Electrochemical Technology in Pollution Control
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Lecture – 27
Process waste handling 3

Greetings to you. We were discussing the chromium removal from their electroplating effluents, and I had shown you in my previous slide some schematic diagrams for the removal of chromium.

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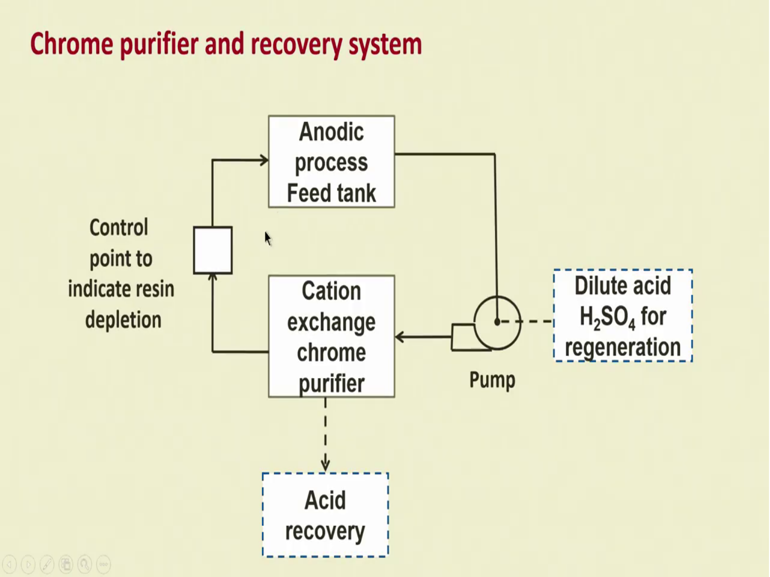

Chrome purifier and recovery system

And I had shown you these slides. My anodic process and cation exchange process, chrome purifier, etcetera, etcetera these are all different schematic diagrams which can handle different quantities of chromium generated from a variety of operations. So, it is not that the process is same or uniform for all situations that you must understand.

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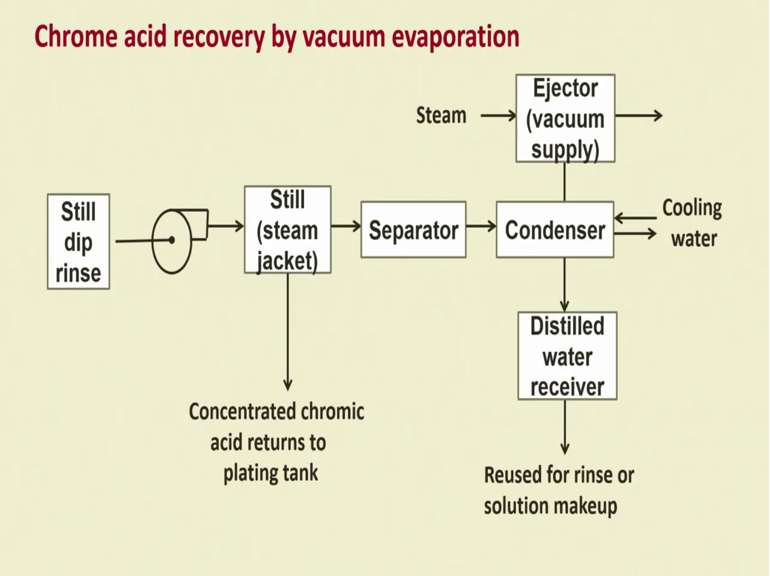
Chrome acid recovery by vacuum evaporation

Even though the chemistry remains the same we have to we can change the design to suit the industrial operations depending upon the quality and quantity of the effluents.

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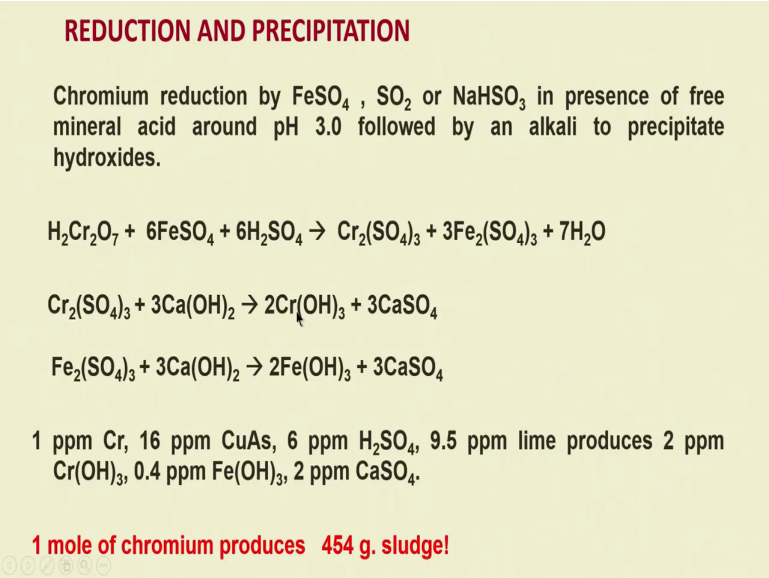

REDUCTION AND PRECIPITATION

Chromium reduction by $FeSO_4$, SO_2 or $NaHSO_3$ in presence of free mineral acid around pH 3.0 followed by an alkali to precipitate hydroxides.

$$H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3 + 3CaSO_4$$

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3 + 3CaSO_4$$

1 ppm Cr, 16 ppm CuAs, 6 ppm H_2SO_4, 9.5 ppm lime produces 2 ppm $Cr(OH)_3$, 0.4 ppm $Fe(OH)_3$, 2 ppm $CaSO_4$.

