

**Course Name: Industrial Wastewater Treatment**

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**Week – 05**

**Lecture 5: Coagulation, Precipitation and Heavy Metal Removal**

Welcome back. So, we are in module 5, lecture 5 and we are discussing about the coagulation, precipitation and heavy metal removal. So, the concepts covered in this topic will be on chemical precipitation for removal of heavy metals. We will talk about the solubility product. We will talk about the steps in the precipitation method. Then we will talk about the removal of various heavy metals by chemical precipitation method, the limitations of the chemical precipitation methods for the removal of heavy metals and then we will do some numerical based on the solubility product.

So, the heavy metals in wastewater, we know that there can be metals present in the water or wastewater. So, the metals or the heavy metals are defined as the metals with high density atomic weight or atomic numbers. So, when the density of these metals is greater than 5 grams per cubic centimeter or they are having a relative mass which ranges from 63.5 to 200.6. So, they may be classified as heavy metals. So, these heavy metals may be essential nutrients for example, iron, cobalt or zinc. So, they may be necessary for the body and that is why they are essential nutrients and similarly they can be harmless also for example, the ruthenium, silver, indium. So, they can be termed as harmless and there can be heavy metals which are of a major concern for example, the metals like arsenic, cadmium, mercury, lead, chromium.

So, they can be highly toxic, they can be highly poisonous as well as they can be highly carcinogenic in nature. So, there can be natural factors which may induce these heavy metals into the environment for example, it can be by the weathering or the soil erosion, it can be the surface runoffs, it can be the volcanic eruptions that can induce these metals into the environment. The anthropogenic reasons for the induction of these heavy metals into the environment is generally the industrial effluents for example, the industries like metal smelting, electroplating processes, the leather tanning, textile, mineral extraction and nuclear power. So, they can induce these metals into the environment. So, the municipal effluents may also contribute to the heavy metals for example, it has been reported that the municipal effluents may contain lead, chromium, mercury and arsenic.

So, the major concern is that these heavy metals can be quite toxic and they can bioaccumulate, they are non-biodegradable in nature so that's why they generally bioaccumulate inside the body as they are not metabolized and they remain into the body

and slowly and slowly they may accumulate inside the body and then once the threshold level is exceeded and then they start showing their effects. So, these metals can be the threat to human life as well as to the environment and because of their bioaccumulation tendencies, so they can also bio magnify in the food chain and that may cause problem to the secondary consumers who are in the food chain. So, the irrigation with wastewater which contains heavy metals, so it can also result in the contamination of the soil, it can result in the contamination of groundwater as well as these metals can also accumulate inside the vegetation, and this may also form a part of the food chain. So, that's why it is very important that the wastewater treatment must take into account the removal of the heavy metals so that the environment can be protected as well as the human health can be protected from these metals. So, there can be metals like arsenic, barium, cadmium, copper, mercury, nickel, selenium, zinc, chromium, lead.

So, these metals must be removed from the water or the wastewater so that these may not come into the food chain, and this may ultimately not come to us. And there can be number of methods which can be employed for removal of these heavy metals from the wastewater. For example, we can take help of the chemical precipitation which we will be discussing at length during this lecture. We can also go for the carbon adsorption, we can go for ion exchange processes, we can also go for the membrane processes like reverse osmosis. So, for the treatment of the wastewater the most common methods that is employed is the chemical precipitation.

However, the choice of the method will depend upon the factors like the type and the concentration of the heavy metals which are present in the wastewater, the characteristics of the wastewater will also decide about the choice of the method and similarly the environmental regulations, the affluent standards that is the level up to which these metals need to be treated so that also decides the choice of the method. So, commonly when we go for the chemical precipitation so we can precipitate these metals in form of hydroxide, sulfides or sometimes carbonates also. So, here when we go for the precipitation methods, so solubility equilibrium plays a very important role during the precipitation of certain ions. Obviously, when we are talking about the heavy metals here so the precipitation of the metals will be influenced by the solubility equilibrium of these compounds. For example, if we consider a slightly soluble compound  $CaAb$ , let's take it as  $C$  is the cation and  $A$  is the anion which is present in this compound.

So, it may dissociate into the anions and the cations as given in equation 1. So, here you can write down the equilibrium constant for this equation. So, this will be the  $K$  equilibrium is equal to  $C^a$  and  $A^b$  as given by the equation and here we are not taking any denominator because denominator represents the solid form that is here  $CaAb$  it represents the solid or the precipitated form and solid is pure and basically it represents the unit activity. So, that's why it is taken to be 1 and that's why the equilibrium constant here is taken to be  $C^a$  and

$A^b$  in this case. And this equilibrium constant can also be referred as the solubility product constant, and we generally use a term that is  $K_{sp}$  for the solubility product constant.

