Environmental Soil Chemistry

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Lecture-34
Redox Chemistry of Soils - Continued

Welcome friends to this fourth lecture of week 7 or module 7. And in this week we are talking about the redox chemistry of soils. In the previous 3 lectures we have covered what is redox reaction, what is redox potential, what is the relation between redox potential as well as pH and how we can calculate it and what is the relationship between what is pe and what is the relationship between the Eh and pe.

And how can we represent the relationship between pe, pH and logarithm of equilibrium constant, how to calculate the logarithm of equilibrium constant from the thermodynamic principles point of view considering the Gibbs free energy and how to use this value of logarithmic of K 0 to calculate the value of pe at different pH, also we have discussed the stability lines of different oxidized and reduced species couple.

And also we have discussed the practical implication of Eh as well as pe as far as the submerge conditions are concerned, we have briefly talked about the practical implications of Eh, how it can affect the composition of microorganisms or the flora and fauna which are present in the soil and what type of micro flora are more prevalent in case of oxic condition and all also in case of anoxic condition depending on Eh we have discussed.

And so, in the last slide of our last lecture, we have started discussing about the submerged soils. Now, these submerged soils as we know the soils that are submerged in water for a sufficient period of time to give the distinct horizon, development.

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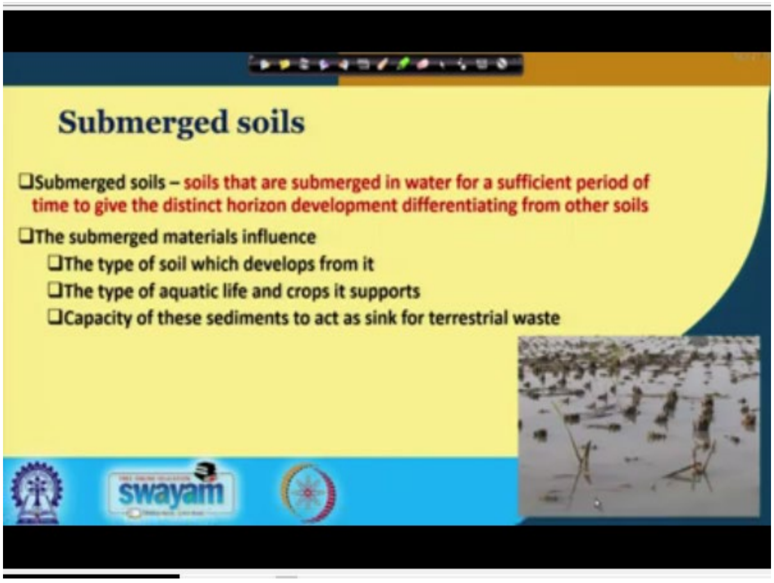

And differentiating from other soils. Here you can see one picture is given, this is a typical rice field where you can see the water is basically stagnant over the soil surface and this is basically the you know the condition which is created to make these soil you know you know under the you know soil waterlogged is basically useful for growing the rice crop. Now, this is a typical condition, typical example of a waterlogged soil where the Eh values is always very low.

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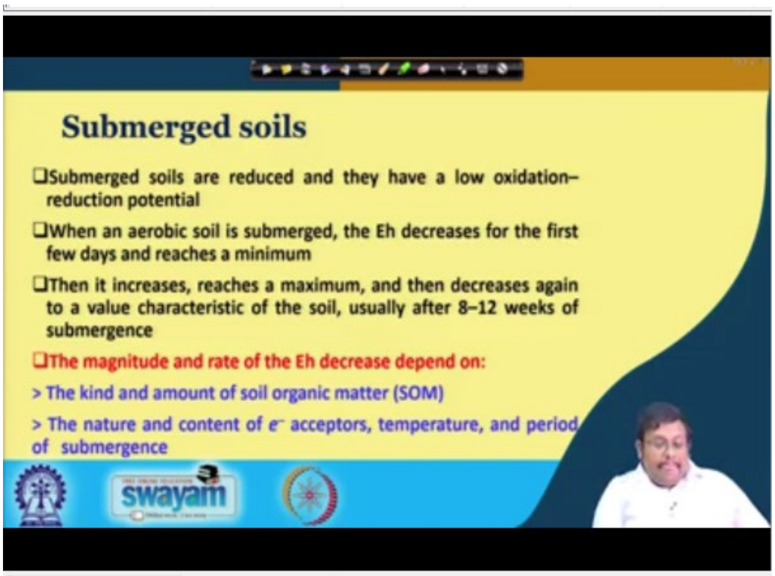

Now, submerged soils are reduced and they have a low oxidation reduction potential obviously, because all the pore space are filled by water. So, there is no oxygen, whatever oxygen was there earlier it was totally you know, you know utilized by the plant root as well as the aerobic microorganisms. As a result of that, you know, there is no free oxygen or trapped oxygen only. So, these are anaerobic condition, anoxic condition.

