Environmental Soil Chemistry
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Lecture – 43
Pollutants - Soil Solution Interactions (Contd.,)

Welcome friends to this third lecture of week 9 of this NPTEL online certification course of environmental soil chemistry and in this third lecture, we will be talking more about some environmental pollution issues. We will be talking about acid rains and also alkaline soils and gypsum dissolution but before going to you know, discuss those things, I just like to give you a quick recap of whatever we have discussed so far.

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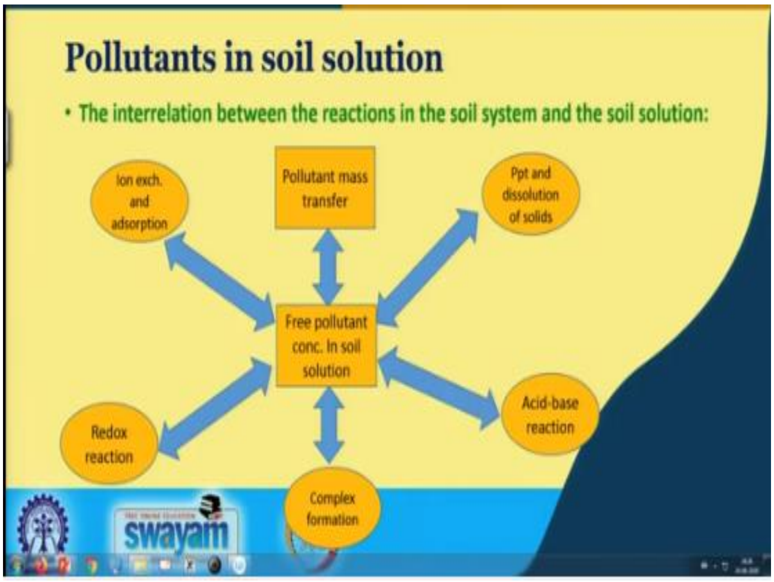

So, in our first 2 lectures, we have started with the pollute; discussion with the pollutants in soil solution, I showed you this slide where I showed you that how the free, you know free pollutant concentration in soil solution shows different dynamics and they can be converted to different forms and vice versa, I have shown you this pollutants in soil solution.

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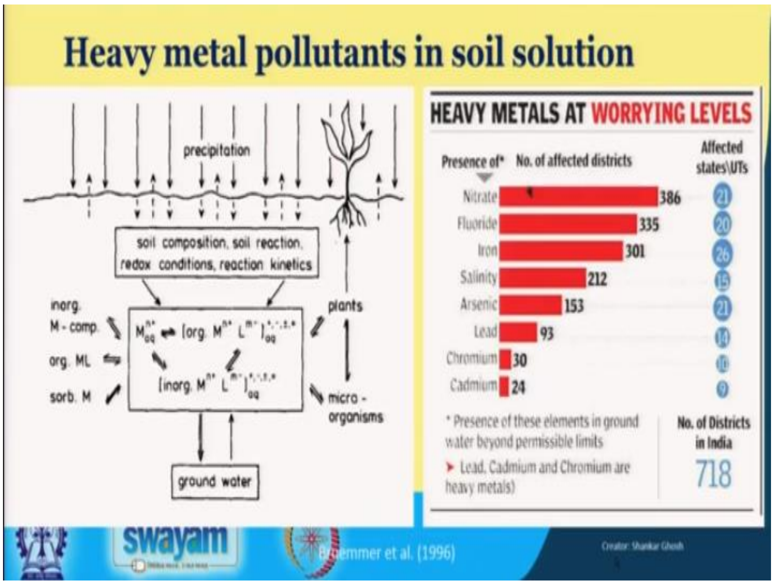

Then, we have discussed what are the dynamics of heavy metal pollutants in soil solution, we have discussed how heavy metals are present in worrying levels in ground water in especially, Indian concern you know, Indian states and union territories are concerned.

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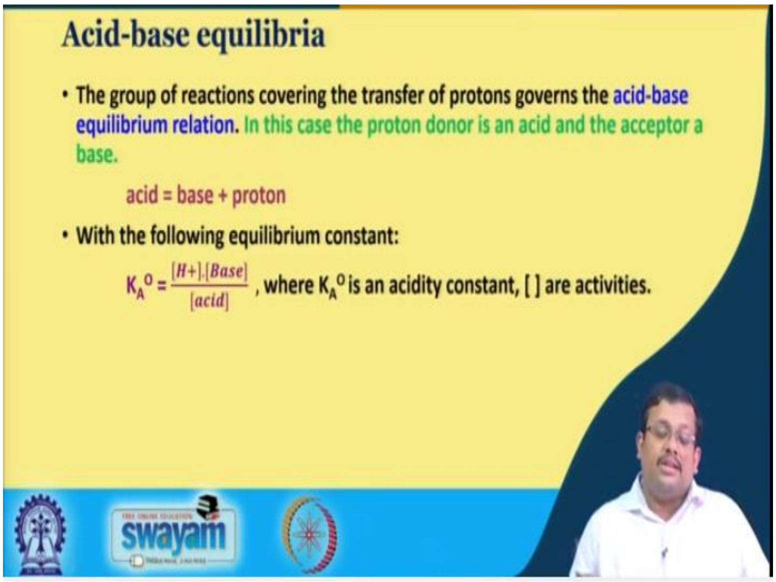

Then, we have talked about the in details about the acid base equilibria; we have seen the relevant reaction for 1 acid, 1 base.

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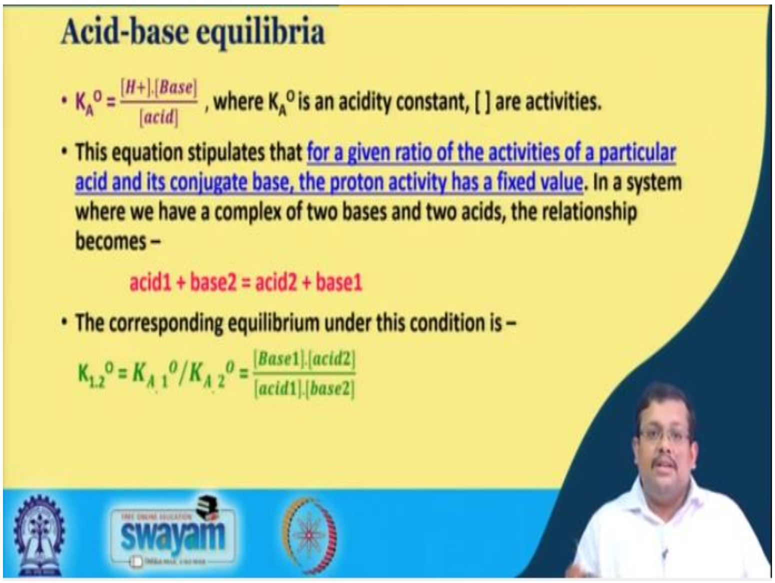

And then, we have seen more complex of 2 bases and 2 acids and how this you know, corresponding equilibrium condition changes for these complex 2 acids and 2 bases reaction.

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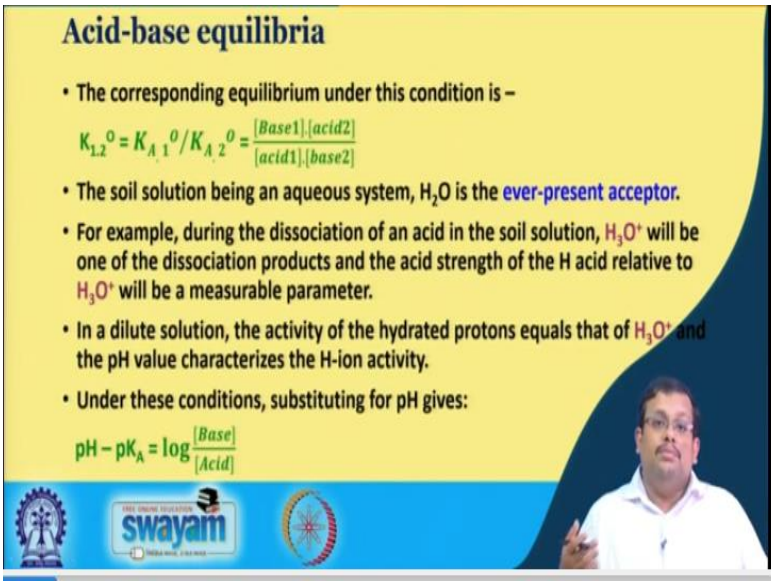

Then you know, we have discussed what is the importance of these hydronium ions, H3O+ as far as the you know, dissociation of acids is concerned.