So, this solubility product constant can help us in determining that whether the precipitation will happen or not. For example, if suppose the ionic product of C and A here is less than the  $K_{sp}$  values at the given temperature. So, we can say that the solution is under saturated, and we need to add more ions here so that the saturation will happen and then precipitation of these ions basically of the compound that is formed by this reaction of these ions so that can happen. Similarly, if the value of the ion product is  $C^a$  and  $A^b$  is greater than the  $K_{sp}$  values that is the solubility product constant. So, we say that the solution is over saturated, and the precipitation will happen and if this ionic product is equal to the  $K_{sp}$  value, so this means that at that point the precipitation started to happen.

So, the  $K_{sp}$  value is higher always for the freshly formed precipitate in comparison to the old precipitates and this phenomena is also known as the aging phenomena and this happens because the freshly precipitates may be more soluble in comparison to the old precipitates as the old precipitates are having the crystals which are ordered which are inactive which are less soluble and larger in size that is why the old precipitates are having the lower  $K_{sp}$  values in comparison to the freshly formed precipitates. Similarly, we can have a common ion effect also which will affect the solubility equilibrium for example according to Le Chatelier's principle if either C or A is added to the system so if we see the equation 1 here so this basically if we are adding C or A to the system so this equilibrium will shift towards the left side. So, this means that it is shifting more towards the precipitation side so this means that the solubility of the precipitates then decreases, and this effect is known as the common ion effect. For example, we may have seen that if we are using the sea water which contains high amount of sodium and if we try to use soap with it so soap does not leather because of the common ion effect and this basically may be taken as the hardness in the water and that is also referred to as the pseudo hardness because it is due to the high sodium ions concentration which is there in the sea water which basically does not allow the sodium salt which is present in the soap to basically leather. So, this effect is called the common ion effect.

Similarly, if we are adding ions which are other than the ions present in the precipitate or which are also known as the indifferent electrolytes so this will reduce the activity of the C cations as well as the anions because the ionic strength will increase as the ionic strength increases the activity of the cations and anions present in the solution so they will decrease and let's say now the  $K$  equilibrium will be equal to  $\gamma_m$  where  $\gamma_m$  is the activity of cations and  $\gamma_m$  also presents the activity of the anions. So, the new value of the  $K$  equilibrium that is  $K$  equilibrium dash so this will be equal to  $K$  equilibrium divided by the  $\gamma_m$  whole square where  $\gamma_m$  is always less than 1 because the activity in high ionic strength is less than the natural concentration that has been added to the

system. So, this will increase the solubility of the precipitate and on addition of the indifferent electrolyte you will always find that the solubility of the precipitate will increase. So, these are the value of the  $pK_{sp}$ .  $pK_{sp}$  here refers to the minus log of  $K_{sp}$  so these values are given for various type of metal hydroxides as well as sulfite so for example you can see here that the cadmium hydroxide and cadmium sulfite so the values of  $pK_{sp}$  is 13.93 and 28 and so on for the different type of metals precipitates for example chromium hydroxide, copper hydroxide, copper sulfite, iron hydroxides and sulfites, lead hydroxide and sulfites, mercury hydroxide and sulfite so they all are given in this table and we can refer this table so that we can find out that what would be the solubility product for such type of precipitations and then we can calculate that how much precipitate will form obviously how much ions needs to be added so that the precipitation of these metals can occur. The heavy metal removal technologies include the conventional precipitation that we are just discussing so we can precipitate the metals in form of hydroxides we can precipitate the metals in form of sulfites we can precipitate the metals in form of carbonates. We can also go for co-precipitation where the metals may precipitate it along with the precipitate of different compounds so these metals can also be entangled or adsorbed onto the precipitate which is otherwise not for of the metals which are there right so this leads to the co-precipitation of these metals. Similarly, when we are having industrial waste water so in that case it is possible that the metals may present in complex form or they will be chelated industrial waste water so these chelated or complex metals can be removed by using advanced precipitation method where we use di-methyl thiocarbonate where we use di-ethyl thiocarbonate or we can use tri-mercapto-striazine or tri-sodium salt for the precipitation of such complex metals in the waste water. The other methods which can be used for the removal of the high metals may be adsorption for example we can use here activated carbon so the adsorption we have already studied, and we know that how we can use different type of adsorbents like activated carbon, or we can also use new type of materials cheap materials also for the adsorption of the metals by using certain adsorbents like biochar etc.