As a result of that these soils have low redox potential or pe values. Now when an aerobic. So, in case of these anoxic soils, the redox potential generally goes below 0 as you know it is minus negative. Now when an aerobic soil is submerge the Eh decreases for the first few days and reaches a minimum. So, you will see a typical kinetics of the Eh change when you submerge a previously aerobic soil.

So, when we submerge a previously aerobic soil then you will see that the Eh value will decrease for the first few days and reaches a minimum. Then certainly it will it will increase, reaches a maximum and then decrease again to a value characteristics to the soil usually after 8 to 12 weeks of submergence. So, you will see there is a change in dynamics of Eh once you submerge a soil or aerobic soil.

And the magnitude and the rate of Eh decrease depends from one soil to another soil and it basically the decrease the magnitude and this rate of Eh decrease depends on the kind and amount of soil organic matter and soil organic matter is a reducing agents and it has got a tremendous influence on these you know chemical dynamics of these anaerobic soil. So, the kind and amount of soil organic matter.

And the nature and content of these electron acceptors, temperature and period of submergence. So, all these play a you know key roles for determining the magnitude and rate of these redox potential decrease.

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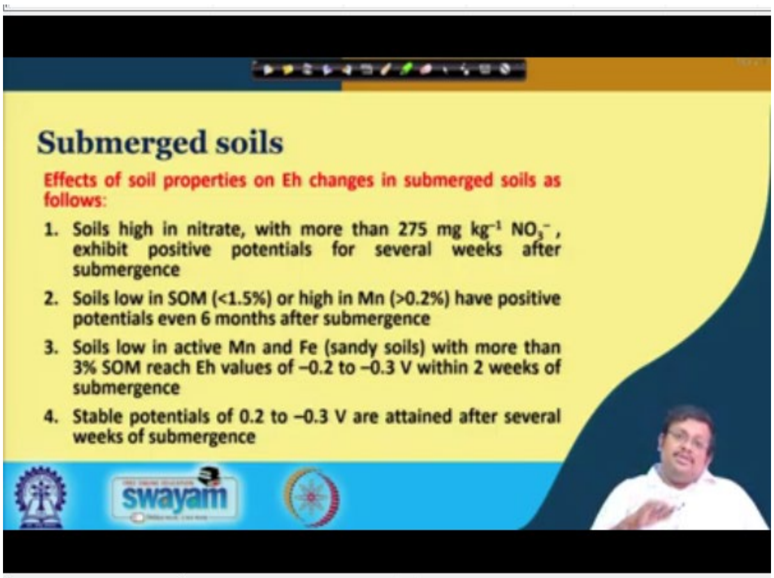

So, let us see what are the, what are the trends we can see; in case of submerged soils. Now, what are the you know the effects of soil properties on Eh in submerged soil basically can be summarized within the following points. First of all, soil which are high in nitrate because nitrate is NO 3 - you know that which is oxidized form. So, the soils which are high in nitrate with more than 275 ppm of nitrate exude positive potential for several weeks after submergence.

So, that means, a soil which has high you know which you have previously in high oxidized condition which, which which is indicated by the high concentration of nitrate will remain positive will remain in will basically show a positive Eh or redox potential for several weeks after the submergence and soil low in soil organic matter that is less than 1.5% or high in manganese which is greater than 0.2% will have positive potential even 6 months after submergence.

Because the soils which are having low amount of soil organic matter that means the soil organic matter being a reducing agent. So, as a result of that, they have more or higher redox potential characteristics to an oxidized condition. Now, soil low in active Mn and iron for example, in case of sandy soil with more than 3% soil organic matter reach an Eh value of - 0.2 to - 0.3 within 2 weeks of the submergence.