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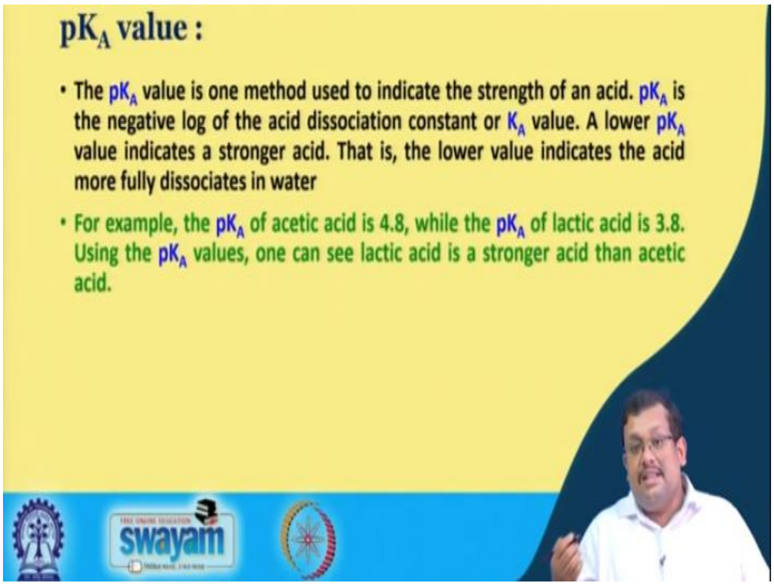

And also we have discussed about the pKA value remember, you know pKA is the negative logarithm of the acid dissociation constant KA. So, a lower pKA value indicates a stronger acid and we have seen the example of acetic acid and lactic acid, where the lactic acid has a lower pKA value and as a result, lactic acid is stronger than you know, lactic acid is stronger than that of acidic acid.

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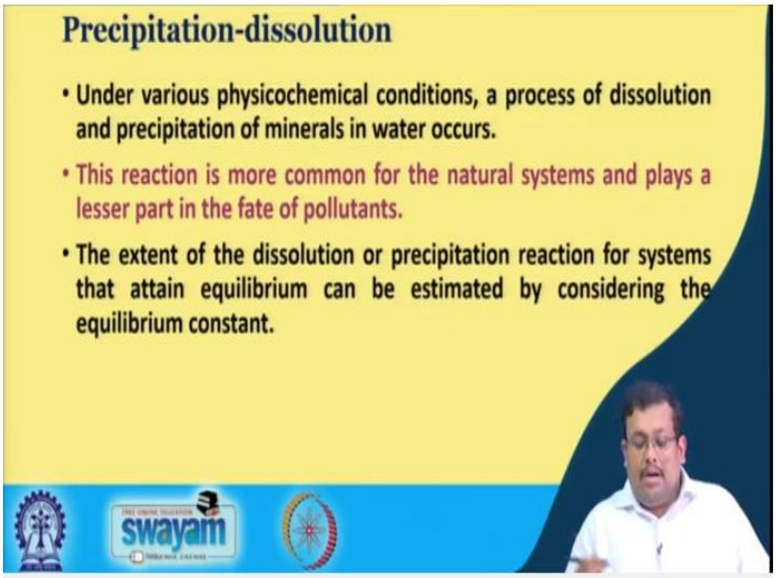

Now, if you consider you know, we have also discussed precipitation dissolution the reactions.

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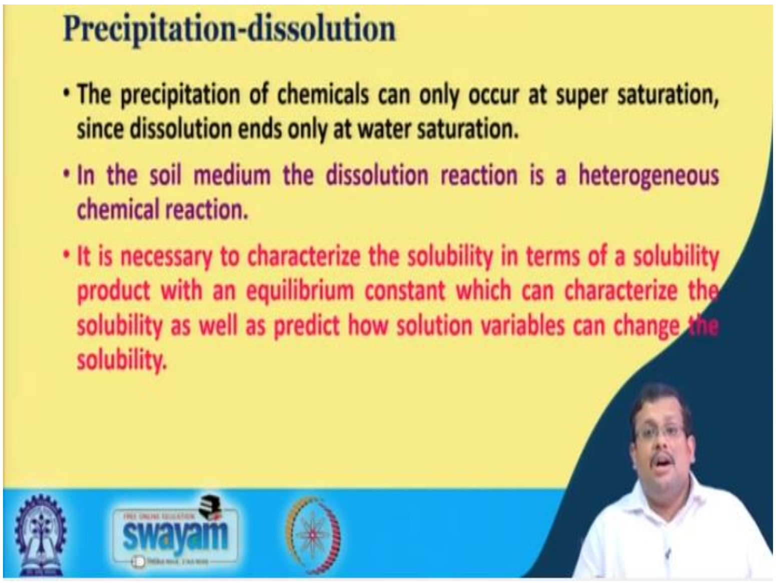

And you know, we have seen different conditions of precipitation and dissolution, what is the condition of getting so, you know precipitation, what is super saturation, what is under saturation we have discussed all these things.

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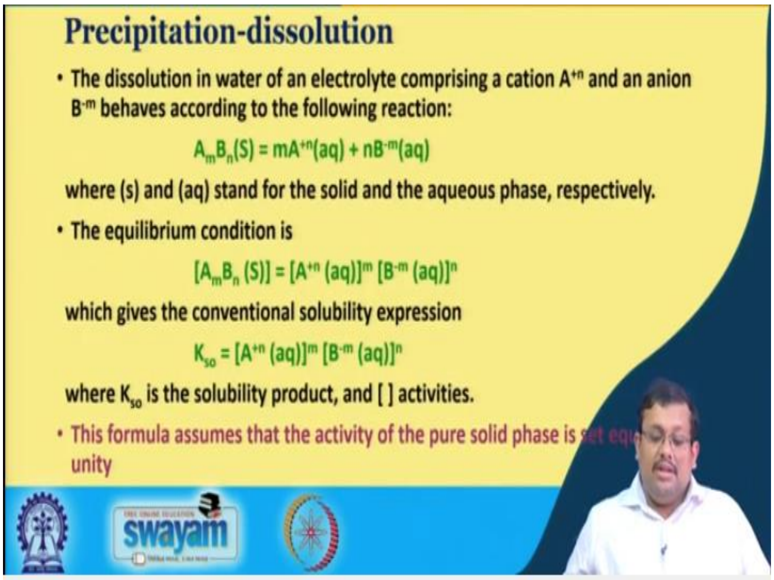

And then in terms of this you know dissolution of in water of an electrolyte comprising these cations and anions, we have discussed this example, in terms of the solubility product constant and the activities of those anions and cations.

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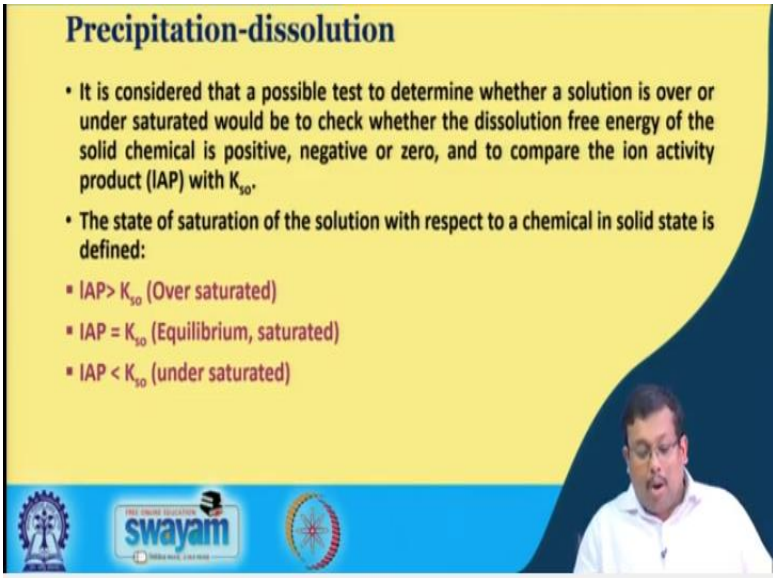

So, we have seen that ion activity product, how these ion activity products linked with this solubility product to infer whether the solution, when there will be over saturation or saturation or under saturation and in this 3 condition, how this precipitation and dissolution will occur.

