Electrochemical Technology in Pollution Control

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Lecture – 25
Process waste handling 1

So, greetings to you. Welcome to my next class on Metal Finishing Industries.

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Because metal finishing industries is, one aspect of industrial scenario that is very important and highly classified as a red category industry. And red category industry means the effluents or waste generated in metal finishing industry are considered as highly dangerous. Therefore, I thought it is prudent to include metal finishing industry, operations and knowledge about that even though it has nothing to do with the nothing much to do with the electra pollution

monitoring as such, environmental pollution monitoring as such, but it has all the things to do with electrochemistry and pollution and the metal treatment.

There are basically four electroplating four metal finishing industries which are very prominent. One is Electroplating; another is PCB Manufacture; third one is Phosphating, Anodizing and other Coatings and Painting. You can imagine that almost every industry almost every operation of our modern life is associated with metal finishing industry. We may not have much to do, but right from day one right from the morning to evening we are all dealing with metals and most of the metals that we deal have undergone some sort of metal finishing operation, either electroplating or PCB manufacture, phosphating, anodizing, coating, painting everywhere.

We all wake up with a painting of our walls and our houses. We live in such houses and painting is nothing but it may not be exactly metal finishing, but your house gates and other things, they are all metals we have painted; 99 percent of the time, they are all electroplated or painted. And sometimes, there many of your gates and walls and grilles etcetera, they are all phosphatized, anodized, coated.

There are many thing depends what you hold, may be coated; the watch is what you wear, are coated with the electroplating, titanium, gold, silver; the handle, door handles what you handle all are metal finished materials and the TV screens what you see, they are all coated with plastics and metals and powders; the gadgets what you hold, they are all metal coated, metal finished, anodized.

Thousands of things what you handled in day to day life, they are all result of metal finishing operations. Basically as I have told you metal finishing operation are classified into these four major of operations and among them electroplating is a very large occupies a very major industry place. Even though electroplating is by itself is not a major industry. There are thousands of small, small, small electroplaters, who do not come under the purview of the pollution control; but they produce electroplated materials and byproducts or effluents or emissions from such industries are hazardous anyway in particular.

So, it is important for us to know about metal finishing industries, especially with respect to the effluents and emissions. The next comes PCB manufacture, printed circuit boards are part

and parcel of our life. Our TVs and washing machines, microwave ovens and many day to day life, day to day equipment what we use in our house, office etcetera most of them contain PCBs and our buses, transport TVs, scooters, many gadgets they all require PCBs and PCB manufacture is sort of specialized electroplating, I would say. Because PCB manufacture involves the not only metal coating, cladding and other things including lacquering and other metal gum finish finishing etcetera and it is a fairly intense industry that is highly mechanized including, even electroplating is highly mechanized.

Then, there are other industry such as phosphating, anodizing and coating and these are these things do not come under electroplating as such. But you can classify them as supporting industries. Quite often before electroplating many of the metals undergo cleaning and after cleaning of oil and grease etcetera, they undergo phosphating, anodizing. Especially, all aluminum compounds are marketed as anodized compounds including many of the day to day materials which we handle and coating definitely yes, not only metal coating; but paints and other things. And painting of course, as I have explained to you that we all live in painted houses 99 percent of us anyway.

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So, after metal fabrication for any particular use, you can imagine, they are finished to a final product require requirement basically. So, this involves metal stripping, metal removal of undesirable oxides on the metal and cleaning, processing, plate processing involves plating, phosphating, anodizing etcetera and then, rinsing and drying. You can imagine in all these operations metal fabrication; what does it mean to a normally lay person? A metal fabrication is a an operation, where a metal is given a particular shape for a function for which it is intended.

Suppose, you take a metal and bend it like this and then make a car, the fabrication of the car metal plates for car to what it looks like in the final finished shape, without the painting, electroplating or painting and other things that is known as fabrication. It mean fabrication may involve something like the riveting and then joining, bending and then fixing and then forging have many other operations are there, they are all involved in metal fabrication. A welding also is one of the important thing in metal finishing and they are the basic requirement of a of any machine or requirement function for a function and they are finished afterwards,

they have to be beautified or functionalized to specific tasks for which they are intended to use.

For example, if you have a metal body bent for making a car, car bonnet will you have a different shape, car dicky will have a different shape, car door will have a separate shape and all these things require need to be finished electro chemically or mechanically for the function, they are intended for. And they may be finished in such a way that all of them look same color for aesthetic purposes or they may look different colors, some of them may be plated some parts.