So, this method can be used for transferring the metals from the water to the solid form. Similarly, ion exchange process also we have discussed, and we can replace the metals which are present in the water or wastewater by sodium or H plus ions which basically goes into the water, and we can also recover the metals from this ion exchange process. We can also use the membrane filtration for the removal of the high metals like reverse osmosis, nanofiltration, ultra filtration so that the metals can be removed from the wastewater. Biological methods have also been used for example the bioremediation by using different species of bacteria algae and fungi so they also can be used for the removal of the heavy metals from water or the wastewater. Similarly, we can also use method which is called electrochemical methods and here we can go for either electro coagulation of the metals or we can deposit these metals onto the cathode by passing the electrical current through the wastewater.

So these methods can also be used but we have already discussed that the method which is commonly used because we are having a very large volume of the waste water which we have to handle so the efficient method by which we can remove the metals from the waste water can be the chemical precipitation and if you want to recover the metals so we can go for the methods like ion exchange, we can use membrane methods or we can also go for the electrochemical methods for the recovery of the metals from the waste water. So then the selection of the appropriate method it depends upon the characteristics of the waste water and the desired treatment goes or basically we can say that which method will be best for certain characteristics of the waste water so that we have to find out and then we also have to look that what are the desired treatment goals, how much reduction of the metals or how much removal of the metal needs to be done so that appropriate method can be chosen from whatever the methods we have discussed till now and similarly we have to also see that whatever the methods we are using so it has no adverse environmental impact and it should also basically comply with the regulatory standards. So when we go for the precipitation methods so the steps that we follow are generally adding of the chemicals to the waste water so that precipitate with the heavy metal ions it can form then we can go for the sedimentation or filtration process so that we can remove we can separate out the sludge from the waste water and here we can use the salts like for example we can use lime here calcium hydroxide we can use sodium hydroxide and we can also use other metal salts when we want to remove it in form of carbonates or in form of sulfides. So, we have to first of all identify the heavy metal that what type of heavy metal is present in the wastewater what is the concentration of the heavy metals that is present and then we have to look for the appropriate precipitation agent that can be used for the optimum precipitation of such heavy metal. We know that the optimum pH is required so that the metals can be precipitated out from the waste water so this means that we have to optimize the precipitation process and we have to adjust the pH of the waste water so that the metal hydroxides or the metal sulfides or the metal carbonates they are least soluble at that pH and they can be removed easily from the system and generally for many heavy metals this pH range is generally alkaline.

So, then we have to add the precipitating agents where we can add one precipitating agent, or we can use a combination of the precipitating agents where we can use either lime, we can use sodium hydroxide, or we can use the metal salts. So once these precipitates are added so they will form insoluble metal hydroxide precipitates, and these metal hydroxide precipitates can be separated from the wastewater. However, we have to ensure that a thorough mixing should be done as soon as we add the chemicals so that the proper contact is established between the precipitating agent as well as the heavy metal ions as we have already discussed that the rapid mix is very much required for the coagulation and flocculation process and similarly we can also add some flocculants so that the precipitate that is formed so that we form a larger flocs. After this we may pass it to a sedimentation tank where these precipitates may be settled out or we can pass it through a filtration system

where the precipitates can be separated out from the wastewater. After this we may also take it to other treatment steps also if it is required for example if we are having a presence of other contaminants in the waste water so we may take it for adsorption process or we take it for the filtration or we would take it for other processes like oxidation etc so that the water is treated for the requisite contaminants which are present in the waste water and then we can polish the water in that way.

And the last step is that we also have to monitor and control the processes for example a continuous monitoring is required like for example we have to always monitor what is the pH, what is the metal concentrations which are coming out in the effluent, we have to also see that what is the effectiveness of the precipitation that we are doing so that we can maintain the optimum treatment conditions. So, the stoichiometric ratio of the reactions so it needs to be studied so that we can calculate that how much precipitation agent is required for the optimum precipitation of certain metals and so this will also help us in minimizing the addition of the excess chemicals in such a way. So, we can see here that this graph shows that how the concentration of the various metal hydroxide it varies with the pH. So we can see here that a number of metals like for example cadmium hydroxide is there which is having a minimum solubility at a pH of nearly 12 and similarly we can also see here that the copper hydroxide is having a minimum solubility of nearly 9 also and so this means that for a different type of metal hydroxides we are having some optimum values of the pH at which the solubility of those hydroxide is minimum. As these metals may be amphoteric in nature so at the low pH as well as at the high pH they may be in the soluble form and there can be an optimum pH values at which these metals may precipitate as hydroxide and the solubility may be minimum at a certain pH values and these curves that we are seeing here so this is based on the mononuclear species right and if you want to find out that what can be the range for the wastewater treatment we have to perform the actual test or pilot scale test so that we can find out that what can be the optimum value for a certain type of wastewater.