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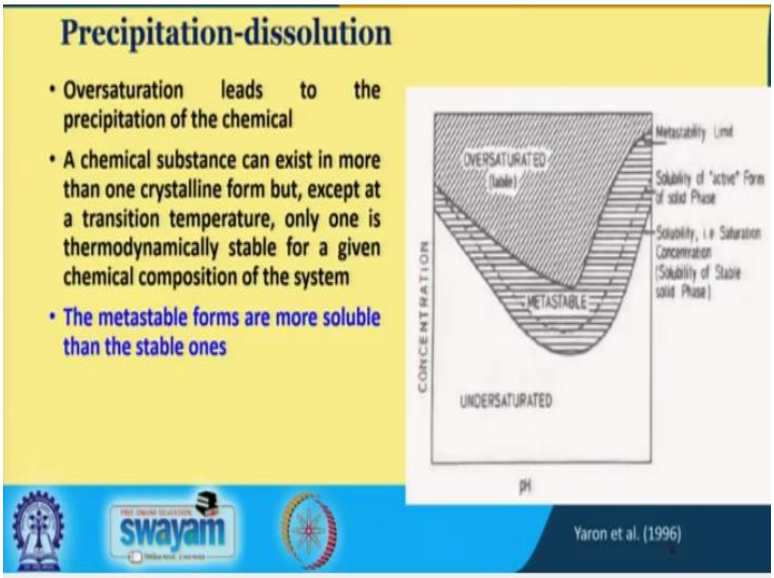

Then, we have seen the relationship between pH and concentration; I have shown you the zones of under saturation, zones of over saturation as well as the metastability limits and metastable zones.

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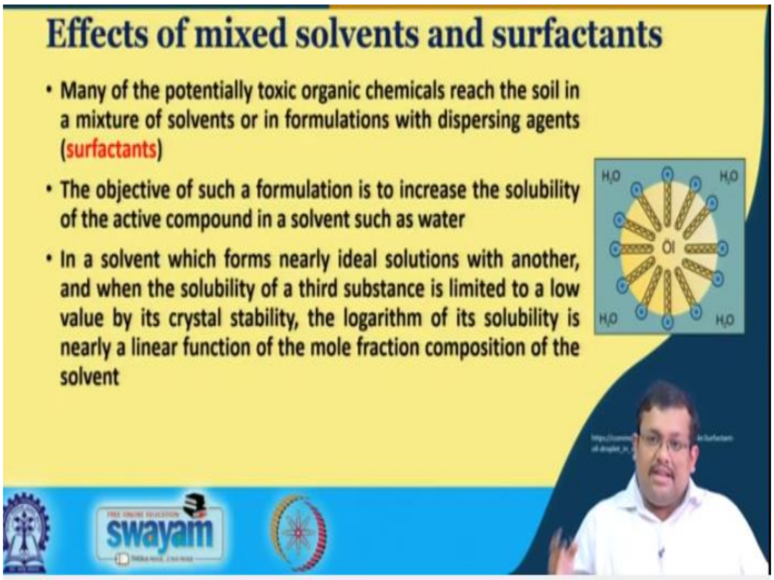

Then we have started a, we discussed an important aspect that is effect of mixed solvents and surfactants, we have discussed the you know, we have discussed the structure of the surfactants and how their solubility, how they act as a dispersing agent to increase the solubility of non-polar, you know non polar molecules in the water. So, what is their implication as far as the solubility of toxic organic chemicals like pesticides in water and their movement from one part of the environment to another part of the environment is concerned, we have discussed in details.

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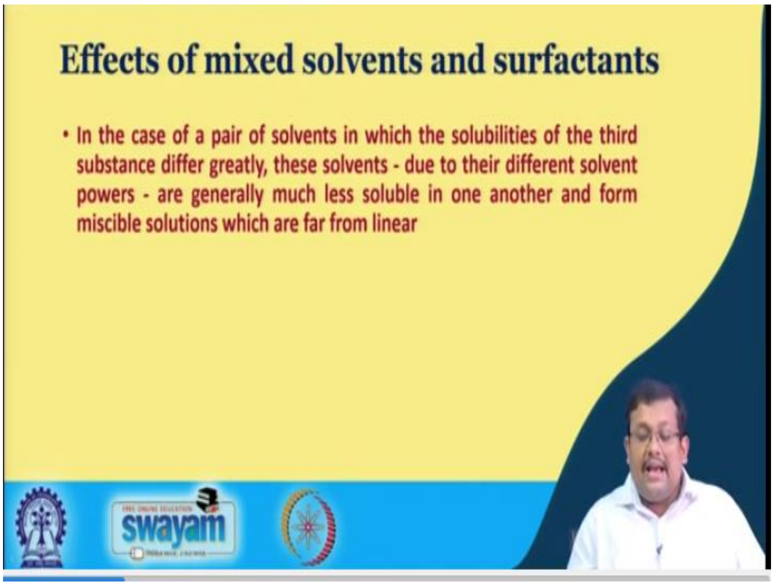

Then we have seen the effects of mixed solvents and surfactants.

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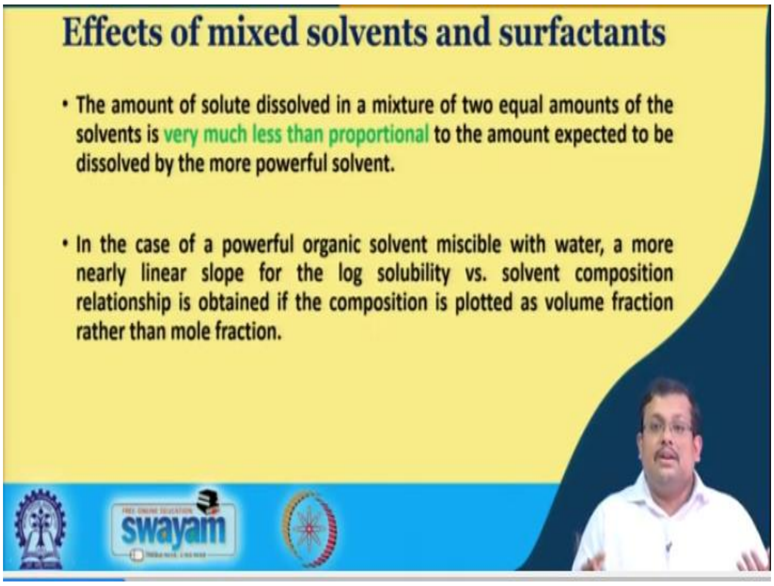

We have discussed when there is a cosolvent in the water, how this you know mixture affects the, you know solubility of a third substance.

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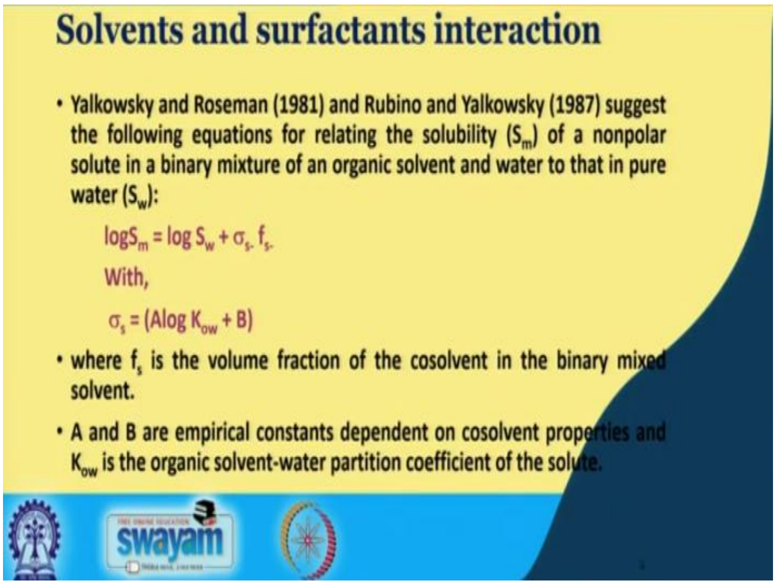

We have discussed this in terms of this, you know relationship between the solubility in a mixture of solvents, which is basically the summation of solubility in pure water plus this you know, this component that is sigma s you know, fs, where this sigma s is basically you know taking this form Alog of Kow, where Kow is the organic solvent water partition coefficient and A and B are basically the empirical constant depend on cosolvent properties.