For example, the front bonnet may be plated. The back side may be red color, blue color etcetera; doors maybe is different color; glass will be there, all those metal finishing things are there involved in the metal surface finishing. So, the finished metal piece must undergo several operations before it takes the shape of the material which you see in your real world. First thing is it must be stripped of its oxygen, oxide corrosion particle corroded particles; nobody would like to see corroded particles on the metals and it will look ugly.

So, metal must be stripped off, the deposits of mud and other things and then it must be cleaned. So, metal cleaning and stripping of oil etcetera is a very important aspect that is part of electrochemical treatment also and then, removal of undesirable oxides; sometimes there will be deposits, corrosion and then sometimes if it is like aluminum or silver or something, there will be oxide deposits and all those things are removed to be removed. And then, it must be clean to a shiny nice finish. So, for that either mechanical treatment like buffing and other things are involved or it can be cleaned chemically also, put acids alkalis etcetera until they are ready for further processing.

What are the further processing operations? They are plating, phosphating, anodizing etcetera. There are many other operation lacquering and etcetera, I had already told you and then, once you in e after each of these operations like stripping, removal of oxides, cleaning, processing, plating etcetera; there are number of operations in between where the metal has to get rid of the memory of the previous operation. For example, after cleaning, after removal of the oxides, corrosion etcetera, it must be cleaned and washed and this kind of washing is best

done by dipping; taking the material and dipping it in water or acidic or alkaline solutions and then again not just once, but two or three operations; first dip, second dip, third dip etcetera.

So, many of the rinsing operations are generators of effluents which may not have good properties with respect to environment. So, rinsing operations are also important followed by drying. So, again drying one has to be careful, it can be done by done mechanically or it can be done by heat or it can be done by simple air blowing etcetera. So, these are the basic requirements of metal finishing treatment, stripping removal of undesirable oxides, cleaning, processing, rinsing and drying.

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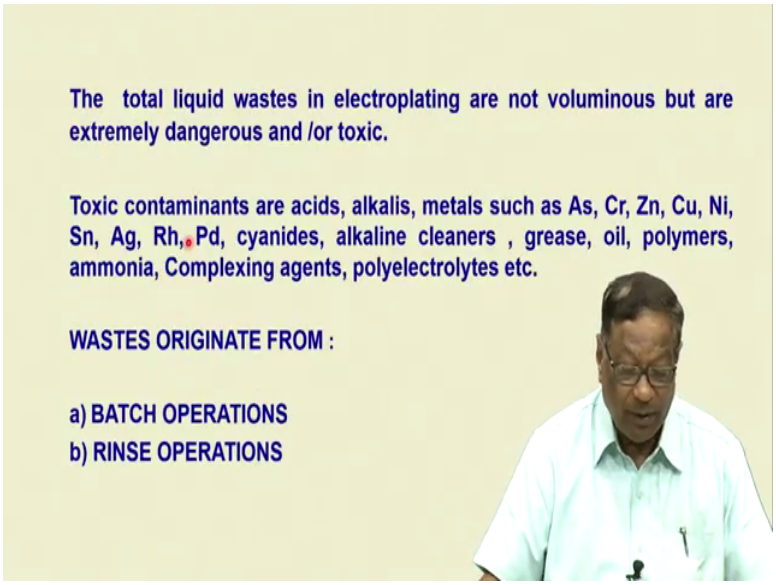

So, the total liquid waste in electroplating are not really voluminous, but they are extremely dangerous or toxic. Quite often, we end up using acids, alkalis and metals such as metals means metal salts in electroplating such as arsenic, chromium, zinc, copper, nickel, tin, silver, rhodium, palladium. And then, anions such as cyanides, alkaline cleaners, grease, oil, polymer,

ammonia; you can see everything I have written here, grease, ammonia, complexing agents, polyelectrolytes and many more things in a that are required in electroplating units.

So, you may assume that all these chemicals are there in every electroplating unit. No, the answer is no. There may be somebody may be using only acids; somebody may be using only alkalis, acids alkalis; somebody may be only making chromium plating unit; somebody may be having others, maybe having just zinc plating unit. And somebody may have a copper plating unit, PCB, most of the PCB manufacturers will have copper plating units and then, some people may try to coat things with metals with nickel, ion is coated with nickel and to make your specs, spectacles nickel coating and many other elements will be there; our ships are all coated with tin because tin as an undercoat in a shape keeps the marine animals at bay.