So similarly, we can see here that precipitation of sulfites with the pH right is given here, and we can find out that for the mononuclear species if the only those species are present in the water so what can be the optimum pH at which these metal sulfites can precipitate. So, it will also depend upon the characteristics of the wastewater that it will also depend upon the concentration of organic matter it will depend upon the temperature optimum pH values that's why it is very important that we go for the bench scale or pilot scale test before we find out the optimum pH for the precipitation of a certain metal. So now we will discuss about the different type of metals which can be present for example we will talk about the arsenic and the arsenic may be used in the metallurgical in the glassware in the ceramics in the tangeries in the dye making pesticides and petroleum refining so this arsenic if it is taken by the humans in high amounts so it may lead to the nervous system disorder it can lead to the liver cancer it can lead to kidney and bladder cancers it can lead to skin cancer

it can lead to diabetes lung cancer as well as the cardiovascular diseases. So, for the drinking water standards it is required as per IS10500 that the total arsenic should not exceed 0.01 milligram per liter in the drinking water whereas the effluent discharge into the inland surface waters the arsenic should not be greater than 0.2 milligrams per liter. So, we can remove the arsenic by precipitation and when we want to remove the arsenic by precipitation, we should ensure that the arsenide that is arsenic 3 should be converted into arsenate that is arsenic 5 because it precipitates better than the arsenide. So, this means that we have to oxidize the arsenic 3 to arsenic 5 before we go for the precipitation method, and we can treat the arsenic by using hydrogen sulfide or sodium sulfide at pH 6 to 7 followed by filtration which can lead to 0.05 milligram per liter of arsenic in the effluent. Similarly, the filtration through the activated carbon filter may also lead to 0.06 milligram per liter of arsenic in the effluent.

However, the co-precipitation with ferric hydroxide have shown to be the best removal and we may get around 0.005 milligram per liter of arsenic in the effluent. So, the barium is used in different industries for example in paints and pigments for glass, ceramics, dye manufacturing, vulcanizing of rubber, explosive manufacture. So here this the barium if it is taken in high amounts it may lead to the muscle weakness, it may cause brain swelling, it may cause difficulty in the breathing, we may have increased BP and stomach irritation etc. As for IS10500 the barium should not exceed 0.7 milligrams per liter in the drinking water. So, if we target barium so the precipitation as barium sulfate is very efficient as the barium sulfate is having very very low solubility. So, if we go for barium sulfate precipitation, we may get around 0.03 to 0.3 milligrams per liter in the effluent and typically we can get a concentration of nearly 0.5 milligram per liter in the effluent. Though ion exchange and electrolytic treatment may also be used but they can prove to be expensive. So, cadmium may also find in the water or the wastewater and this may happen because of its use in number of industries like it can be used in nickel cadmium batteries, it can be used in solar cells, it can be used in metallurgy, alloys, ceramics, electroplating, photography, pigments, plastic stabilizers and it also absorbs neutrons so it can also be used in the nuclear reactor. So, if we take high cadmium so it may basically lead to a disease which is called Itai-Itai disease. So once this has happened that during the zinc mining it has led to the very high concentration of cadmium in the Jinzu River in Japan, so which led to the replacement of calcium bicadmium in the bones which leads to the softening of the bones, and it also led to the kidney disease.

So nowadays it is being seen that the trend for the cadmium in the rechargeable batteries and solar cells is increasing whereas in the pigments, coating and plating, stabilizer or alloys it is decreasing and in the drinking water it should not exceed 0.003 milligrams per liter and the effluent which is discharged to the inland surface water so it should not exceed 2 milligrams per liter. So, if we talk about the removal of the cadmium by precipitation methods, so hydroxide precipitation at pH 10 to 11 may lead to 0.05 milligrams per liter in

the effluent. If we co-precipitate the cadmium with ferric hydroxide so it may also lead to around 0.05 milligrams per liter in the effluent whereas sulfite precipitation is the best which leads to around 0.008 milligrams per liter of cadmium in the effluent. So, chromium may also come into the environment through various industries like chrome plating, diamond fetching, textile industries, aircraft, leather tanning, wood preservatives and mud drilling. So, the chromium may be present in the water in major two forms for example it may present in trivalent form, or it may present in the hexavalent form. So, this hexavalent form is quite toxic basically cytotoxic in nature, mutagenic, carcinogenic, it can cause chromosomal damage and also it can cause oxidative protein changes.