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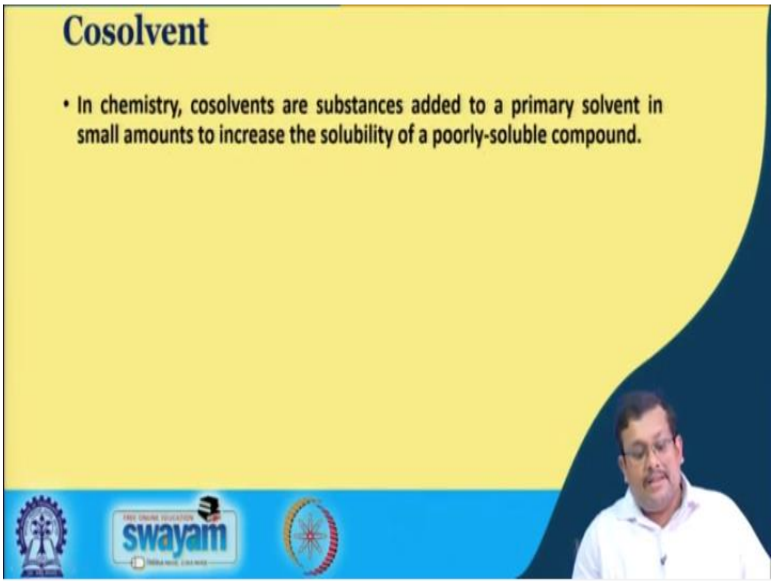

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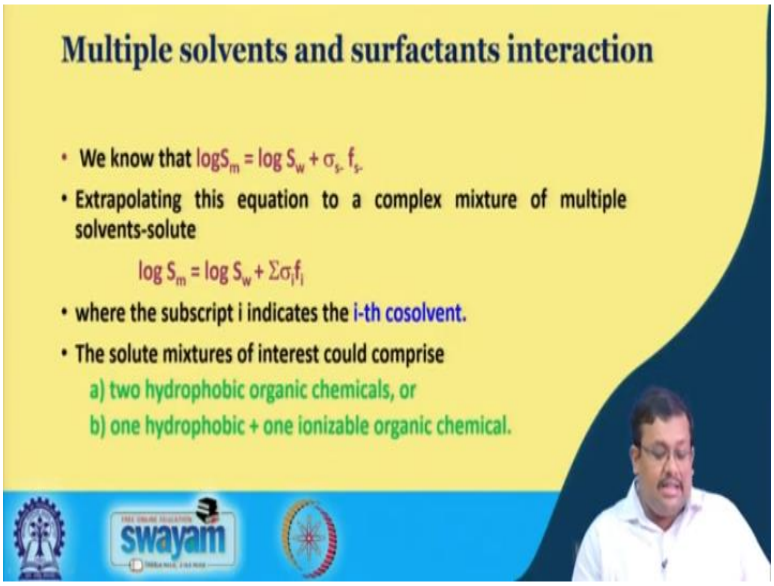

So, we have discussed about the cosolvent and you know based on that what are the compositions, possible composition of this solid mixture we have discussed.

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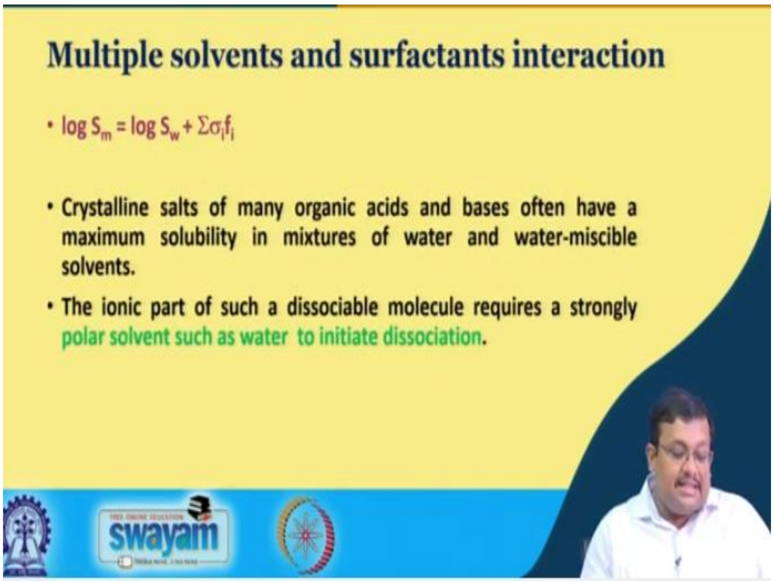

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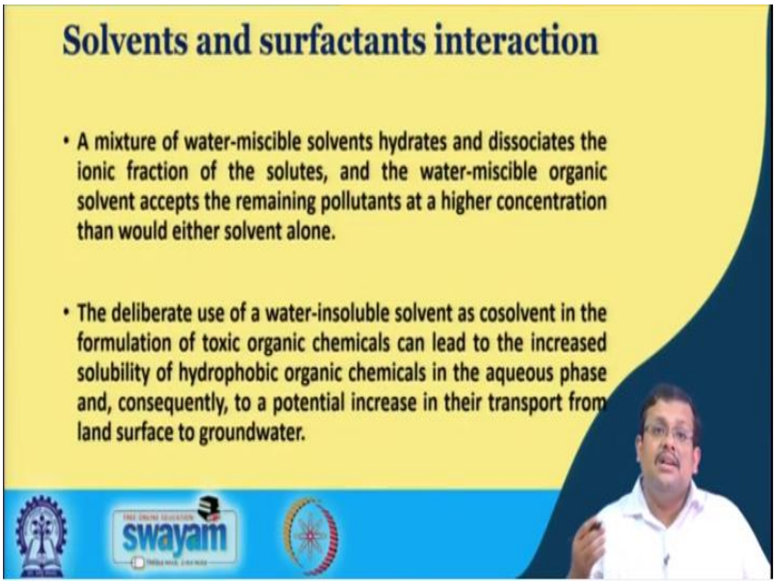

Then, we have discussed the solvent and surfactant interactions.

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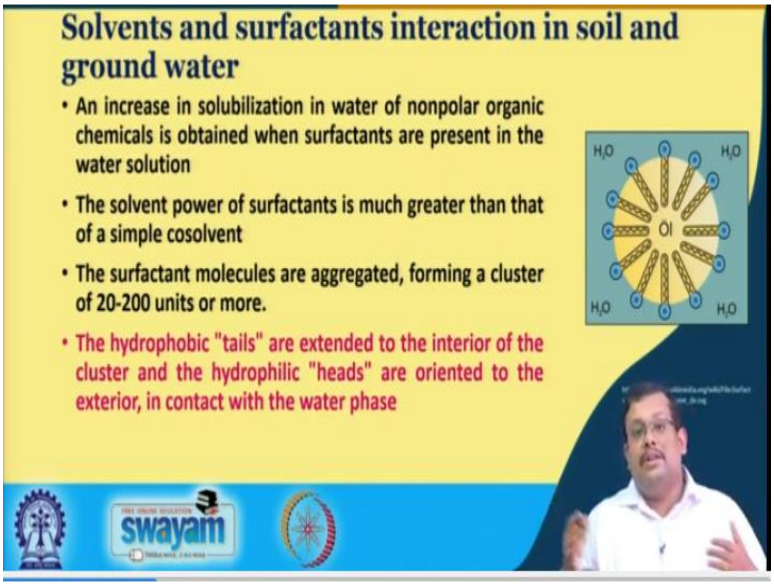

How these hydrophobic tails are extended into the interior of the cluster in the hydrophilic heads are oriented to the exterior in contact with the water phase and how they affect the dissolution of non-polar compound in the polar water solvent.