Fungus will not grow on the chips coated with tin on the bottom, but it has got its own environmental implications. I may not be going into detail, except to say that the most of the tin that we use in our organic compounds, as ships coating disturbs the marine ecology making them sort of lose their identity in terms of male female characteristics ok. So, there may be alterations in genes, we use trioctyl tin and tri. Then we use tetra, not tetra octal tin; but trioctyl tin is very well known tributyl tin and many other things we use for painting in our ships.

Silver coating of course, everybody knows that many of our household items are silver coated. There was a big industry of silver coating on household vessels in Madhya Pradesh, Indore they are known as Devar Steel that is a place, where a silver coating use to go on a large scale and silver coating again used to use cyanides and cyanide salts of silver. Gold of course, cannot be plated without cyanide. Even now 90 percent of the gold plating has be is based on cyanides, but slowly things are changing, not slowly even quite fast now and cyanide plating is banned nowadays, but still cyanide is a very important chemical. Usually, I will say that with cyanide we die and without cyanide also we die, that is my bottom line with respect to cyanide.

Cyanide is so important industrially; we cannot really imagine. Sometime cyanide is used in pharmaceutical companies to prepare specific compounds and cyanide is in electroplating is definitely dangerous and platinum, palladium, gold many of them are coated with cyanide, electrolytes and then again, continuing on the same line, I can say alkaline cleaners again are a

problem in our environment. Because alkaline cleaners essentially as effluents celanides the soils. They were agriculture if we let them into the environment without treatment, alkaline the salts will make the soil unfertile, infertile. So, they are not comfortable acids, definitely not people are not comfortable because they cause burning and other things.

Grease nobody likes, but we generate lot of grease anyway in all industrial operations. Oils, we store metals, we dip the metals in oil when we when we stack them one above another. So, that there should not be much corrosion and oil removal again is a very important operations, we coat them with polymers so that there should not be any scratches and other things.

And then, ammonia, complexing agent, polyelectro; every one of these are environmental hazards and there is nothing like environmentally safe compound. And electroplating is definitely a problem with the effluents. They generate gaseous emissions, they generate liquid effluent, then they generate solid sludge which we do not know how to deal with that because of the ignorance until 1970s and 80's.We did not know that the things could be so dangerous and after 1980's, we have developed quite a few treatment options and alternate options for several electroplating operations that are really dangerous.

Now, coming back to our discussion on the electroplating, what I would like to tell you is electroplating wastes originate from batch operations that is every electroplating has to all these operations which I had described to you as cleaning, surface removing, oil de-oiling, degreasing and all these operations, they are all batch operations and then, there are rinse operations. After the batch operations, there will be just dipping it in water, taking it out into another and taking it into another water bath etcetera and they are all dilute effluents which are which cannot be treated economically. So, but hazardous all the same.

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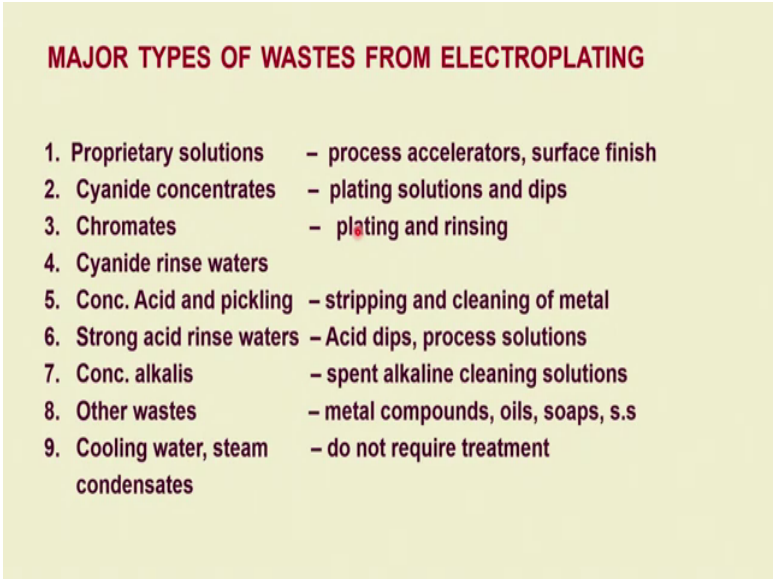

So, that is another part and what are the major types of wastes, coming from electroplating? Here they are. One is Proprietary solutions and process accelerators and surface finish chemicals. Here and now I am going to put you on to the different operations involved in the electroplating and I wanted you to understand that the chemicals that are involved in electroplating can be made by the manufacturer by dedicated manufacturer who supplies you the chemical equipments or chemical salts and solutions etcetera and then, sometimes they can be made by the electroplated himself. He can buy the salts and make himself.