So, when we submerge the soil within 2 weeks of the submergence, you will see that you know the soils with the low Mn and Fe with more than 3% of soil organic matter will reach an Eh value of less than 0. That is varying from 0.2 to 0.3 volt. Now, stable potential of 0.2 to - 0.3 volt are attained after several weeks of submergence. So, you can see that it will be kind of stabilized from 0.2 to - 0.3 volt after several weeks of submergence.

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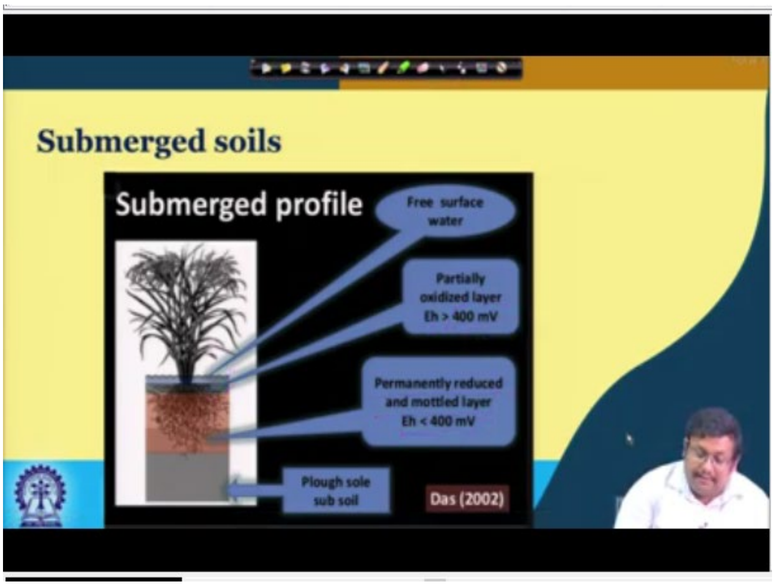

So, when we see the cross section of a submerged soil, we will see some morphological features. So, what are the morphological features obviously, it is quite clear from the submerge soil profile, if you see this is a free surface water obviously, let us consider this as a rice field, then you can see just below these you know free surface water you will see a dark partially oxidized layer with an Eh value of greater than 400 millivolt okay.

So, it is a partially oxidized layer as indicated by the positive Eh potential. Now, below this partially oxidized layer you will see a permanently reduced and mottled layer with the color change with the Eh value of less than 400 millivolt. So, you can see the distinct difference between these 2 layers by seeing their color change and obviously, their associated redox potential also will change in case of these partially oxidize it will show higher than 400 millivolt.

However, when it is when it is this mottle layer it will show less than minus you know you know less than 400 millivolt. Below these permanently reduced and mottled layer you will see a plough sole or sub sole. So, this is basically in general you will see the submerged soil profile like this.

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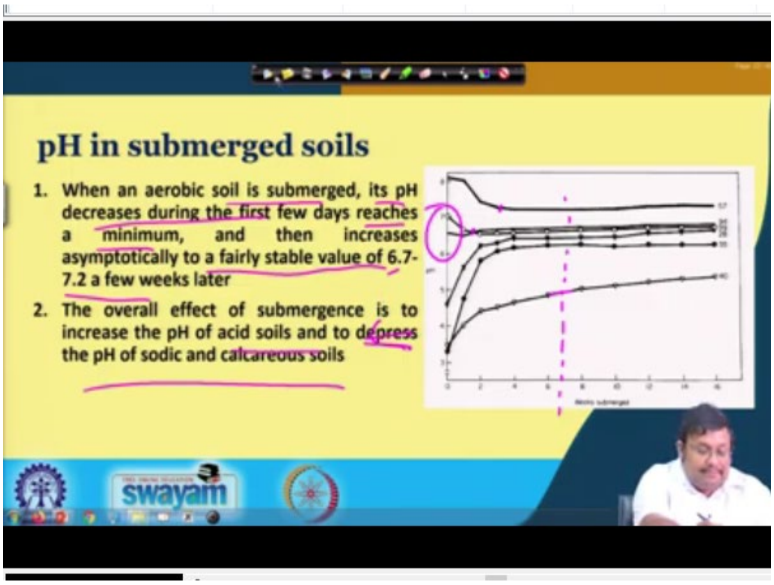

So, what is the dynamic of pH in submerged soils? Now when an aerobic soil is submerged, its pH decreases during the first few days. So, when aerobic soil when you submerge it, it will see that if it has high pH, the pH will be you know decrease during first few days and then it will reach a minimum and then it increases asymptomatically to a fairly stable values of 6 to 7 and 7.2 a few weeks later.