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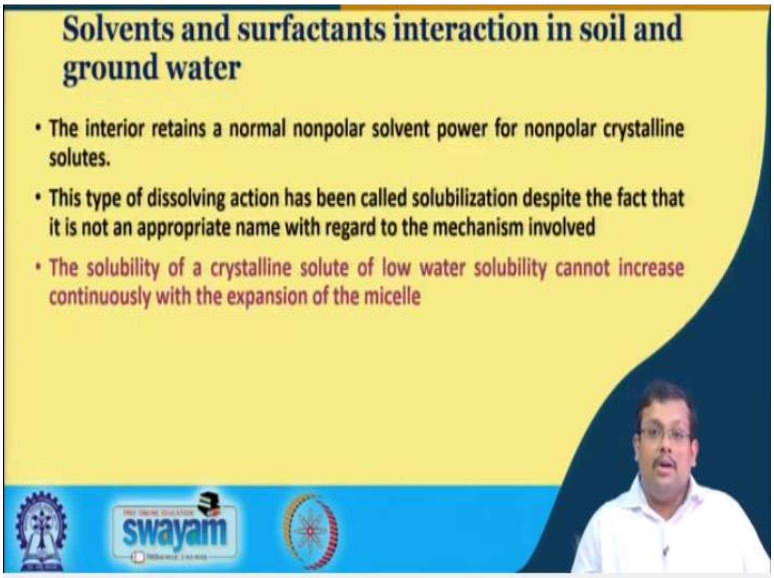

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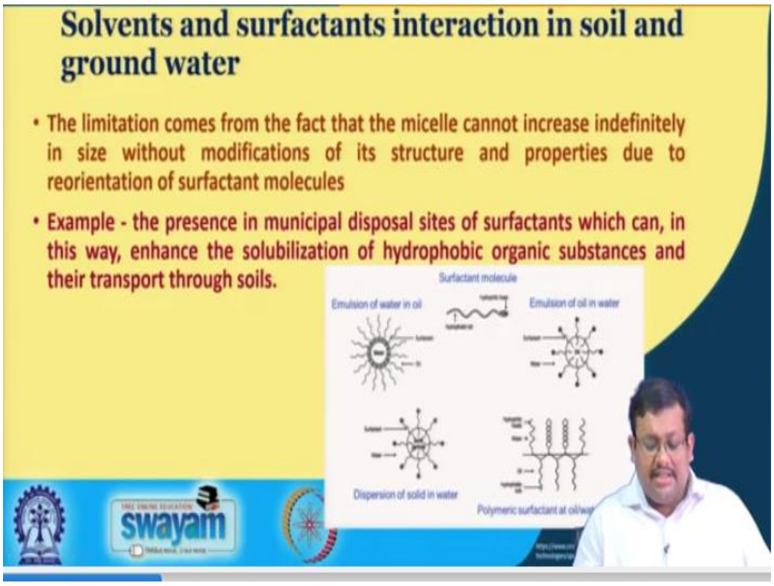

We have discussed all these things.

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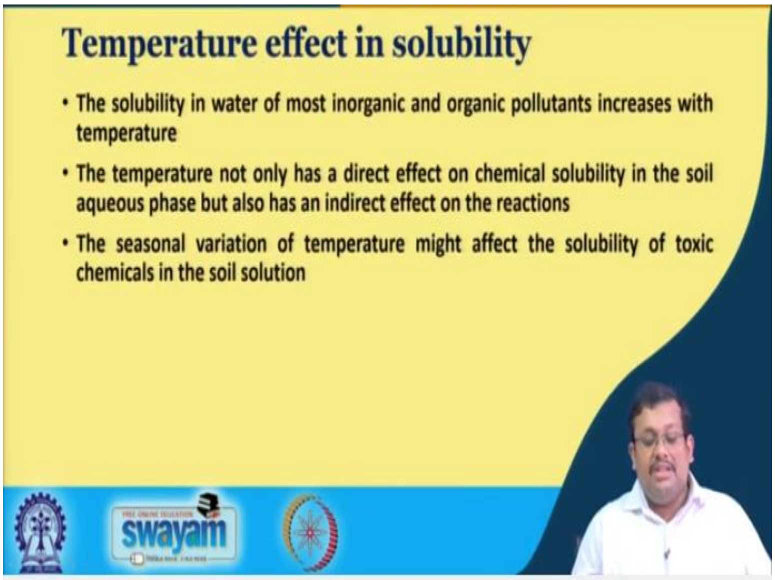

And also finally, we have discussed the temperature effect in the solubility, you know remember that the solubility in water of the most inorganic and organic pollutants increases with the temperature and the temperature not only has a direct effect on chemical solubility of the in the soil aqueous phase but also has an indirect effect on the reactions.

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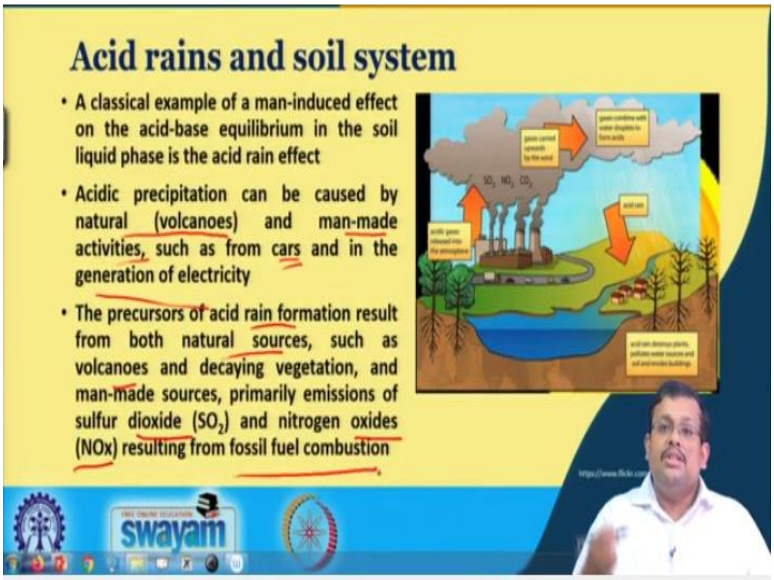

So, today we are going to start with the acid rains details about; detailed discussion about the acid rains and you know how they interact with the soil system and what is the relationship between acid rain and soil system. So, a classical example of man induced effect on the acid base equilibrium in the soil liquid phase is the acid rain effect. Now, we have already briefly talked about the acid rain effect in our previous lecture.

Remember that when there is an acidic precipitation and this acidic you know, we call it acid rain and this acidic precipitation generally occurs when there is a reaction of different gases with the water vapour which is present in the atmosphere creating different acids. So, acidic precipitation can be caused by natural volcanoes, as you can see it is a natural volcanoes and man-made activities.

So, man-made activities; what are the man-made activities? So, they can be you know, this gas can generate for example sulphur dioxide; this sulphur dioxide can be generated from the car exhaust you know and in the also, generation of the electricity also they can produce these gases. So, this acidic active you know, these gases when go to the you know, atmosphere and mix with you know water vapour, then it they produce the acidic rain.

Now the precursors of acid rain formation results from both natural sources such as volcanoes and decaying vegetation's and manmade sources you know, primarily emission of sulphur dioxide and this sulphur dioxide basically emit from different automobiles and nitrogen oxides you know, the nitrogen oxides can be represented as NOx, resulting from fossil fuel combustion.

So, this when we you know, when we burn the fossil fuel either petroleum or coal, they basically you know generate the sulphur dioxide and nitrogen oxides and this sulphur dioxide as you can see these acidic gases released into the atmosphere and you know, for example sulphur dioxide, nitrogen dioxide and carbon dioxide. They can be also generated from the smokestack of you know industrial you know, industrial release.

So, gas carries to; after they are released these gases carried upwards by the wind and goes combined with the water droplet to form different acids. We are going to see the chemical reactions which are responsible for forming those acids and ultimately, then you know come back ultimately in the form of acid rain. So, acid rain basically what happens when there is an acid rain, acid rain basically destroy plants, pollutes water sources and erode different buildings and so these are some of the ill effects of the acid rains. So, we have seen that the precursor of this acid rain formation the mainly, the gases; sulphur dioxide and nitrogen oxides are forming as a result of fossil fuel combustion.

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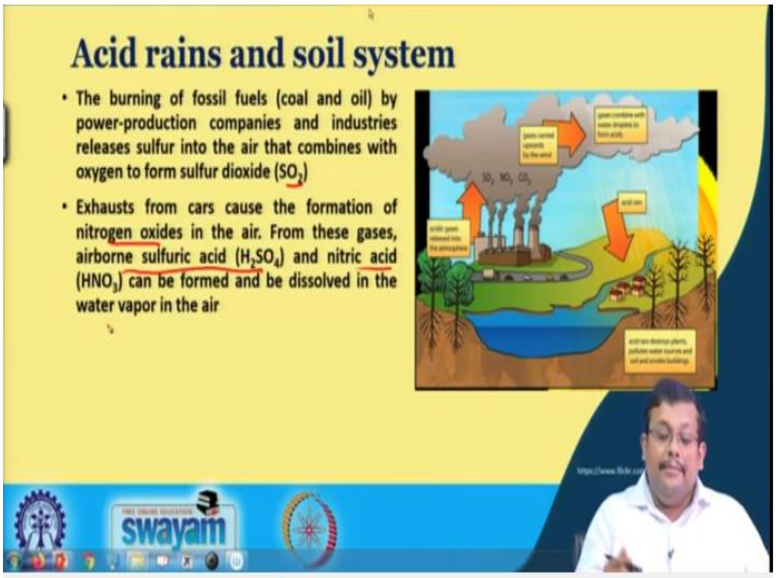

So, the burning of this fossil fuels like coal and petroleum by power production companies as we have seen here power production companies and industries release this sulphur into the air and combines with the oxygen into in the form of sulphur dioxide, so that is how a sulphur dioxide gas is produced. Now, exhaust from the cars cause the formation of nitrogen oxides in the air, from these gases you know airborne sulphuric acid.