Whereas if we are inhaling the high amount of hexavalent chromium so it can cause a lot of problems like it can cause nose ulcers, irritation, anemia, it can basically cause face erythema, and a number of problems related to the lungs. So, the removal of the chromium may take place that is we have to first of all convert chromium 6 to chromium 3 and then this can be precipitated as chromium hydroxide. The chromium in the drinking water should be very low that is it should be nearly 0.05 milligram per liter in the drinking water and when we are discharging the effluents to the inland surface water so it should not exceed 2 milligram per liter as total chromium whereas the chromium 6 plus it should not exceed 0.1 milligram per liter. So when we want to reduce the chromium 6 to chromium 3 so in that case we have to use iron salts for example ferrous salts we can use sulfur dioxide we can use and sodium thiosulfate we can use so that we can reduce chromium 6 to chromium 3 and in turn the ferrous is oxidized to ferric and sulfur dioxide is oxidized to sulfate and this happens in an acidic medium and after that we have to add lime so that the chromium hydroxide can be precipitated out. So if we want to remove 1 ppm of chromium so we may require around 2.81 ppm of sodium thiosulfate which is 97.5 percent pure 1.52 ppm of sulfuric acid 12.38 ppm of lime and 1.85 ppm of sulfur dioxide and we have to always use excess of sulfur dioxide so that we can counteract the dissolved oxygen which is present in the water for example here we have to add 35 milligram per liter of sulfur dioxide additionally. So, we can go for the removal of the chromium in the batch system also as well as in the continuous system also so when we are having very very small plants which are having discharge less than 114 cubic meter per day in that case we may go for the batch system where we add the chemicals simultaneously in a batch reactor and then we may treat the water or the wastewater in batches. Whereas if we want to treat it continuously so then we have to have different reactors for example the first reactor that we are seeing here in this reactor the chemicals may be added like sulfur dioxide will be added from here we can add the ferrous salt we can add sodium thiosulfate and we can also add here acid so that the chromium 6 is reduced to chromium 3 in this reactor and then we take this effluent to another reactor where we increase the pH where we add lime to it so that the pH may be increased and the chromium which has been converted to chromium 3 now it can be converted to chromium hydroxide precipitate and then we can take it to a settling tank where basically this sludge may be settled out and the effluent



may go to the disposal and this is used for the large plants where basically we are having the flow greater than 114 cubic meter per day. So, the copper is also used in number of industries for example it is used for the metal process it is used for pickling baths and plating baths chemical manufacturing units etc. and high doses of copper may lead to the liver damage abdominal pains cramps nausea diarrhea and vomiting, and it can also cause wilson disease which where basically the copper may get accumulated into the brain or the liver.

So, we can use different methods here for the removal of the copper for the precipitation ion exchange evaporation or electrolysis so they can be used for the removal of copper and as per the ricky water standards the copper in the ricky water should not exceed 0.05 milligram per liter and as well as in the effluent discharge it should not exceed 3 milligrams per liter. So if we want to remove the copper by using precipitation method so we have to have alkaline pH where the copper may be converted to copper hydroxide and it may result in 0.02 to 0.07 milligram per liter in the effluent but if the sulfate is present and we are using lime so in that case the calcium sulfate may be precipitated out and which may interfere with the recovery of the copper from the copper hydroxide sludge.

Similarly, we can also use oxidize the copper-to-copper oxide which is having a minimum solubility between pH 9 to 10.3 and it can also result in 0.01 milligram per liter of copper in the effluent. Copper can also be precipitated as copper sulfate at pH 8.5 and it may result in 0.01 to 0.02 milligram per liter of copper in the effluent. So iron can also come into the environment because the different industrial uses for example from the mining operations from ore milling from chemical industries diamond fracturing metal processing textile mills petroleum refining so there can be number of industries through which the iron basically can come into the environment and this when we take very high doses of iron so it can lead to the fibrosis and the liver enlargement it can basically also lead to the insulin resistance and diabetes it can lead to hypothyroidism it can also lead to cardiomyopathy. So, we want that the concentration of iron in the drinking water should not exceed 0.3 milligram per liter as well as in the effluent discharge the iron should be limited to three milligrams per liter. So if we want to remove the iron by using the precipitation method so we have to add lime at nearly pH 7 so that the ferric which is present it can be converted to ferric hydroxide but if we take it to a higher pH in that case the  $\text{FeOH}_4$  minus it solubilizes and again the solubility of this iron may increase because of which it may be difficult for the removal by the precipitation method.