1 mole of chromium produces 454 g. sludge!

So, now, coming back to the; but the chemistry does not change, no. So, coming back to the chemistry of this chromium reduction I want to tell you that basically chromium reduction is can be accomplished by ferrous sulfate, sodium sulfur dioxide or sodium sulfide, hydro sulfide and many of these reaction these are all reducing agents. So, in presence of free mineral acid around pH 3 followed by an alkali addition to precipitate the hydroxides. Basic reactions can be presented like this.

This is potassium dichromate, sorry hydrogen dichromate. If I put potassium here it will be potassium dichromate otherwise it is chromic acid, H 2 Cr 2 O 7 is chromic acid reacted with ferrous sulfate followed by sulfuric acid addition and it will get reduce to chromium 3 and ferric.

So, this will be chromic sulfate and chromium chrome sulfate and this will be ferric sulfate followed by water that is part of the reaction and this Cr 2 SO 4 thrice can react with lime now, because we are going to add lime it will produce chromium hydroxide and 3 moles of calcium sulfate. It is just an exchange reaction, but calcium chromium hydroxide will precipitate.

And this ferrous sulfate also, ferric sulfate now the ferric sulfate also will react with 3 moles of calcium hydroxide to give ferric hydroxide and calcium sulfate. The problem is the 1 ppm of chromium and 16 ppm of CuAs, 6 ppm of sulfuric acid, 9.5 ppm of lime produces 2 ppm of chromium hydroxide and 0.4 ppm of ferric sulfate and 2 ppm of calcium sulfate.

If you convert all these things into moles, a molar concentrations, then you will be surprised to know that 1 mole of chromium produces 454 gram of total sludge out of which chromium will be a small component of the total sludge that comes out of chromium operations.

So, chromium reduction followed by hydroxide precipitation is always a losing proposition if you want to convert it into chromium hydroxide for disposal. Obviously, disposal does not mean recovering. So, in the end all the precipitated chromium hydroxide, ferrous hydroxide, lime hydroxide, lime calcium sulfate all those things will be disposed of either in a landfill or in TSDF. What is TSDF? Toxic Substances Disposal Facility.

So, for 1 mole of chromium for disposal if I had to produce 454 grams of sludge, you can imagine if I had to dispose of several tons of chromium, what happens to the sludge quantity and how it will be disposed off and if it is not disposed of properly what will be the fate of the environment or the soil in which it is deposited or the water in which it will seep down. So, that kind of problems are always there associated with the chromium disposal.

As it is in Bengaluru there are number of factories in Peenya and other places where chromium plating is has been done extensively since last almost 5 decades, and at the about 3-4 decades before till that time till around 1970s until the environment act came into force. Most of the people used to dump their chromium in their own factory dump yards from there chromium has gone underground.

Nowadays, wherever you dig in Peenya area, Peenya industrial area you will get affluent something like Fanta or gold spot and that kind of color containing approximately 165 parts per million, 165 to ppm of chromium will be there, hexavalent chromium that too and that is very dangerous; will be there.

If you dig any bore well anywhere in Peenya right now a whole aquifer under underground area where waters are effluents are collected from the bottom collected in the bottom of the earth from where bore wells are dug approximately 800 square feet depth. All these chromiums, hexavalent chromium have accumulated and it becomes very very difficult to treat that kind of waste.

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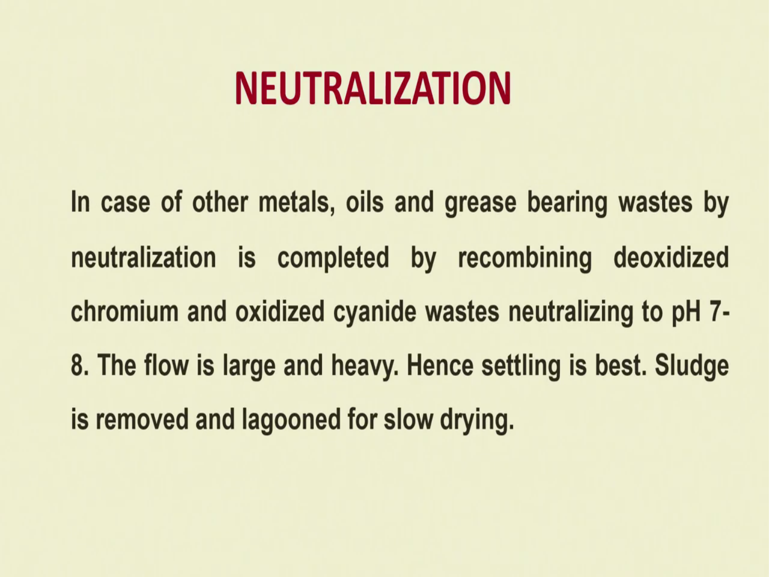

NEUTRALIZATION

In case of other metals, oils and grease bearing wastes by neutralization is completed by recombining deoxidized chromium and oxidized cyanide wastes neutralizing to pH 7-8. The flow is large and heavy. Hence settling is best. Sludge is removed and lagooned for slow drying.