For example, from this you know, from this sulphur dioxide, these airborne sulphuric acid and nitric acid, this nitric acid can form from this nitrogen oxides can be formed and dissolve into the water vapour in the air.

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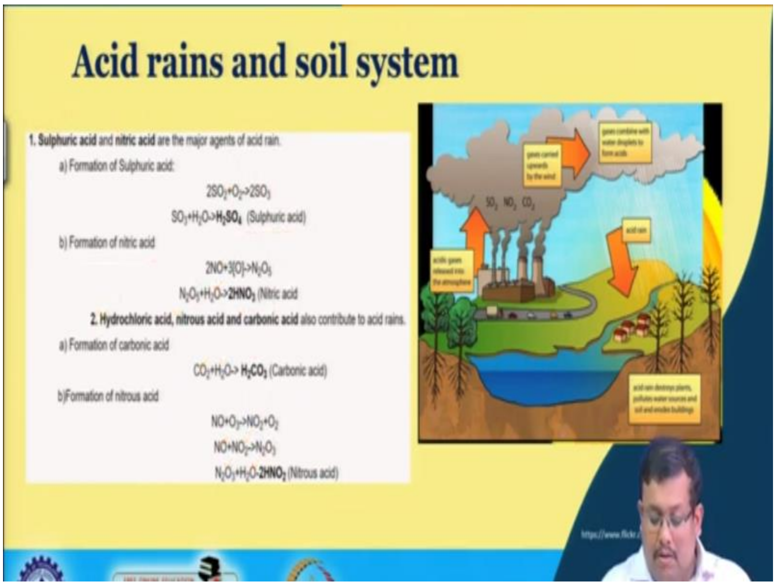

So, these are some of the reactions which are responsible for producing the acid rains, so let us see. So, sulphuric acid and nitric acids are the major agents of the acid rains, they are the strong acids. So, let us consider the formation of sulphuric acid, as we have seen that sulphur dioxide, this sulphur dioxide which is produced by burning of the fossil fuels when they exhaust and then basically, reacts with the oxygen to form sulphur trio oxide.

This sulphur trioxide when reacts with the water vapour, they will produce H2SO4 or sulphuric acid similarly, formation of nitric acids, here you can see nitric oxides, these nitric oxides when reacts with the oxygen, they produce N2O5 and this N2O5 when reacts with water vapour they produce this nitric acid and so you know, hydrochloric acid, nitrites and then nitrous acid and carbonic acids are also can contribute to acid rain.

So, major contribute of these acid rains are sulphuric acid and nitric acid, apart from that hydrochloric acid, nitrous acid and carbonic acids also contribute to acid rains. How carbonic acid form; we create is generated, this carbonic acid is generated because of the carbon dioxide reaction with the water vapour, as you can see here the carbonic acids, carbon dioxide when reacts with the water vapour, it produces the carbonic acid.

Formation of nitrous acids; so here you can see nitric oxides when it reacts with the ozone, it produce nitrogen dioxide and oxygen and you know these nitric oxides also can react with this nitrogen dioxide to produce this N2O3 and this N2O3 when reacts with the water vapour, it produces this nitrous acid. So, what we can see; we are seeing that the sulphur dioxides or the nitrogen oxides which are exhausting from which are emitting due to the industrial activities as well as the burning of the fossil fuels or car exhaust anthropogenic activities.

They basically undergoes to different reactions, chemical reactions and ultimately they reach into the atmosphere, mix with the water vapour and then form the acid and comes back into the soil in the form of acid rain.

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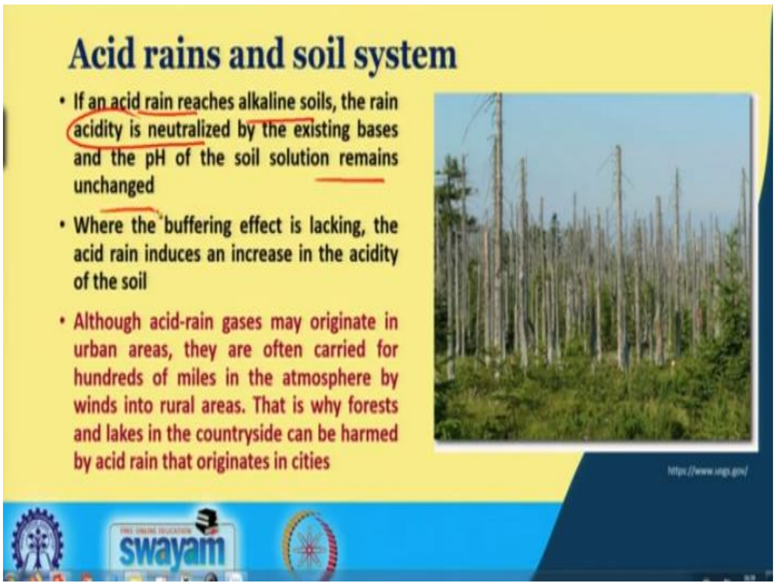

Now, if an acid rain reaches alkaline soils, the rain acidity is neutralized by the existing bases and the pH of the soil solution remains unchanged. So, again you know, if you know so to simplify this, when the acid rain which is basically acidic in nature, when reaches the alkaline soil, the rain acidity is neutralized because of the presence of the you know, bases in the alkaline soil by, in the alkaline soils and pH of the soil solution remains unchanged, so there is basically neutralization.

Where the buffering effect is lacking, let us consider a soil where the buffering effect is you know for example, the soil which has low amount of clay or low amount of organic matter, these soils are lacking their buffering capacity. So, when there is an acid rain in this type of soil, the acid rain induces an increase in the acidity of the soil, so although acid rain gases may originates in urban areas, they are often carried for 100’s of miles in the atmosphere by winds into the rural areas that is why forests and you know and lakes in the countryside, the rural areas can be harmed by acid rains that originate in the cities.

As you can see here this is a photograph of acid rain effect in the forest which is published by USGS, so you can see this, due to the acid drain a large tract of forest area are getting you know are getting affected and plants are getting defoliated. So, this is basically the interaction of acid rains in the soil solution.

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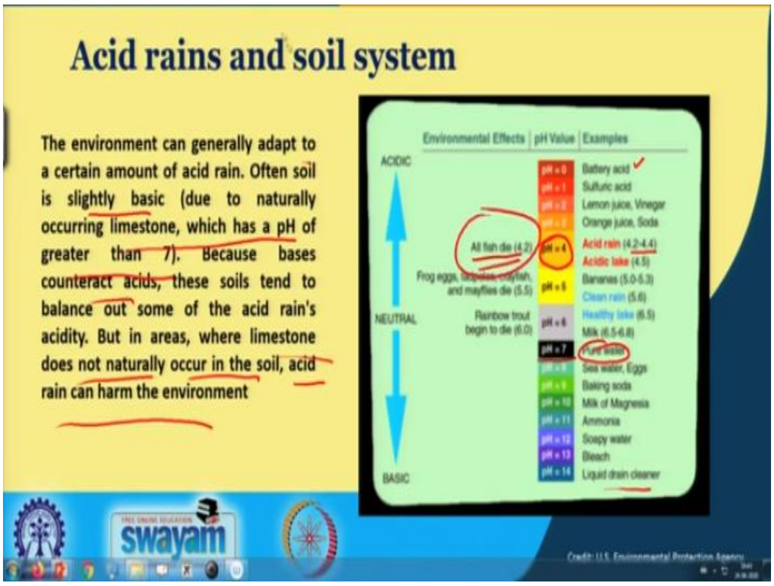

So the, if we see the pH of the you know acid rain, so obviously these chart or these graph will give you a better idea, this chart will give you better idea, so we can see in case of battery acid which is highly extremely acidic, the pH will be 0, whereas liquid drain cleaner which has the highly basic, are having the pH 14. When we are talking about pH 7 that is the pH of a pure water.