So, you can see the trend is like this. So, initially with an aerobic soil the pH was higher. So, it reduced drastically after first few days. So, it reaches a minimum and then from there it increases asymptomatically and to a fairly stable values of around 6 to 7 and then you can see it will be kind of stable at this pH range after around 6.7 to 7.2 weeks later. So, you can see around these time after the after the submergence they will achieve a kind of stability.

Now, the overall effect of submergence is to increase the pH of acid soil and to decrease the pH of a calcareous soil. So, it is decrease or depress the pH of the sodic or calcareous soil. So, this is a general trend, when you submerge a previously aerobic soil you will see if the soil is acidic its pH will increase and reaches a stable condition and if the soil is a sodic condition, previously sodic condition calcareous condition the pH will decrease and appears and show a stability.

As you can see here in case of acidic soil, it is increasing after the submergence and then reaches the stability after 6 to 7 weeks. Similarly, for a soil, for a calcareous soil with a pH of greater than 8, it will reduce drastically and then will reach a, you know, kind of a plateau or kind of a stability. So, basically irrespective of the pH of the soil when we submerge the soil, it will basically try to stabilize its pH around the normal pH range that is from 6 to 7, it is a general observation.

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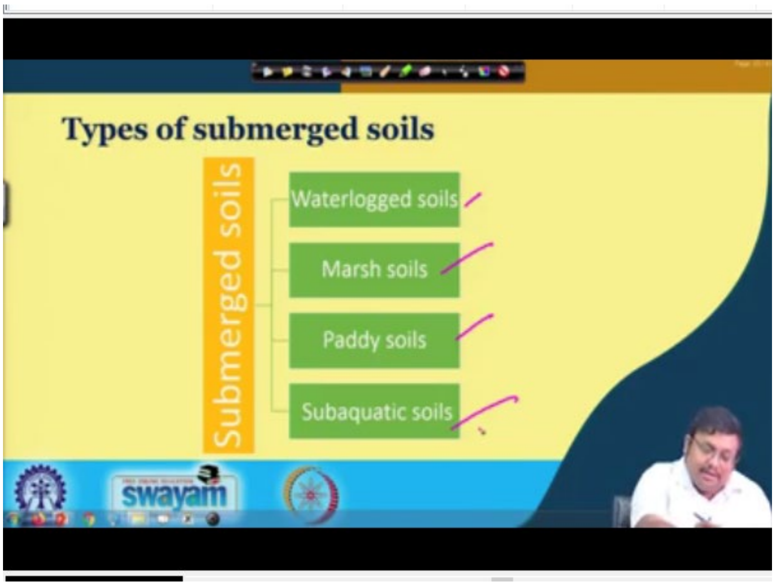

Now, what are the different types of submerged soils, there are 4 different types of submerged soils, as you can see, one is called waterlogged soil another is marsh soils. Third one is paddy soils or rice soils and the fourth one is subaquatic soils.

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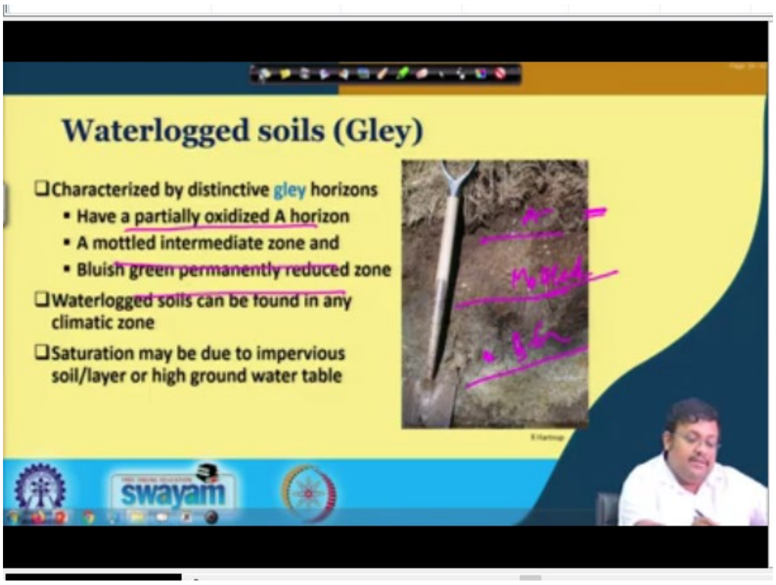

So, if we see the waterlogged soils, the characteristics of the waterlogged soil as I have told you in case of rice soil, if you take a cross section, you will see the color change and it will show a distinctive gley horizon. So, gley horizon are basically are characterized by a partially oxidized A horizon which I have already told you with Eh potential of greater than 400 millivolt.