So, the major types of ways is especially if electroplating is done by not so educated people, then they would prefer to buy a readymade solution containing the operations of plating etcetera. Because somebody has set them an industry, you dip it here, dip it there, dip it here wash it and then put on the switch, it will start plating, remove it from the plating and then, your material is ready, sell it away.

So, that kind of operations who do not have basic degree in basic required knowledge in the chemistry of operations also could be a very prominent electroplater. So, such people use

proprietary solutions. Those who have certain knowledge, they can use their own solutions. And among the proprietary solutions, we still have many operations we do not know, they will not reveal the chemical components or the concentrations of the proprietary solutions.

And then, there are additional chemicals that go into proprietary solutions, they are known as process accelerators and surface finish quality, surface finish chemicals; they will give you a mat finish. Sometimes they will give you a very shining, very polished surface; sometimes they will give you a designer finish and all those things, they are all proprietary chemicals designed to give you specific appearance. But they generate a waste for who the characteristics of the waste are not known because the proprietor makes the chemicals and he keeps on making changes, he does not bother to educate you or the people who use them are not educated enough to understand, what are the kind of chemicals that come out from the electroplating operations.

Now, second type Cyanide concentrates. Lot of people use as I had told you that people use cyanides for gold plating, silver plating and several other types of plating and these cyanide plating's again as I had explained to you involve batch operations, rinsing; batch operation, rinsing all containing cyanides now. So, end of the day, end of the operations there will be cyanide waste from parts per million level to several percentage level. So, again one has to worry about how to treat cyanide plating solutions and cyanide dipping solutions. So, same thing is true with Chromates. Chromates what we have? Chromate plating is very important in our day to day life. Many of the shining things we are made on steel, they are all chromate plated.

Many of our table spoons and other things, industrial operations, steel, there it gives impart certain hardness. Metal finishing is never about the finishing alone, but it also imparts particular kind of functionality to the metals. So, if you want a particular metal surface to be very hard because it is going to be exposed in a very harsh environment, then you may it you make it chromium and there are two different types of chromium; hard chromium and hard chromium plating and light chromium plating.

A light chromium plating is what we use for spoons and other things, we can give coating, make it look shiny and they will work for some time and then, that is the end of it. But hard

chromium plating is a permanent fixture on the metal plate which will be exposed to high harsh conditions and it will be there for years to come.

Many of our earth mover equipment etcetera, they need to survive harsh environments and they are all coated with hard chromium plating. Hard chromium plating is a very important industrial activity nearly 90 percent of chromium plating is done with hard chromium and again, chromium itself is a very bad environment polluter because chromium is a poisonous. Chromium plating is bad and especially hexavalent chromium causes cancer. Many of the plating metals used in plating, they are all mutagenic, teratogenic and then toxic and then hazardous, carcinogenic. So, almost all electroplating wastes normally end up being hazardous. Then, I am talking about Cyanide rinse waste waters, I have already talked enough.

Then, I am talking about Concentrated Acids and pickling. Here, I want to tell you that stripping and pickling is again a very important operation, especially in steel plating, steel operations mild. There are different types of steel; mild steel, stainless steel, you must have all heard and then, many of the acids and alkalis are used for cleaning the metals to give a nice finish. Copper material, if you take and dip it in a nitric acid, it will give you a very nice finish of copper color. But the waste are dangerous anyway because they contain acids its now strong acids. So, most of the metals are dipped in acids and process solutions.

Now again, what kind of acid dips we are talking about? When metals are dipped in acids, we do not want the metals to damage also. So, it should inhibit corrosion that is the whole idea. So, we add inhibitors. So, inhibitors have got a property to increase the concentration of the acid so that they can be effective. These inhibitors again is a separate topic, electroplating itself is a separate topic, but since we are dealing with the pollution control aspects.

I just want to touch these aspects of electroplating and metal finishing and apart from strong acids and rinse waters, we will also have concentrated alkalis which end up as spent alkaline cleaning solutions. These spent alkaline cleaning solutions also are sort of waste hazardous substances that affect the fertility of the soil. I have already explained to you.