So, the apart from chromium there are not many other cases which will cause so much of heartburn and you know public discussion and technology development, no not many other metals are there at all. So, in case of other metals oil and grease bearing waste can be neutralized, they can that can be completed by recompiling the deoxidized chromium and oxidize the cyanide waste, neutralizing to pH 7 to 8. The flow is large and heavy, hence settling is best.

So, sludge is removed and lagooned for slow drying and afterwards again sludge is disposed off in the usual manner. Part of it could be burnt also and things can be reduced handling this thing.

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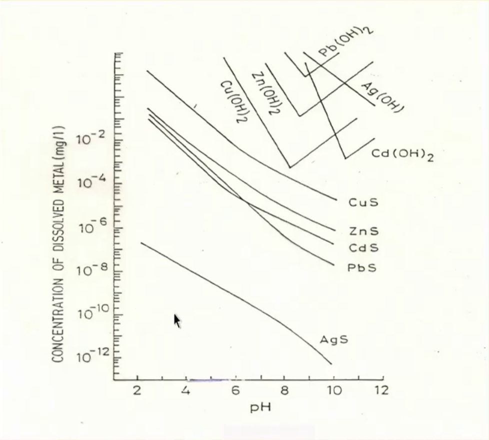

Solubility curves for hydroxides and sulphides

Now, here is a solubility curve for sparingly soluble salts of dissolved metals versus pH. Here I have written the bottom one if we take it is silver sulphide, here you can see around pH 2 solubility is approximately 10 raise to minus 6 milligram per liter that is ppm and as you increase the pH to about 10 it still decreases, decreases, decreases and falls to almost 10 raised to minus 12 around pH.

So, it makes sense to convert all the metal bearing waste into alkaline treatment subject them to alkaline treatment, so that most of the metals whether they are sulfides or hydroxides or oxides can be converted into insoluble salts. Now, look at lead sulfide. Lead sulfide is here that is around pH 3 solubility is approximately 10 raise to minus 2 that could be 10 raise to minus 1 let us say, ok. So, 10 raise to minus 1, this could be 10 raise to 0, this could be 10 raise to minus 1, the most of these 3, zinc cadmium and lead sulfide are approximately in 10 raise to minus 1 range around pH 3.

But as the alkalinity increases, as the pH increases to let us say around 10 the solubility will decrease to 10 raise to minus 4 minus 6 minus 8 level that is a ppm level and at this level ppm parts per million level these salts are not so dangerous. Now, look at the hydroxides copper hydroxide initially it dips, but then as the after around pH 8 again there will be certain amount of solubility and it does not make sense to take them all the if you are precipitating them as hydroxides to take them to come total alkaline conditions.

For example, here it is for zinc hydroxide it is approximately 9, calcium hydroxide copper hydroxide it is approximately 8, 8 and 9 and afterwards the solubility keeps on increasing. So, it is similarly for cadmium, cadmium hydroxide, cadmium sulphide, cadmium sulfide is better if I want to dispose it off as a sludge, but not cadmium as hydroxide.

Now, because cadmium hydroxide starts dissolving precipitating from 10 raise to minus 1 to 10 raise to minus 2 around pH 10, if you increase the pH condition alkaline conditions it will increase, the solubility will increase and cadmium will go into a solution again. Same thing is true with later hydroxide and silver sulfur, silver hydroxide is the only exception where the precipitate keeps on the solubility keeps on coming down. So, this kind of graphs help us to decide what should be the pH of the sludge before we start filtering it.

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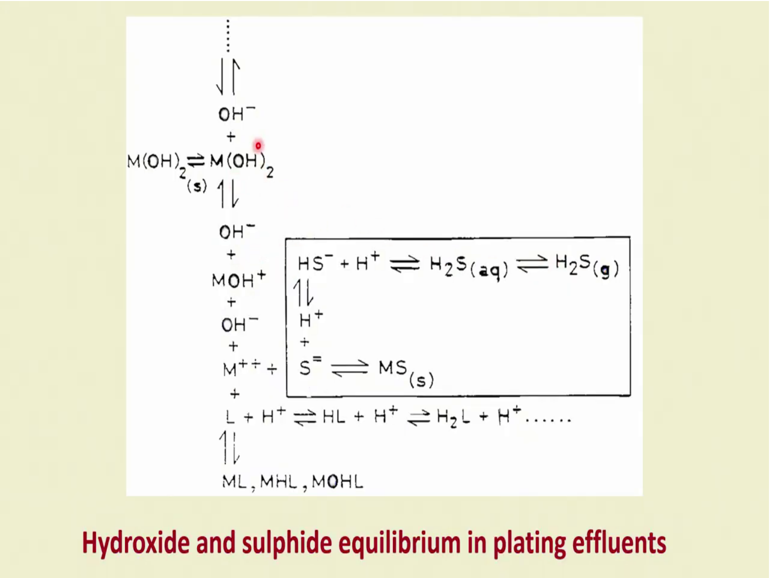

