called **Fatty Acids or Soaps**.
- Examples are salts of **oleic acid and linoleic acid**.
- Soaps have an advantage over other ionic collectors that though they have long carbon chains, they are soluble in water.
- These are strong in nature and have low selectivity.
- They are used for flotation of **Ca, Ba, Sr, Mg** and salts of alkali and alkaline earth metals.

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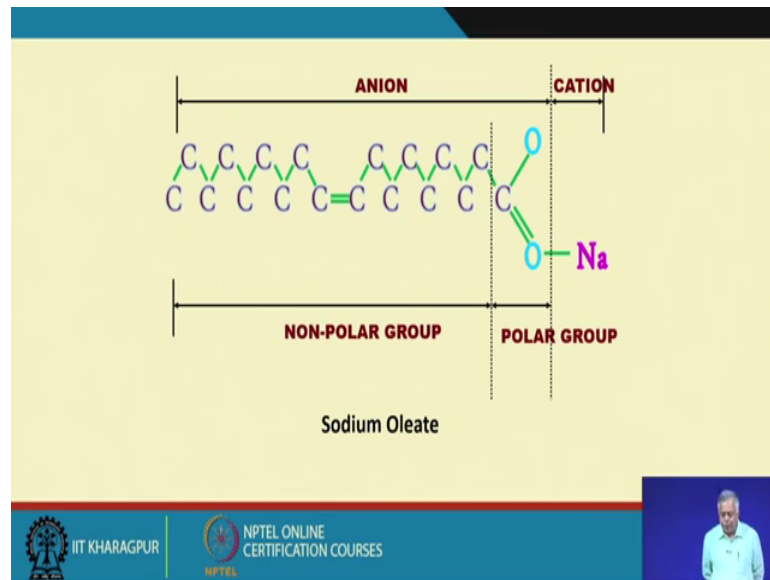
These collectors possess non-polar and a polar group in the anionic part; that means, in an anionic part it has got a non polar and a polar group and the cationic part has no significant role in the reagent surface reaction; that means, the collector has got an anionic part and a cationic part in this type of your anionic collectors the non-polar and polar group; that means, basically your anionic part is hetero polar that it has got a non polar and a polar group and that is what we try to use that property examples like carboxylates it is an oxyhydril your collector, these are also called the fatty acids or soaps.

They come into this category example real example are salts of oleic acid and linoleic acid soaps, they have an advantage over other ionic collectors in such a way that they have long carbon chains and they are soluble in water too. So, what is the what is the issue here that your collector must be fast dissolve into your solution and then it should have that your cations and anions to be released and that anionic part in this type of your anionic collectors it has two polar groups that is your polar and non-polar part.

So, the cationic part does not have a significant role to play and that polar and non-polar group will try to make my mineral surface my targeted mineral surface to be hydrophobic in that context the soaps as has got advantage over other ionic collectors in such a way that although they have a long carbon chains they are soluble in water why I mentioned have a long carbon chains; that will discuss later on these are basically strong in nature and have low selectivity, this is a very this gives you a very stable bonding, but

they have got lesser selectivity where they are used they are used for flotation of calcium barium cerium magnesium and your salts of alkali and alkaline earth metals this is an example of an anionic collector; you see that this is the structure of sodium oleate very popular collector; you see that it has got a cation part that is the sodium.

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Now within this anionic part, you have got a polar group and you have got a non polar group here. So, this polar group should get adsorbed onto the surface of the mineral and this nonpolar group should be projected towards my fluid part. So, that my entire surface of the mineral becomes hydrophobic.

So, if you look at the structure here, it is very fascinating that this is called a; this is basically a of no use; this cation part and this is how they are basically oriented towards. So, how big is the chain how long is the chain that determines that whether it is a short chain or whether it is a long chain collected there is another example; the sulphonates and sulphates.

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Sulphonates and Sulphates (OXYHYDRYL):

- These have lower collecting power and have greater selectivity.
- They are used for flotation of Barite, celestite, fluorite, apatite, chromite, cassiterite, mica, kyanite and scheelite.

Xanthates (SULPHYHYDRYL):