And also they have a mottled intermediate zone and bluish green permanently reduced zone. So, this is how the waterlogged soils have been characterized. So, at the top, it will see in case of you know, you will see a partially oxidized A horizon then you will see kind of a mottled soil and then you will see bluish green you know, bluish green permanently reduced zone here, bluish green permanently reduced zone and here you will see a kind of mottled intermediate zone and here you will see a partially oxidized you know A horizon.

So, this is how the color difference will be clearly visible when we see a waterlogged soils or gley soils, the feature is known as a gleying of the soil. Now waterlogged soil can be found in any climatic condition and saturation may be due to the impervious soil layer or high groundwater table, when the groundwater table is high obviously, there will be saturation and if you see the previous slide where we discuss the cross section of a waterlogged soil there is a plow sole or impervious layer.

As a result the water cannot move further and as a result the, you know, the whole profile remains saturated all the time. So, this is the, this is the feature of a waterlogged soil or gley soil.

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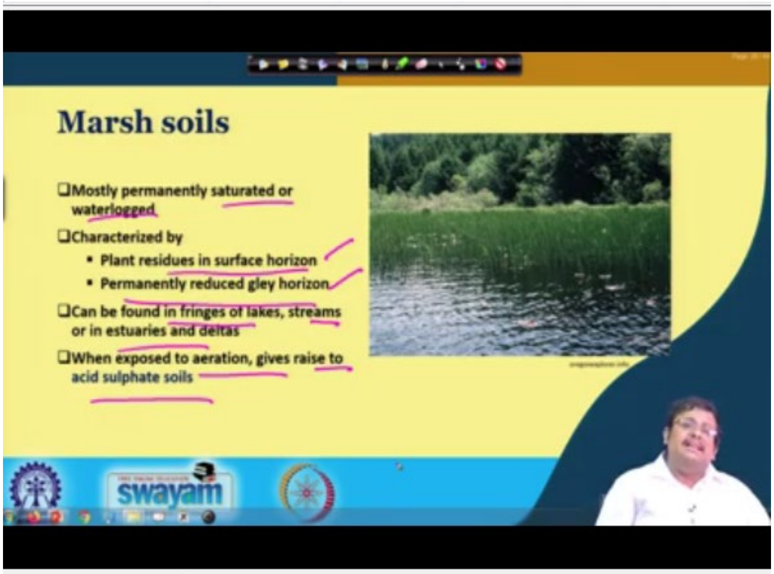

Now another type of soil is marsh soils. So, marsh soils are basically mostly permanently saturated on waterlogged soil. So, they are permanently they are not periodically saturated, they are permanently saturated for a quite long period of time. And they are characterised by plant residue in the surface horizons obviously, they do not decompose easily and permanently reduced gley horizons obviously, there is a permanent reduced gley horizons.

And they can be found in fringes of lakes, streams and estuaries and deltas. So, the areas which are more or less throughout the year are submerged with water are basically showing these marsh soils. Now, when exposed these marsh soils are exposed to addition gives rise to acid sulphate soil because they have huge amount of sulphide and these sulphide get oxidized to produce the acidic sulphate soils.

Some of these sulphates, acidic sulphate soils in India are you know can be found in case in the state of Kerala, we call it curry or pokkali soils, the name is curry or p o k k a l i pokkali soils. So, these are highly acidic in nature, because of the formation of you know formation of sulphuric acid due to the oxidation of sulphide. So, these are basically marsh soils. These are the characteristics of the marsh soils.

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Another important and most dominant type is paddy soils or rice soils. These soils are specially managed by paddy production and horizon developed depends on the period of waterlogging you will see the development of different horizon color horizons depending on the period of waterlogging, iron and manganese usually eluviated from top soil and deposited below the plow sole you will see that due to the water movement, the iron manganese which are present in the top soil, they will eluviate or move down and deposit below the plow sole.