Hydroxide and sulphide equilibrium in plating effluents

So, here you can take a look at some of the reactions that are involved hydroxide and sulfide equilibrium in the plating effluents. So, you can see this box, the there is H 2 S here gas and if it is in aqueous medium it will be H 2 S aqueous that will be in equilibrium with HS minus and H plus. This is all these are all in solutions, and HS minus can give you H plus and S 2 minus, and if there is metal these sulfide ions can combine with the metal to form sulfides as solids which can be filtered and removed.

Now, here the moment you add alkaline we have an equilibrium reaction M OH twice going to solid to liquid, M OH twice liquid and these can get ionized OH minus and then OH plus metal or hydroxide, and then another OH. So, if it let this loose is OH, I get metal salt, divalent metal I have put.

And if there is a ligand I get ML ligand, this is again an equilibrium reaction, and if there is an acid the ligand can also combine with acid to give HL that is the ligand in the acidic form and H 2 L as the complex form. And then metal also can react with a MHL to give MHL and M OHL, L is always elegant, OH are additions coming from the solutions.

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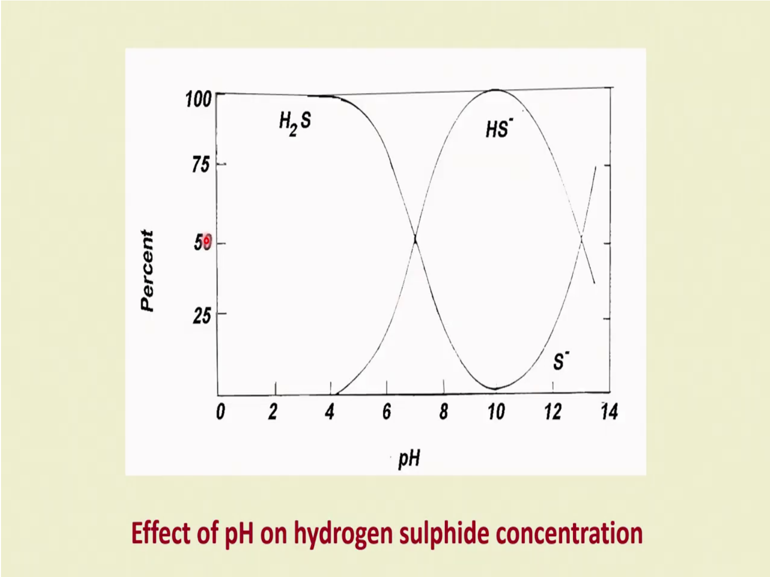

Effect of pH on hydrogen sulphide concentration

Now, here is a graph that explains what is happening in the precipitation of sulphide. If I have a sulphide solution as H 2 S the solubility is almost 100 percent around pH 2, 2.53 and then slowly solubility decreases and then reaches minimum and then again it will increase, solubility will increase here in this case.

So, if it is HS minus ion, it will start the formation of HS minus ion will start around pH 4, reach here maximum around 10 and then the concentration of HS minus ion decreases. So, we should always find a point where both these curves interact, so that the solubilities of both are optimum here. If I choose pH 10 sulfide will be solubility will be minimum, but as HS minus solubility will be maximum, that is not desirable. But somewhere here the solubilities of both sulfides and HS are minimum here and that is the point which I will have to choose for treatment of sulfide bearing wastes.

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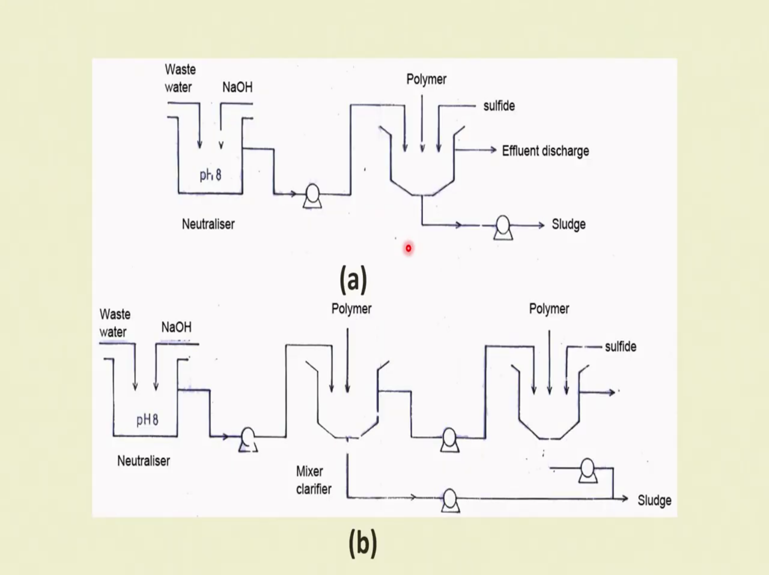

So, based on these reactions I can have something like a, I can design a schematic program for the treatment of waste containing the samples that is effluents containing the alkali acid and alkali waste. So, I have wastewater coming in here, I add NaOH, pH will be 8, I pump it into the reactor and this reactor will have a input of polymer. This waste is coming into a holding tank, this is the holding tank and sulphide I can add as a separate stream and the effluent discharge can happen from here.