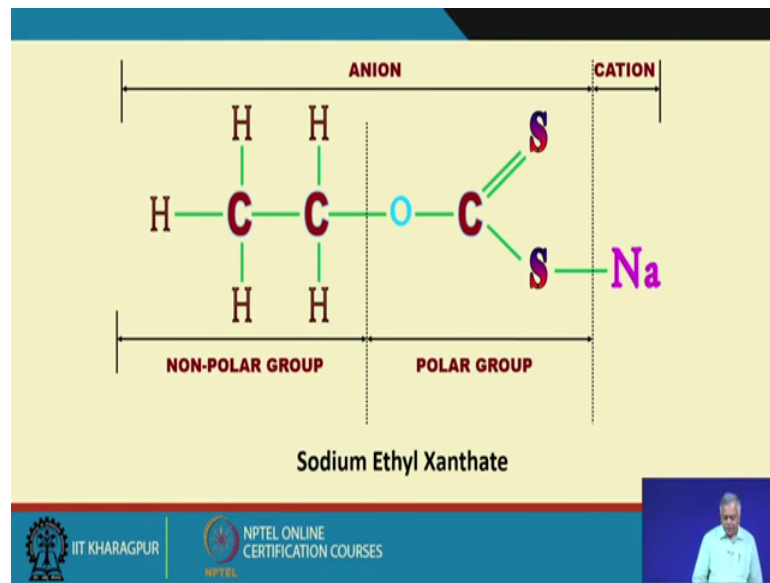
- They are most widely used THIOL collectors. Also called Xanthogenates.
- They are formed by reacting Alkali Hydroxides (eg. KOH), Carbon Disulphide (CS₂) and Alcohol (ROH).
- They contain normally 1 to 6 Carbon atoms.
- Sodium (the cationic part) Alkyl Xanthates decreases in efficacy with age.

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These are called the oxyhydril, these have lower collecting power and have greater selectivity and means it can sit selectively onto your targeted mineral surfaces, but its collecting power is very less where the bonding may be weak bonding between the particle surfaces and this collector may be weak and that is why its collecting power may be your low, but it will not have friendship that is in terms of bonding with anyone; that means, with any mineral it will only have friendship or the bonding with its certain class of material or mineral which you have targeted to be flouted.

So, they are used for flotation of barite, celestite, fluorite, apatite, chromite, cassiterite, mica, kyanite, seheelite, etcetera, then there are another group of collector that is called xanthates; it is also known as sulphyhydril group rock collectors. So, they are most widely used thiol collectors also called xanthogenates; they are formed by reacting alkali hydroxides like KOH and carbon disulphide and alcohol. So, how they are made now by reaction by reacting with alkali hydroxides carbon disulphide and alcohol, you can make this type of your collectors they contain normally 1 to 6 carbon atoms, sodium, the cationic part and the alkali xanthates decreases in efficacy with age; that means, if it is freshly produced, it will have much more efficiency than if it has produced earlier.

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This is an example of that is called sodium Ethyl Xanthate see that this is the again the cationic part is the sodium.

Now, this is the polar part and this is the non-polar part. So, you see that there are structural changes, it has got now two carbon atoms and here you have got two sulfur atoms. So, this call this is another group of your collectors this is also very popular, it is called sodium Ethyl Xanthate.

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Adsorb chemically on the sulfide mineral surface and form insoluble metal Xanthates

Used for collection of oxidised ores like malachite, cerrusite, anglesite and native minerals like gold, silver.

The diagram shows the chemical structure of a Dithiophosphate (Sulphydryl) group, $\text{P}(\text{S})_2\text{OR}$. It consists of a central phosphorus atom (P) bonded to two sulfur atoms (S) and one oxygen atom (O) which is part of an RO group. The other sulfur atom is bonded to a sodium or potassium ion (Na(K)).

Dithiophosphates (SULPHYHYDRYL):

Comparatively weak collectors. Possess pentavalent Phosphorous in the polar group.

Also called Aerofloat Collector. They are effective selective collectors for Copper sulfide minerals.

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Now, how does it work? It adsorbs chemically on the sulfide minerals surface and form insoluble metal xanthates, they are used for collection of oxidized ores like malachite, cerussite, anglesite and native minerals like gold and silver where they found applications.

However whatever the examples I am giving; does not mean that all varieties of such ores will have equal responses to these collectors, why? Now the mineral surfaces may not be that clean though the mineral surfaces may be also having some impurities and there are many other your varieties of parameters could be there now depending on the cleanliness of that material surface depending on the surface properties of that mineral the effectiveness of a particular collector will depend, but normally when we start working with that whether the what type of collector we should start with.

So, these are the general guidelines that you can start with this type of collectors based on your mineral if it does not work, first, you have to before he conclude that whether it works or not you have to optimize the doses and other two parameters like your machine related issues and your material related parameters also you have to optimize and then you can say that whether the collector is appropriate or not.

There is another group of collectors that is called dithiophosphates or the sulphhydryl collectors these are basically comparatively weak collectors, it possesses pentavalent phosphorus in the polar group also called aerofloat collector, they are effective selective collector for copper sulfide minerals. Now what it is revealing that for different types of minerals for different your targets and for different needs that is how much of that what is the recovery you want and even the particle sizes and various other factors, they ultimately help you to decide you have to consider everything before you decide that which chemical as a collector, I will be using and how much of that I will be using, we will continue this discussion in the next lecture; till then.

Thank you very much.