Agriculturally, if you throw them on the soil, the soil is gone and there are other kinds of waste containing metal compounds, oil, soaps etcetera and these oils and soaps are used oils and soaps and they are environmentally nuisance. So, oils of course, cannot be used and

reused even though a lot of people efforts are going on regarding the use of oils and reuse recycling of the oils. But still there will be lot of problem with soaps and oils. Then, there are other requirements of an electroplating industry, where we need hot water, cold water etcetera and then, we have a air cooler system, water cooling system etcetera temperature because many of the operations electroplating operations are done at higher temperature.

So, the wastes need their sample, the bath should be kept at higher temperature and for that you need the steam. Then, cooling towers etcetera, water circulation, they are all required and even though these things do not require treatment as such, but the condensates etcetera need to be handled properly with respect so that they do not become environmental nuisance value.

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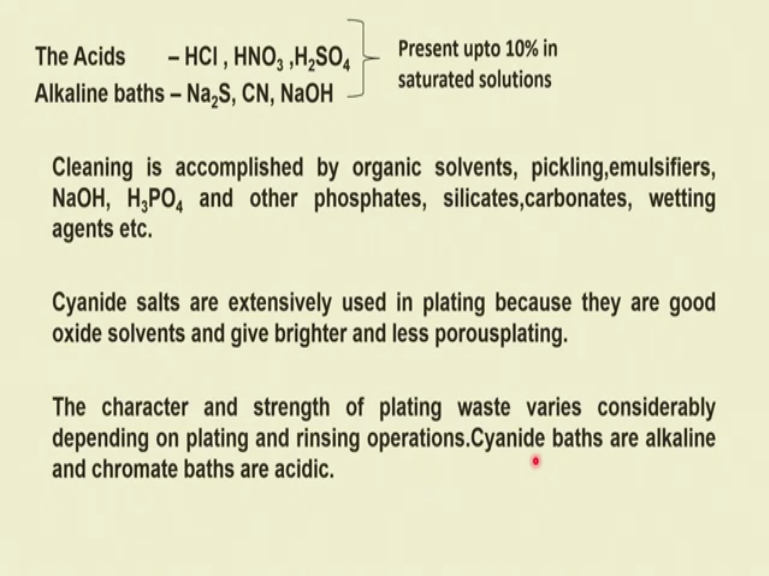

So, the acids; how much acids are there in the industrial effluents containing in the industrial electroplating units? The acids are hydrochloric acids, nitric acid, sulfuric acids, axenic acid, acetic acid and thousands of the hundreds of I won't say thousands, but they could be and there are could be hundreds of acids technic, malic acid, succinic acid, tartaric acid; many of

them are being regularly used. And those in the business know quite a few things about the acids, much more than what I am trying to tell you.

But they could be present up to 10 percent of the solutions of the total effluents and sometimes alkaline baths also contains sodium sulfide and then, cyanide, sodium hydroxide, many other alkalines are there, alkaline solutions. So, the total acidic and alkaline wastes themselves can be approximately about 10 percent of the total effluents, that itself poses a great danger because you just cannot hope to combine acids and alkali is to produce neutral water that react, equation does not work even though in theory everything works. But the simple chemical reaction of mixing acids and alkalis is no more there because of the complications involved in the matrix of the electroplating solutions.

What are the matrix? The matrix could be oils, grease and anions, cations and several other things which are there in the electroplating solutions. So, cleaning is normally accomplished by organic solvents, pickling emulsifiers, sodium hydroxide, phosphoric acid and other phosphates, silicates are there, carbonates are there, and wetting agents; all these things end up as a composition of only metal cleaning operations.

As I told you, if you remember metals are stacked one above the another and when electroplating is to be done, they are all to be pulled out. Oil to be removed, grease to be removed, acid must be the metal surface should be cleaned of the corroded particles like that there will be hundreds of operations for such operations, there are not only acids or alkalis; but there could be organic solvents, there could be other phosphates, there could be silicates, there could be carbonates, there could be wetting agents, there could be many other organic compounds, which I have been investigated and used industrially in millions of tones, in electroplating industries. That is why the electroplating industry effluents are something which are really risky hazardous and toxic.

So, cyanide salts are normally extensively used in plating because they are good oxide solvents and give brighter finish and less porous plating. So, cyanides we are still not able to get rid of. The cyanide as a component in the effluents in the component in the process baths, but largely nowadays its happening; someday we will be getting rid of it. Even then, there is no way of getting rid of cyanide in our day to day life. As I had told you earlier with cyanide, we die without cyanide also we die. So, the character and strength of the plating wastes generally

varies considerably depending on the plating and rinsing operations. Cyanide baths are alkaline and chromate baths are acidic. Usually, this is the condition.