So, whatever is the sludge, that will settle down at the bottom here which can be taken out through this pump and to a sludge drying bed. Then I can have another system something like this waste water sodium hydroxide, neutralize it and then take it to a mixing tank. Here I add a little bit of polymer and the polymer will act to settle whatever solids are there, settling here and then the clarifier, the liquid which is on top is taken through the pump into another reactor and sulphide is added, polymer is added and everything is precipitated and the liquid clear liquid is taken from the top and from the bottom sludge is drawn off and this can be disposed off in a proper manner.

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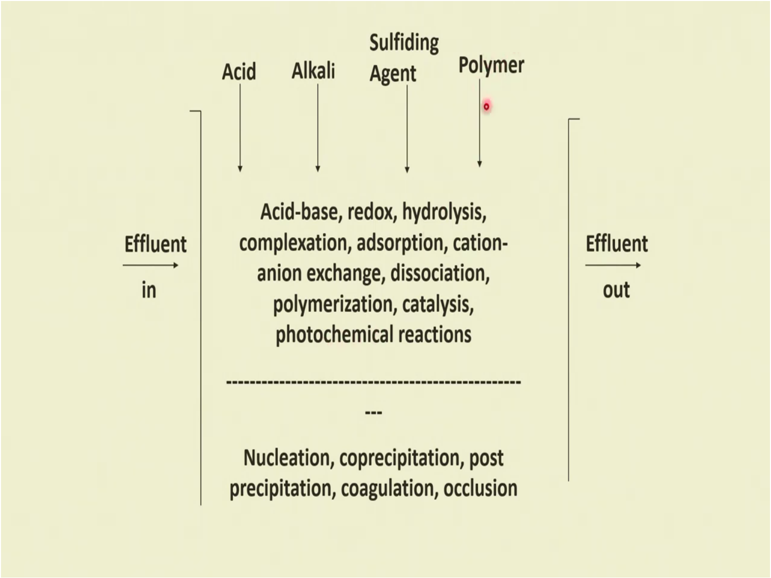

Acid

Alkali

Sulfiding Agent

Polymer

Effluent in

Acid-base, redox, hydrolysis, complexation, adsorption, cation-anion exchange, dissociation, polymerization, catalysis, photochemical reactions

Nucleation, coprecipitation, post precipitation, coagulation, occlusion

Effluent out

So, this is what happens when effluent comes in, I have an acid input, alkali input, sulfiding agent input and polymer input, this is our own research work. Here we are mixing acid-based, redox reactions, hydrolysis, complexation, adsorption, cation exchange, resins, dissociation, polymerization, catalysis, photochemical reactions etcetera. The reactions that can happen could be nucleation, coprecipitation, post precipitation, coagulation, occlusion and several other things that can happen and they way they precipitate will be at the bottom. From the top I can take out the effluent.

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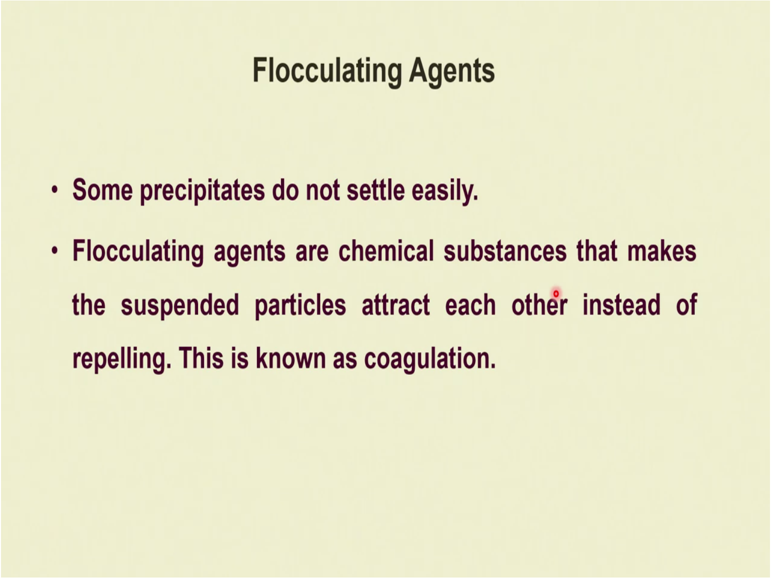

Flocculating Agents

- Some precipitates do not settle easily.
- Flocculating agents are chemical substances that makes the suspended particles attract each other instead of repelling. This is known as coagulation.

So, some flocculating agents are necessary because some precipitates do not settle easily. So, it is important to add 1 or 2 ppm solutions of flocculating agents. What are flocculating agents? Flocculating agents are chemical substances that makes these suspended particles attract each other electrostatically instead of repelling. This is also known as coagulation.