Similarly, if cyanide is present then the iron can also combine with the cyanide to form complexes this may interfere with the precipitation of the iron. The two-state hydroxide or sulfate precipitation it can result in around 0.01 milligram per liter of iron in the effluent. Lead can also go into the environment because of different uses like for example battery manufacture the paints and alloys so they use lead a lot and lead is quite toxic so it can lead to adverse impact on the central nervous system and the bair can lead to the adverse

impact on the reproductive systems on kidneys on cardiovascular systems blood and immune system so basically it can reduce the IQ levels it can impair the learning ability and it can also have a risk of behavioral problems in the individuals the lead is taken by the individuals. So here in the drinking water the lead should not exceed 0.01 milligram per liter as well as in the effluent discharge when we are discharging the treated wastewater to the surface water so in that case it should not exceed 0.1 milligram per liter. So for the removal of lead by precipitation methods we can go for lead carbonate or lead hydroxide so when we are using sodium carbonate at 9 to 9.5 pH we can get 0.01 to 0.03 milligram per liter of lead in the effluent if we are precipitating out the lead with lime at 11.5 pH then we may get concentration of nearly 0.01 to 0.2 milligram per liter in the effluent similarly precipitation with sulfites at pH 7.5 to 8.5 will lead to 0.01 milligram per liter of lead in the effluent. So manganese can be used in number of industries for example it may come from steel alloys, dry cell batteries, glass and ceramics, paints, varnish, inks and dyes etc. and manganese can basically impact the human health if we are taking very high concentration of manganese then it will lead to the problems in the stomach it may cause the anxiety effect in the stomach and for the drinking water the manganese should not exceed 0.1 milligram per liter whereas in the effluent discharge it should not exceed 2 milligrams per liter. So, we can remove the manganese by aeration that is we can convert this manganese into manganese dioxide which can be precipitated out from the system but if we are going for very very enhanced aeration so it will also lead to soluble  $MnO_4^-$  ions which are soluble and that's why it may interfere with the  $MnO_2$  precipitation.

So aeration is not also efficient if we are using the pH above 9 so basically we should try to do the aeration below the pH 9 and copper may also enhance the manganese removal through the aeration so if the copper is present so then  $MnO_2$  precipitation is better in that case and chlorine dioxide can also be used for the precipitation of manganese similarly ozone and lime can also basically remove manganese from the water or base water. Mercury is also a very very notorious element which may find its way into the environment from the chlor-alkali industries, cements, electrical electronics, explosives, photography, fluorescent lamps, batteries, pesticides and preservatives and chemicals, petrochemicals, power generation so everywhere a lot of mercury is used and this mercury if it goes into the environment if it basically comes back to the people so it may cause a lot of problem that is it may impair the central nervous system of the humans and they may lose their control on the body. For example, the case has happened in Japan it is also known as Minamata disease where 900 people they died because of the very high mercury pollution which has basically aggravated which is bio-magnified through the food chain and it has come into the fishes which ultimately has come to the humans and this episode is also known as dancing cats because the cats were dancing at that time because they also lost control on their body because of very high mercury pollution in the body. So, the mercury in the drinking water it should not be more than 0.001 milligrams per liter and in the effluent discharge it should not exceed 0.01 milligram per liter. So, if you want to go for

the removal by precipitation method so the sulfite precipitation can lead to around 10 to 20 micrograms per liter of mercury in the effluent. Alum co-precipitation may lead to around 1 to 10 micrograms per liter of mercury in the effluent. Iron co-precipitation may lead to 0.5 to 5 micrograms per liter of the mercury in the effluent. Iron exchange can lead to around 1 to 5 micrograms per liter whereas the carbon absorption may lead to as low as 0.25 micrograms per liter of mercury in the effluent. So, nickel may be used in metal processing, steel foundries, motor vehicles, aircrafts, industries and printing and as well as the chemical industries. So, when we take high amount of nickel so it may lead to allergy, cardiovascular and kidney diseases, lung fibrosis, lung and nasal cancer. So, in the drinking water the nickel should not exceed 0.02 milligram per liter whereas in the effluent discharge it should not exceed 3 milligram per liter. And when you want to remove it by using the precipitation method so nickel hydroxide has a very poor setting characteristics and the lime treatment, lime sulfide treatment and the filtration may lead to the removal of the nickel.