And submerges decreases the redox potential Eh which promotes the growth of the paddy. So, for the growth of the paddy it is required to reduce the, you know, Eh potential and when the Eh potential is reduced obviously, some of the nutrients are change their dynamics strength okay. For example, Fe 3 + will be converted to Fe 2+ become more available. Mn 4 + will be converted to Mn 2 + become more available.

Nitrate will be converted to ammonium and plant will take the ammonium for their nitrogen for their for their nitrogen need. So, these type of you know conversion you can see when you basically submerge a paddy soil and remember these paddy soil submergence is basically manmade phenomena and generally we created to provide the, you know, the convenient growing environment for the paddy or rice crop.

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Now, in this paddy soils, paddy soils are these soils which are basically managed by special way of wet cultivation of rice as you can see the standing of water, the water standing on the surface, the management practice how we manage this. So, the management practices basically include the levelling of the land and construction of levees and impound water. So, basically we level the land and then we stagnate the water.

And then we do the puddling. Puddling is a specific process, which in which we basically break the clods. So, when we break the clods, we basically create an impervious layer by breaking the clods and then dispersing the soil in the standing water. So, when the water is standing we are breaking the clods, the soil particles and the clay particles will be dispersed and these dispersed clay particles will basically you know clog the pores through which water can infiltrate.

So, as a result of the clogging of the pores the water cannot further infiltrate. And as a result there will be stagnation of the water. So, this process is known as flood puddling. Plowing and harrowing the water saturated soil. So, remember, puddling is always done in case of you know, in case of water saturated soil by plowing and harrowing. Harrowing basically done to break the clods.

Now, you know levelling of the lands, impounding the water and then puddling and then maintaining the 5 to 10 centimetres of standing water during the 4 to 5 months of the crop of the land. So this is required for the growth of the rice crop, and then draining the drying the field at harvests because it is required to drain the field at the time of harvest to which is required for the maturity of the crop.

And then reflooding after the interval which varies from few weeks to as long as 8 months. So, these are the basically the cultural practices we generally do in case of paddy soils and creating an anaerobic or anoxic condition. Now, these operations and oxygen you know secretion by rice root lead to the development of certain features you know peculiar to paddy soil or rice soils.

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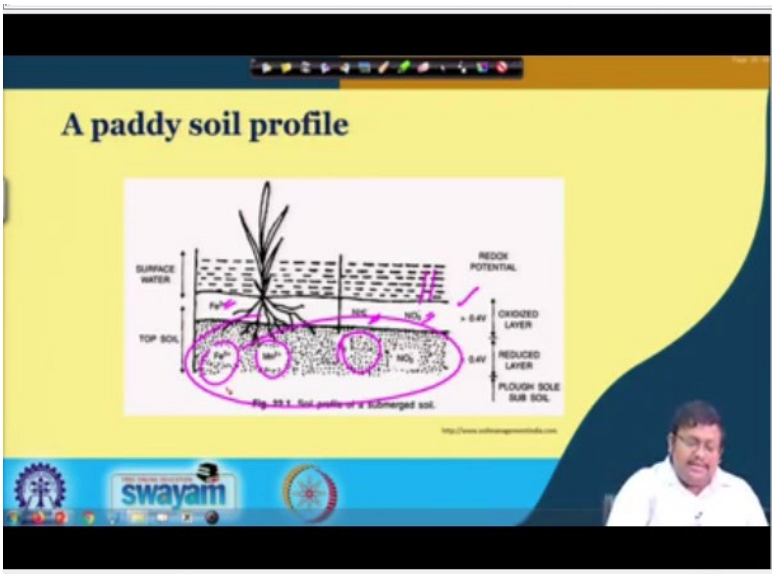

So, if you see the paddy soil profile we have already discussed it again same this is initially the you know surface water layer and then there is a partially oxidized layer with 400, you know, millivolt, greater than 400 millivolt you know redox potentials then a reduced layer with mottled layer reduced mottled layer with less than 400 millivolt and then plow sole sub sole, one thing is important that in the partially oxidized layer you will see both the nitrate as well as ammonium.