So, if we consider the acid rain you know, this acid and has a pH varies from 4.2 to 4.4 and so basically near about pH 4, we can see the as you know, the pH of an acid drain cleaner. So, basically these acid rain is highly acidic and as a result of these very low pH, all fish which are you know present in the aquatic body basically dies. So, this is basically giving an idea about the pH of the acid rain.

So, the environment can generally add up to a certain amount of acid rain and you know often soil you know, when the often the soil is slightly basic due to the naturally occurring limestone which is a pH greater than 7, now because bases counteract the acids which have already discussed in the last slide. So, base is basically counteracts acid and this soils tends to balance out some of the acid rain's acidity.

But in areas, where limestone does not naturally occur in the soil or in the areas where the soil lacks the normal buffering capacity, acid rain can harm the environment as you can see here.

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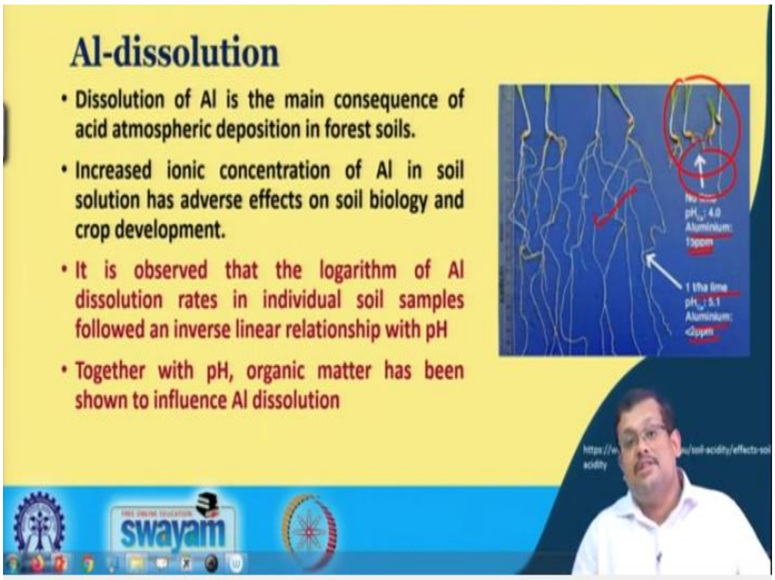

So, let us talk about another important thing, so we have completed the acid rain, let us talk about another important thing that is aluminium dissolution. Now, aluminium is a you know, aluminium is an element which you can see or aluminium is a metal which you can see in high concentration in acidic condition. Now, remember that the dissolution of aluminium is the main consequence of acid atmospheric deposition in forest soils.

So, increase in ionic concentration of aluminium in soil solution has adverse effects on soil biology and crop development. So, basically again the dissolution of aluminium in the, is the main consequence of acid atmospheric deposition of forest soil. As a result of acid deposition or acid rain, the aluminium activity in the soil solution quite increase and these ionic activity you know increase ionic activity of aluminium has an adverse effect on soil biology and crop development.

This picture can give you a better idea about the you know ill effects of aluminium concentration in the soil solution, as you can see here these are you know, the roots which are grown with an aluminium concentration of less than 2 ppm, whereas and here also, here the aluminium is here 15 ppm. Now, here the difference basically is here in this case we are applying 1 ton per hectare lime and here we are not applying lime to neutralize the acidity.

So, obviously when we are adding lime to neutralize this acidity, we can see that there is normal growth of the roots however, when there is no application of lime obviously their concentration of aluminium increases which adversely affect the root growth which you can see in this picture. So, it is observed that the logarithm of aluminium dissolution rates in the individual soil samples followed an inverse linear relationship with pH. Now, remember that together with pH, organic matter has been shown to influence the aluminium dissolution, how? Let us see in our next slide.

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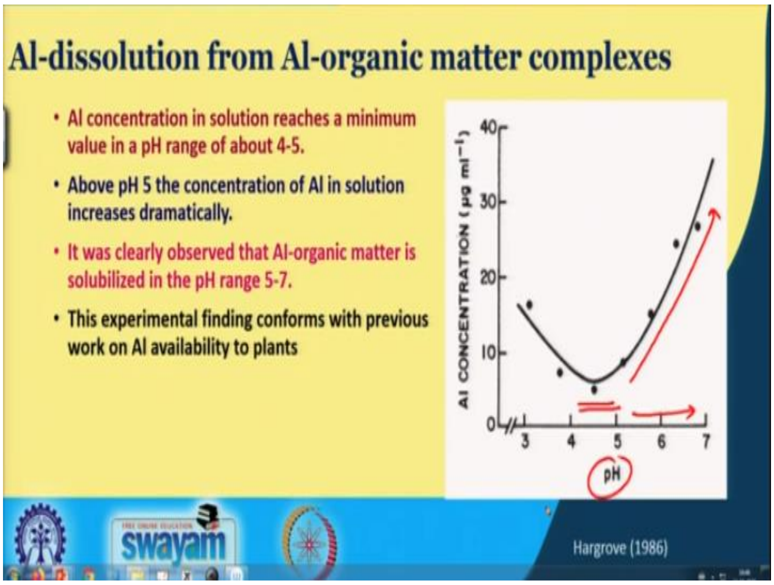

So, this graph basically shows the relationship of aluminium concentration in microgram per ml and pH, so here basically this graph is showing aluminium dissolution from aluminium organic matter complexes. So, one thing is clear that aluminium concentration in solution reaches a minimum value in a pH range of about 4 to 5. So, in this region the aluminium concentration in the solution reaches a minimum value.

Now, above this pH 5, the concentration of the aluminium in solution increases dramatically as you can see it is increasing with the steep slope and it is clearly observed that aluminium organic matter is solubilized in the pH range of 5 to 7. So, obviously when there is a solubilisation, aluminium concentration in the soil solution will increase and this experimental finding conforms with previous work of aluminium availability with the plants.

So, these basically shows the aluminium dissolution from aluminium organic matter complexes and how this dissolution of this aluminium, from these aluminium organic matter complexes are influenced by the pH of the soil solution.

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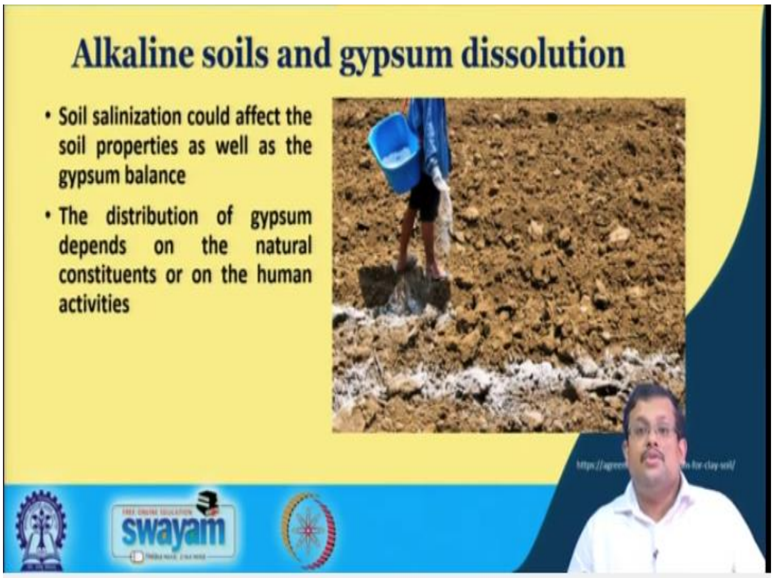

So, another important thing which we need to discuss is the alkaline soils and gypsum dissolution. Now, you know what are the alkaline soil; alkaline soils are those soils in which the exchange complex is saturated with the sodium ions and as a result of the saturation of the sodium ions you know, the soil becomes alkaline in nature. The alkaline soil are having high pH and the alkali soils or alkaline soils are not good for crop production.

Why? Because they have unfavourable physical conditions, what are those unfavourable physical conditions; due to the presence of sodium, the soil particles are dispersed, they do not form the aggregates and as a result of that, the zeta potential is quite high. As a result of high zeta potential, the flocculation never occurs and these individual particles basically block the entry of moisture or soil water through infiltration or exchange of gases from the atmosphere to the soil air.