If the cyanide baths are alkaline and chromate baths are acidic, can you just combine the different kinds of baths emanating out of electroplating industry? Just pause a little bit and think, what happens if it is just sodium hydroxide and acid, it just produces water, but chromate effluents will have chromium and acids. Cyanide baths will have cyanide and alkalis. The moment you try to mix all of them together to produce water, the cyanide will react to give you cyanogen gas which may kill the operator.

Chromium may precipitate and after precipitation, it may land on the soil, making the soil toxic and by some chance even if you treat it and minute quantities of chromate in the water, minute quantities of aluminum in water, minute quantities of any metal in water can affect, can settle down at the bottom of the stream, where the depth of the stream could be vary 1 or 2 millimeter; maybe 1 or 2 half a centimeter. But that half centimeter zone all along the riverbed is a repository of thousands of any variety thousands of varieties of animals including protozoa, small fish and this and that etcetera. All those things will their weight is small, concentration the kind that can affect their composition, also required is small.

So, even parts PPM level of the materials can affect the benthic life forms very seriously. So, that is the challenge the governments face when dealing with the industrial effluents emanating from electroplating units.

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So, in the treatment of metal plating waste, what is required is minimization of waste and rinsing wastes. We cannot really get rid of the rinsing wastes and waste in electroplating at all. It is almost impossible. So, what we can do then? We can minimize the solutions. We can reuse the solutions; filter and reuse like that, there are there could be thousands of operations that can be organized and that is possible. Then, I can have a some sort of a physico chemical treatment of the effluents.

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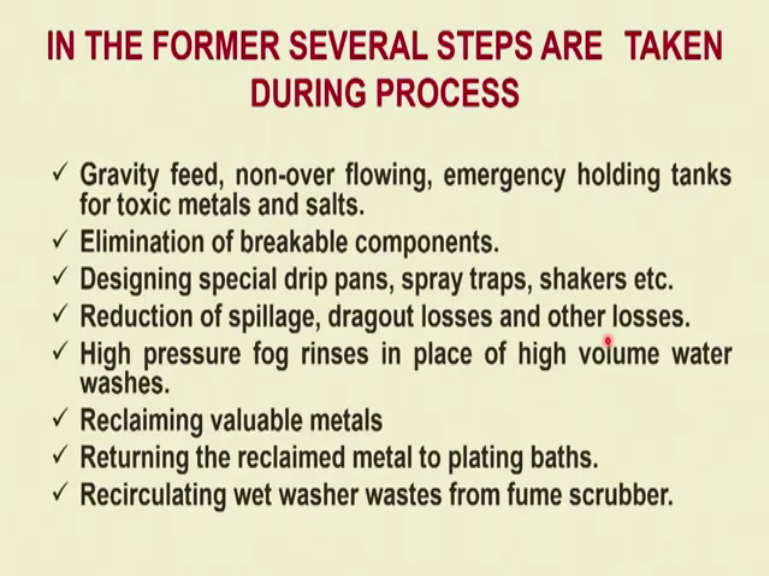

In the physico chemical treatment, again I have several options and there are ways and means of separating the pollutants in a simple way or in complicated way depending upon the requirement of the environment and specific process details are usually dependent on the toxicity, toxicity aspects of the metals which we are dealing with. Suppose, it is iron as a waste; it is not really dangerous in the environment, it can lie around somewhere or it can be precipitated and lying around that is not a big problem. But if it is chromium even in PPM level, we are at a risk. So, the depending on the quantity that we are handling we will be dealing with physico chemical processes.

So, gravity feed is one thing. Non overflowing emergency holding tanks, we can have for toxic metals and salts. Why non overflowing? Because, we do not want the toxic materials to overflow and go out of control and so, if there is overflowing, I can have one more dike around it for holding the chemicals, overflowing chemicals.

So, simple physical tasks and physical gravity a separations etcetera, they all require some additional materials, processes rather additional processes for handling the electrochemical

ways. We will examine more options for electrochemical waste treatment in our next class. Because I think it is very important for all of you to know about the dangers of the electrochemical waste treatment, that is why I have gone a little deeper into this.

We will continue our discussion in the next class.

Thank you very much.