This nitrate basically converts to ammonium and you will see the Fe 3 + which is less soluble however in the reduced zone you will see the you know predominance of nitrogen elemental nitrogen Mn 2 + and Fe 2 +. Remember these Mn 2 + and Fe 2 + are more soluble than their oxidized counterparts. So, this is how you will see the soil profile of a submerged soil and depending on their variation of you know different species oxidized and reduced species of elements.

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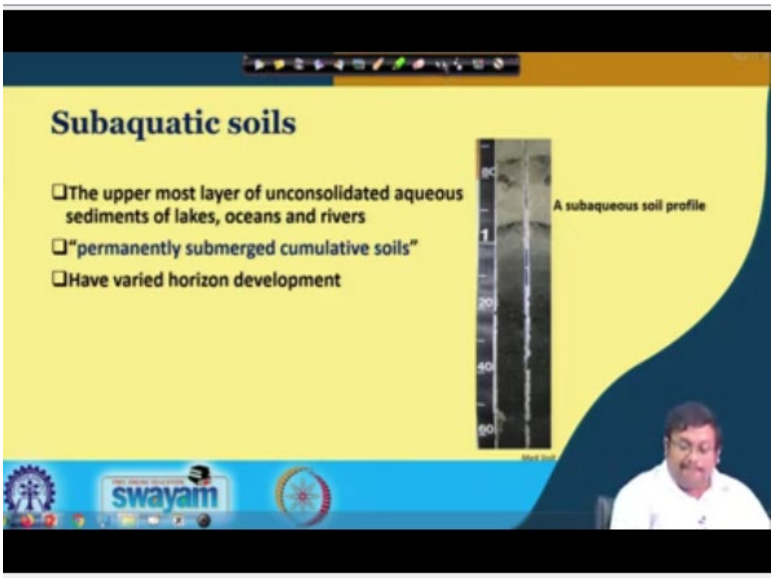

Another is called the subaquatic soils. Now, this subaquatic soils is uppermost layer of unconsolidated aquifers, sediments of lakes, oceans and rivers. So, it is basically uppermost layer of unconsolidated aqua sediments and it is basically permanently submerged by you know cumulative soils and they have varied horizon development.

You can see this is the subaqueous or subaquatic soils which are permanently waterlogged okay. And they basically can be seen in case of they are basically the unconsolidated aqueous you know sediments of lakes, oceans and rivers. Now, what are the characteristics of submerged soils?

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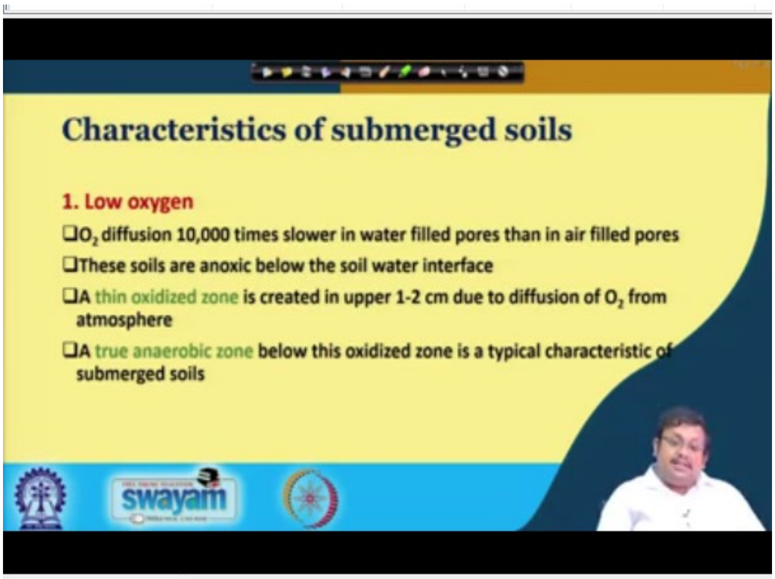

This is very important, the first important characteristics of submerged soil is low oxygen. And as a result of that, because all the pore spaces are filled by water, no water trapped, no oxygen trapped in between, as a result the oxygen diffusion is 10,000 times slower in water filled pores than in air filled pores. So, these soils are anoxic because the soil water interface and a thin oxidized layer is created we have already seen for upper 1 to 2 centimeter due to diffusion of oxygen from the atmosphere.

So, whatever oxygen, some amount of oxygen is diffused from the atmosphere will create these upper 1 to 2 centimeter a thin oxidized zone and below that a true anaerobic zone will be produced which is a basically typical characteristics of submerged soils. So, again, the submerged soil has low oxygen because oxygen diffusion is very, very slow when the water, pore space are filled by water.