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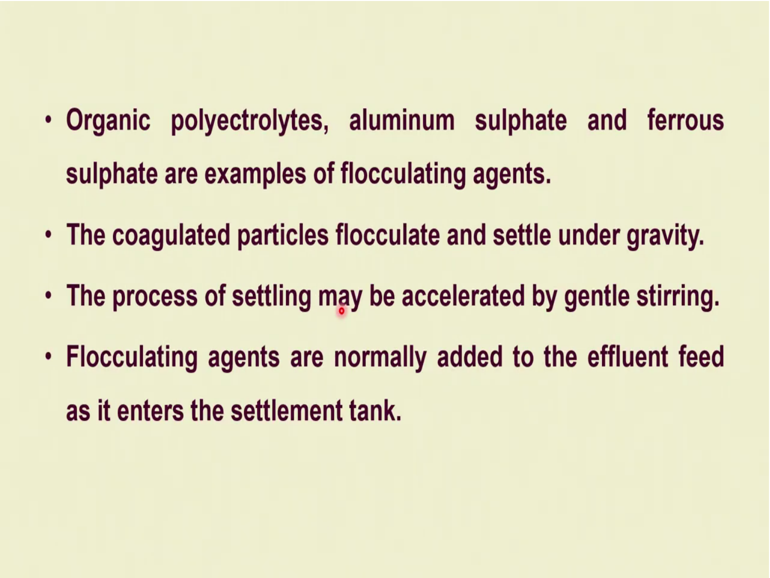

- Organic polyectrolytes, aluminum sulphate and ferrous sulphate are examples of flocculating agents.
- The coagulated particles flocculate and settle under gravity.
- The process of settling may be accelerated by gentle stirring.
- Flocculating agents are normally added to the effluent feed as it enters the settlement tank.

So, use of flocculating agents in industrial scenario wherever precipitation is required is a very common occurrence in all industrial waste treatment operations. So, we can have organic among the flocculating agents there are inorganic as well as organic flocculating agents, and I can have polyelectrolytes as the flocculating agents and I can use aluminum sulfate, this is a very well known and age old system. Ferrous sulfate is again another one, age old system for precipitating many of the things even it is used for water purification.

So, the coagulated particles normally end up flocculating and settle under gravity very easily. The process of settling may be accelerated by gently stirring etcetera, but these are all basic chemical operations which you know one can learn only by experience. So, flocculating agents are normally added to the effluent field as it enters the settlement tank. So, in this figure I can add a what I show here is polymer that is the flocculating agents.

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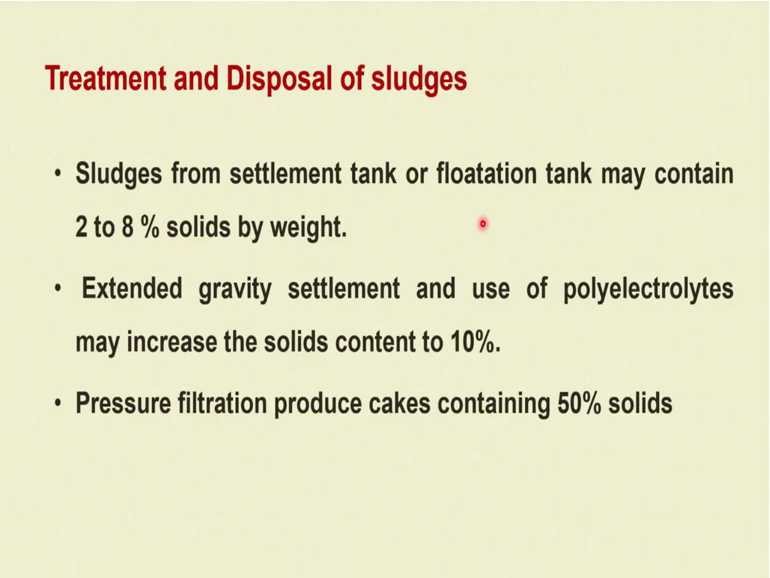

Treatment and Disposal of sludges

- Sludges from settlement tank or floatation tank may contain 2 to 8 % solids by weight.
- Extended gravity settlement and use of polyelectrolytes may increase the solids content to 10%.
- Pressure filtration produce cakes containing 50% solids

So, that brings us to the end of metal, almost end of metal treatment waste. And what is happening here is the what remains to be done is treatment of sludges. Sledges as I have said earlier are not really very convenient to handle, because the characterization of sludge is very important and it is not easy. Once you have a dried sludge in your hand, if somebody ask you to analyze a sludge what it contains it becomes very difficult you have to start a whole chemical operation of dissolving it and then analyzing and all that.

So, sludges from settlement tank or flotation tank may contain solids approximately 2 to 8 percent. Whenever you do the operation from the effluent, from a electroplating waste. When do you call it a sludge? The moment the solids percentage reaches about 5 to 8 percent we call it a sludge; that means, the solid particles should constitute about 8 percent.

So, such sludges are allowed or rather they go by gravity settlement and use of polyelectrolytes helps increase the solids content to approximately 10 percent, not more. But then I will I have to subject the sludge containing 10 percent waste to pressure filtration that produces cakes containing 50 percent solids. So, from 10 percent I graduate to 50 percent of the solids still it becomes a slurry, it does not become solid.