For example, it has been shown that the hydroxide treatment at pH 10 so it can result of around 0.12 milligram per liter of the nickel in the effluent. Similarly, the selenium may come into the environment from various industries like paper, fly ash, from the metallic sulfide ores, from the pigment and dyes where calcium selenide is used. So, these industries may induce the selenium into the environment and if we take very high amount of selenium in our diet so it may lead to the stomach discomfort, it will lead to headache, rashes, hair loss, fatigue, nausea, vomiting and weight loss. So, these are some of the impacts of the selenium which can be there if we take very extremely high doses so it can lead to the organ failures as well as death.

So, selenium should not exceed 0.01 milligram per liter in the drinking water whereas in the effluent discharge it should not exceed 0.05 milligram per liter. So, when we talk of the selenium removal by precipitation methods so precipitation as sulfide at pH 6.6 may lead to effluent concentration of nearly 0.05 milligram per liter whereas the iron hydroxide co-precipitation at pH 6.2 may lead to 0.01 to 0.05 milligram per liter in effluent. Alumina adsorption proves to be best so we can have concentrations as low as 0.005 to 0.02 milligram per liter in the effluent. So, silver can come into the environment of number of industries like jewelry, soldering and brazing alloys, batteries, glass coatings, LED chips, medicines, dentistry, nuclear reactors, photography, photovoltaic or solar cells, solar energy, RFID chips, semiconductors. So, there can be number of industries from where the silver may come into the environment.

So, if we are taking high concentration of silver so it may lead to the discoloration of skin. Silver nitrate or silver oxide may cause breathing problems as well as it can also cause lung and throat irritation in stomach pain also. So, the drinking water standards the silver should not exceed 0.1 milligram per liter. So, if you want to remove the silver by using the chemical precipitation method so we can go for iron and alum co-precipitation which may

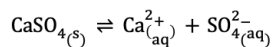
lead to 0.025 milligram per liter of silver in the effluent. The precipitation as hydroxide at pH 11 may lead to nearly 0.02 milligram per liter in the effluents. Activated carbon can also be used for the removal of silver and we can get concentration of nearly 0.005 to 0.02 and iron exchange may also be used because we want to recover this metal so the iron exchange can prove to be beneficial in such cases.

Similarly zinc can find its way in through the steelworks, rayon fiber manufacturer, cooling water systems, plating, metal processing etc. and high zinc may cause problems like nausea, dizziness, headaches, stomach upset, vomiting and loss of peptides we are taking the zinc for a long time so it may basically cause the low levels of HDL it may cause low immunity right and it may also cause low copper levels also and the zinc should not exceed 5 milligram per liter in the drinking water whereas in the effluent it should not exceed 5 milligram per liter when we are discharging the effluents to the surface water. And addition of lime and caustic can remove the zinc and hydroxide precipitation at pH 11 may result in around 0.1 milligram per liter in the effluent. So, there can be some limitation of the precipitation methods for the wastewater treatment for example when we are treating both industrial wastes as well as the domestic waste together so in that case the chemical needs to be added to the primary sedimentation tanks especially the pretreatment processes, they become ineffective so in that case we can go for the chemical addition in the primary sedimentation tank.

Similarly, the sludge that is we are getting from the precipitation of the heavy metals so this may not be stabilized by using anaerobic digestion method because these metals may prove to be toxic to the microbes which are causing the anaerobic digestion. Similarly, the chemical precipitation may also lead to the increase in the total dissolved solids of the wastewater that is being treated so these are some of the limitations of the precipitation methods if we are going for precipitation in a wastewater treatment. So now let us discuss a few problems based on the solubility product that we have already discussed so the problem.

**Question 1. The solubility product,  $K_s$ , for calcium sulfate in water at 25°C is  $1.96 \times 10^{-4}$ . Determine the equilibrium  $\text{Ca}^{2+}$  concentration for a saturated calcium sulfate solution if ideal behavior is assumed.**

**Solution:**



$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

$$1.96 \times 10^{-4} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

$$1.96 \times 10^{-4} = M^2$$

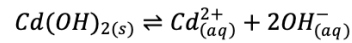
$$[\text{Ca}^{2+}] = M = 1.4 \times 10^{-2} \text{ mole / litre}$$

$$\text{mg Ca}^{2+} / \text{litre} = (1.4 \times 10^{-2})(1000)(40.08) = 561 \text{ mg/L}$$

**Question 2.** Compute the solubility (mg/l) of cadmium hydroxide in water at 25°C. Assume that the solution exhibits ideal behavior and that the solubility product,  $K_{sp}$ , is  $5.9 \times 10^{-15}$ .