And as a result of that these alkaline soils are not good for crop growth, so these alkaline soils need to be reclaim you know, for the reclamation of this alkaline soil the you know, farmers generally use gypsum which is basically calcium sulphate dihydrate and these since the salinization or alkalinisation could affect the soil properties as well as the gypsum balance. So, the distribution of gypsum depends on the natural constituents or on the human activities.

So, generally to counteract the ill effects of alkaline soil we generally apply gypsum; gypsum is basically calcium sulphate dihydrate and this gypsum, the calcium from the gypsum can replace the sodium in the exchange complex and as a result, the clay start you know starts to flocculate or forming the aggregate. So that is why we generally apply the gypsum in the alkaline soil. As you can see here in this picture you know farmers are spreading the gypsum, dusted gypsum in the alkaline soil.

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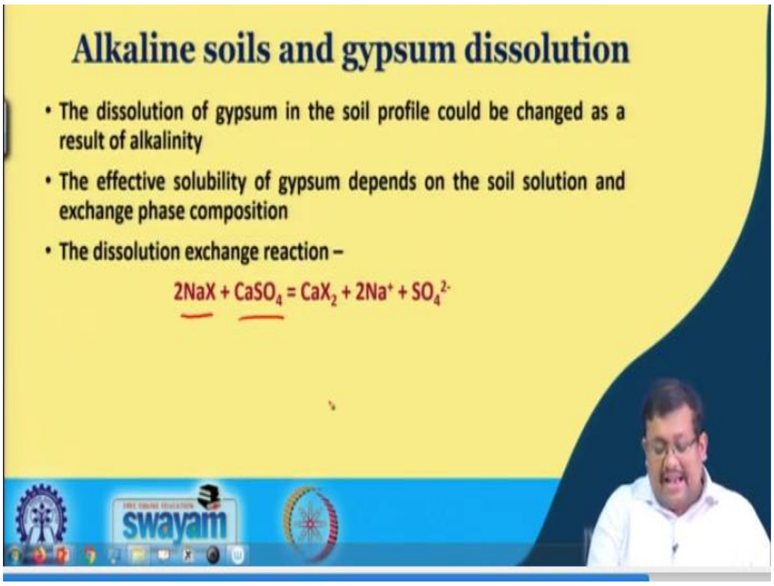

So, the dissolution; let us consider the dissolution of the gypsum in the alkaline soil, so the dissolution of the gypsum in the alkaline soil profile could be you know, change as a result of alkalinity. Now, the effective solubility of gypsum basically depends on the soil solution and exchange phase composition. So, let us see how it occurs, so the dissolution of exchange reaction, dissolution exchange reaction as you can see, so the exchange complex was previously saturated by sodium ions.

So 2, let us consider these 2 sodium ions was attached or adsorbed into the mixture into the clay surface and when we are applying the calcium sulphate, the calcium basically replace this sodium which basically comes into the soil solution. So, as a result of that the calcium binds the you know soil particles and forming the aggregate.

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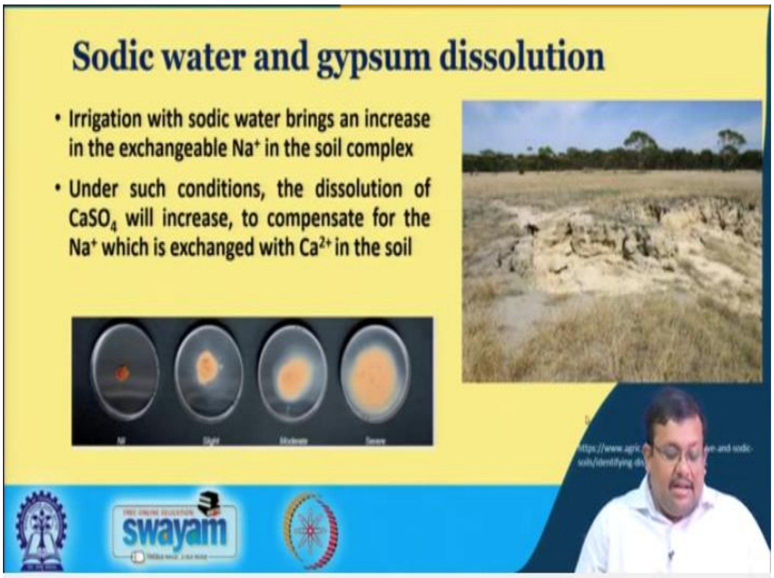

So, the sodic soils or alkali soils are basically, you know the sodium saturated soils, so irrigation with sodic water, if we just do the irrigation with sodic water brings an increase in the exchangeable sodium in the soil complex and creates the unfavourable condition as you can see in this picture and so under such conditions, the dissolution of calcium sulphate will increase to compensate for the sodium which is exchanged with the calcium in the soil.

As you can see this is an ill effect of you know of the sodic soil, as you can see here the exchange complex has nil sodium, here it has got slightly higher sodium content and in this condition they have moderate sodium concentration in the exchange complex and here it has severe sodium concentration in the exchange complex. So, you know as you can see from this slide, from this soil to this soil, there is a, you know continuous increase in sodium concentration.

As a result of that you can see here the degree of dispersion is continuously also increasing with the increase in sodicity, so here this soil is you know highly aggregated and these soils are increasingly disaggregated. So, under such conditions when these you know when the sodicity is increasing in the soil, you know the dissolution of calcium sulfate is also increased because this calcium from this calcium sulphate competes from the exchange site in the soil and thereby replace those sodium from the exchange site to form the aggregates or you know to form the flocculates. So, this is basically the dissolution of gypsum in sodic soils.

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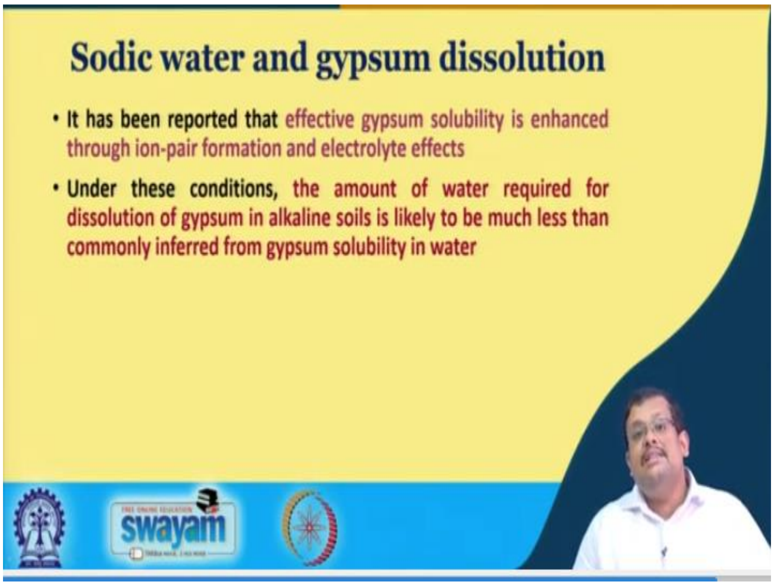

It has been reported that effective gypsum solubility is enhanced through ion pair formation and electrolyte effects, under this conditions the amount of water required for dissolution of gypsum in alkaline soil is likely to be much less than commonly inferred from gypsum solubility in water. Again, the effective gypsum solubility is enhanced through the ion pair formation.

What is ion pair we will discuss and the electrolyte effects, in this conditions the amount of water which is generally required for dissolution of gypsum in alkaline soil, you know here we will require much less than commonly you know what we see which is required for gypsum solubility in the water. So, let us wrap up our lecture here, in this lecture we have discussed the acid rain effect and their interaction with the soil system.

Also, we have seen the sodic soil and how the gypsum solubility is influenced in the sodic soils and also we have seen the aluminium, you know aluminium solubility from the organic matter complexes, aluminium organic matter complexes and how they are impacted by variable pH. So, I hope that you have learnt something new in this lecture, let us wrap up this lecture here.

And the next lecture will be discussing more about you know ion pair effects, what is ion pair which I have discussed here, what is the ion pair and other aspects of pollutant and soil solution interactions. So, feel free to email me or feel free to let me know, if you have any questions, I hope that you know these are pretty self-explanatory, if you need any explanation

just let me know and feel free to email me, I will be more than happy to answer your queries.
Thank you very much, let us meet in our next lecture.