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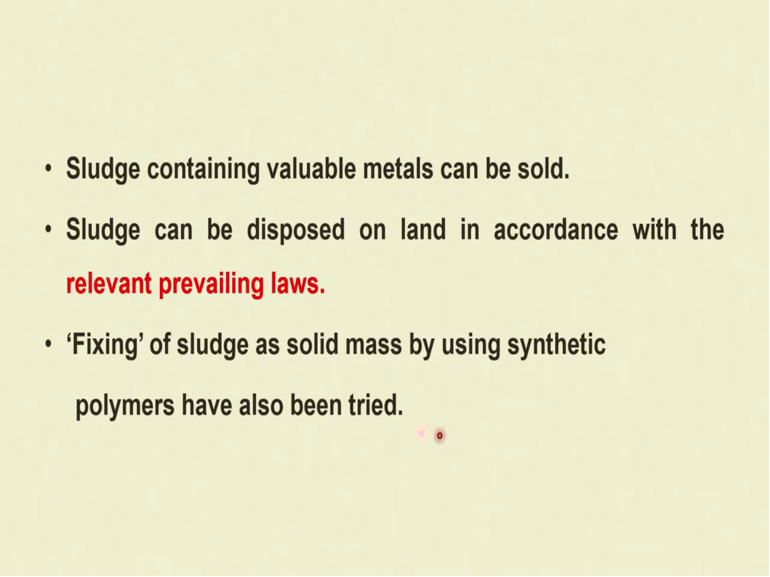

- Sludge containing valuable metals can be sold.
- Sludge can be disposed on land in accordance with the relevant prevailing laws.
- 'Fixing' of sludge as solid mass by using synthetic polymers have also been tried.

So, after that the some sludge containing valuable metals we can we can sell them for resource as a resource material or it can be disposed of on land in accordance with the relevant prevailing laws. So, fixing of sludge as a solid mass by using synthetic polymers have also been tried and it is a it has seen sort of partial success, not always it is a viable solution.

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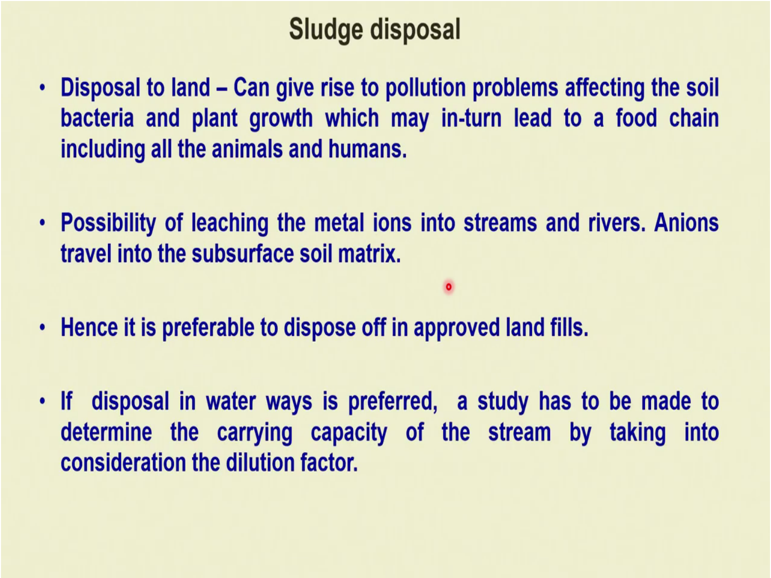

Sludge disposal

- Disposal to land – Can give rise to pollution problems affecting the soil bacteria and plant growth which may in-turn lead to a food chain including all the animals and humans.
- Possibility of leaching the metal ions into streams and rivers. Anions travel into the subsurface soil matrix.
- Hence it is preferable to dispose off in approved land fills.
- If disposal in water ways is preferred, a study has to be made to determine the carrying capacity of the stream by taking into consideration the dilution factor.

So, sludge disposal is again a specialized field by itself where lot of civil engineer specialized in sludge handling and sludge disposal. So, sludge disposal on land can definitely give rise to pollution problems affecting the soil bacteria and plant growth which may in turn lead to a food chain problem including toxic effects on all the animals and humans whoever is contaminated by the sludge dumped there.

So, possibility of leaching, quite often the sludge, quite often the sludge material whenever it rains it leaches. Part of it will dissolve or part of it will be forcibly carried out or transported along with the liquid and then in the solution it can form metal ions, and then once metal ions are formed they can move into the streams and rivers anions traveled to the subsurface soil matrix, that is also another big problem. So, proper disposal of sludge is always a matter of great care and lot of engineering thoughts must be must go in before you finally decide how to dispose of the sludge.

So, it is preferable to dispose of sludge in approved landfills. These approved landfills are basically a pit drawn on a land, so you have to take out the mud, dump your line up the pit with polypropylene or PVC sheets about 2 mm or 3 mm thick on that you dump your waste above that you put some mud to give some soil bacteria a chance to convert the organic material into harmless products. And then after the mud again dump your material, again a soil, like that you keep on slowly building up the waste.