Solution:

1. Write the appropriate dissolution reaction:



2. Write the appropriate equilibrium constant expression:

$$K_s = [Cd^{2+}][OH^{-}]^2$$

Or

$$5.9 \times 10^{-15} = [Cd^{2+}][OH^{-}]^2$$

3. Compute the equilibrium molar  $Cd^{2+}$  concentration.

$$5.9 \times 10^{-15} = [Cd^{2+}](2[Cd^{2+}])^2$$

$$5.9 \times 10^{-15} = 4[Cd^{2+}]^3$$

Thus,

$$[Cd^{2+}] = 1.14 \times 10^{-5} \text{ mole/litre}$$

4. Determine the molar solubility of  $Cd(OH)_{2(s)}$ .

Since 1 mole of  $Cd^{2+}$  ions are produced for each mole of cadmium hydroxide which dissolves, the molar solubility of  $Cd(OH)_{2(s)}$  is equal to the equilibrium molar concentration of  $Cd^{2+}$  or  $1.14 \times 10^{-5}$  mole/L

5. Convert the molar solubility to mg/l:

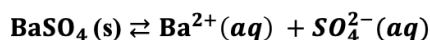
$$\text{Solubility of } Cd(OH)_2 = (1.14 \times 10^{-5})(1000)(146.4)$$

$$= 1.67 \text{ mg/L}$$

**Question:3**

**Barium sulfate** finds application in medical imaging of the gastrointestinal tract due to its ideal properties for this purpose. With a solubility product of  $1.08 \times 10^{-10}$  at  $25^\circ\text{C}$ , it exhibits low solubility, making it suitable for tracking the pathway of a "barium milkshake" consumed by a patient through x-ray monitoring. The question arises: will **barium sulfate** precipitate if 10 mL of a 0.0020 M  $\text{Na}_2\text{SO}_4$  solution is introduced to 100 mL of a  $3.2 \times 10^{-4}$  M  $\text{BaCl}_2$  solution? It is important to note that **NaCl** is highly soluble in water.

**Solution:** The only slightly soluble salt that can be formed when these two solutions are mixed is  $\text{BaSO}_4$



The solubility product expression is as follows:

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.08 \times 10^{-10}$$

To solve this problem, we must first calculate the **ion product**:

$$Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

Using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of  $\text{Ba}^{2+}$  when the solutions are mixed is the total number of moles of  $\text{Ba}^{2+}$  in the original 100 mL of  $\text{BaCl}_2$  solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\begin{aligned} \text{moles Ba}^{2+} &= 100 \text{ mL} \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L}} \right) = 3.2 \times 10^{-5} \text{ mol Ba}^{2+} \\ [\text{Ba}^{2+}] &= \left( \frac{3.2 \times 10^{-5} \text{ mol Ba}^{2+}}{110 \text{ mL}} \right) \left( \frac{1000 \text{ mL}}{1 \text{ L}} \right) = 2.9 \times 10^{-4} \text{ M Ba}^{2+} \end{aligned}$$

Similarly, the concentration of  $\text{SO}_4^{2-}$  after mixing is the total number of moles of  $\text{SO}_4^{2-}$  in the original 10.0 mL of  $\text{Na}_2\text{SO}_4$  solution divided by the final volume (110 mL):

$$\begin{aligned} \text{moles SO}_4^{2-} &= 10 \text{ mL} \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{0.0020 \text{ mol}}{1 \text{ L}} \right) = 2 \times 10^{-5} \text{ mol SO}_4^{2-} \\ [\text{SO}_4^{2-}] &= \left( \frac{2 \times 10^{-5} \text{ mol SO}_4^{2-}}{110 \text{ mL}} \right) \left( \frac{1000 \text{ mL}}{1 \text{ L}} \right) = 1.8 \times 10^{-4} \text{ M SO}_4^{2-} \end{aligned}$$

We can now calculate  $Q$ :

$$Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (2.9 \times 10^{-4})(1.8 \times 10^{-4}) = 5.2 \times 10^{-8}$$

We now compare  $Q$  with the  $K_{\text{sp}}$ . If  $Q > K_{\text{sp}}$ , then  $\text{BaSO}_4$  will precipitate, but if  $Q < K_{\text{sp}}$ , it will not. Because  $Q > K_{\text{sp}}$ , we predict that  $\text{BaSO}_4$  will precipitate when the two solutions are mixed. In fact,  $\text{BaSO}_4$  will continue to precipitate until the system reaches equilibrium, which occurs when  $[\text{Ba}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}} = 1.08 \times 10^{-10}$ .

So, with this we stop here, and these are the references that we have used for this lecture.

Thank you.