And then the most tricky engineering part comes in providing small small pipes where the pressure will act to leach out some of the waste and that waste can be taken out and treated separately. If it is in large quantities definitely it must be done and it is preferable to dispose of the sludge in approved landfills where all these things are taken care of automatically. So, if disposal in water is always preferred, a study has to be made to determine the carrying capacity of the stream, this is also important by taking into consideration the dilution factor.

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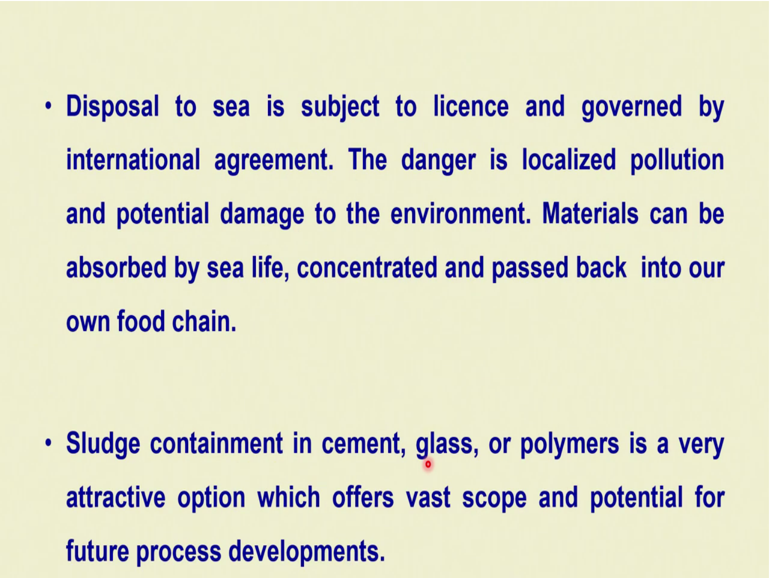

- Disposal to sea is subject to licence and governed by international agreement. The danger is localized pollution and potential damage to the environment. Materials can be absorbed by sea life, concentrated and passed back into our own food chain.

- Sludge containment in cement, glass, or polymers is a very attractive option which offers vast scope and potential for future process developments.

So, it is not always a proposition to go for dilution irrespective of the size of the receiving tank. Normally, if the receiving tank is having does not have the capacity to take this or liquid load then it is very difficult to revive the, it is very difficult to revive the polluted water tanks or water bodies. So, disposal to sea is always subject to license you know waters pollutants going into the rivers and from the rivers into the seas, from the seas into international waters.

So, one every government is very careful regarding the disposal of industrial effluents into the sea because immediately at the point of disposal there will be problems for the flora and fauna in the sea. So, sea animals and they get polluted immediately. So, it becomes very difficult to handle. So, the laws are very strict regarding the disposal of the pollutants into the sea.

The danger is localized pollution, this I this is what I was trying to explain to you. The danger is localized pollution and potential damage to the environment at the point of discharge, near the point of discharge, and if the quantity is large it can move on into international waters also where the ramifications could be much more serious. So, materials can be absorbed by sea life, concentrated and passed back into the food chain and so many related problems, happen especially with respect to electro chemical waste being discharged in the sea.

So, sometimes people have tried sludge containment in cement, people have tried it in glass or polymers that is away seems to be very attractive option which offers vast scope and potential for future processing developments, and effort efforts have been done to use such cements and glass in you know in areas where there is no possibility of leaching. So, obviously, there are problems associated with sludge containment in cement glass and polymers, but it is again an area which requires more and more studies depending upon the severity of the electro chemical waste that is being generated.

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V✧SEP ultra filtration- a new paradigm in effluent treatment

So, that brings us to the end of our discussion on the electrochemical waste. There are of course several types of electrochemical waste which require special type of treatment depending upon the quality of the material we are handling. For example, if there you are doing titanium, then there is not much titanium is not such a harmless element aluminum, but the problem with titanium and aluminum is we do not want to lose such materials.

So, there should there has to be a dedicated titanium recovery, dedicated gold recovery, dedicated silver recovery and chromium and several other metals. Then there are certain elements which will vary with respect to; with respect to the resource, and if we are handling a rare material it makes sense to recover.

Sometimes, many metals are becoming extinct. For example, indium; lot of indium coating and other things go inside go into a mobile. And indium and gold is going inside a mobile and that kind of waste if we let it go and there will be millions and millions of mobiles waste which will be lying around and indium is an element which is going to be extinct very shortly. So, we have to worry about such metals and special treatment techniques have to be developed depending upon the requirement of recovery of the metals.

So, I hope I have given you some indication of the severity of the problem with electro chemical waste. So, thank you very much. We will continue our discussion with the ultra filtration which is a very important concept in the treatment of industrial effluents, and it is something like a new paradigm in the effluent treatment. I will spend some time about maybe 40 minutes or 1 hour on this and then we will go on to batteries, and fuel cells and the other related electrochemical waste which need to be treated in the new modern world where the pollutants cannot be tolerated.

Thank you very much.