These soils are anoxic, they will produce a 1 to 2 centimeter upper partially oxidized layer because of the diffusion of oxygen from the atmosphere and a produce a true anaerobic zone below this oxidized zone which is a characteristics of the submerged soils.

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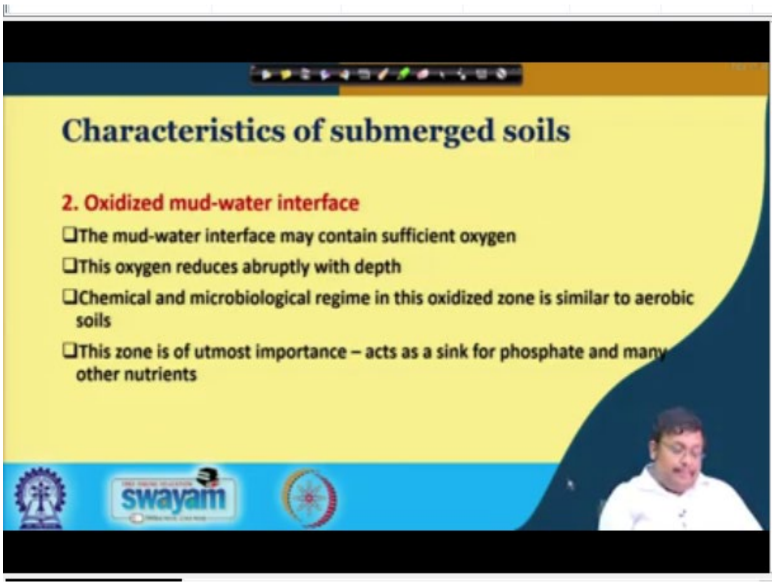

The second characteristics is oxidized mud-water interface, the mud water interface may contain sufficient oxygen and this oxygen reduced abruptly with depth and you know chemical and microbiological regime in this oxidized zone is similar to this anaerobic soils and this zone is of utmost importance. Basically the accessing for phosphate and many other nutrients okay, we will discuss these dynamics later.

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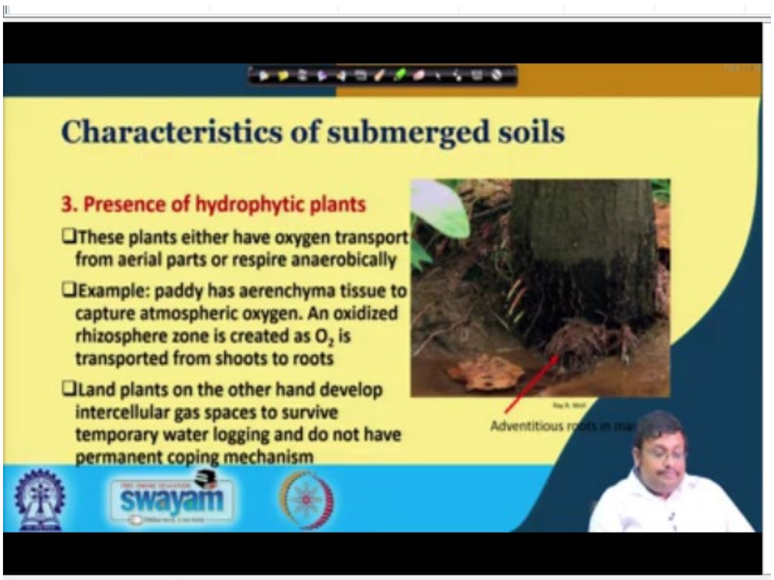

Third is presence of hydrophytic plants. Now these plants basically as you can see here, these the hydrophytic plants are basically grown in this submerged condition and these plants either have oxygen transport from aerial parts or they basically or they respire anaerobically. For example, in case of paddy or rice, they have aerenchyma tissue to capture the atmospheric oxygen and oxidized rhizosphere zone is created.

Or oxygen is transported from shoot to root and land plants on the other hand, develop intercellular gas space to survive the temporary waterlogging and do not have a permanent coping mechanisms. For example, you can see in case of you know, in case of salty land, you will see that you know submerged soils you also see that adventitious roots of different plants which are helpful for their growth.

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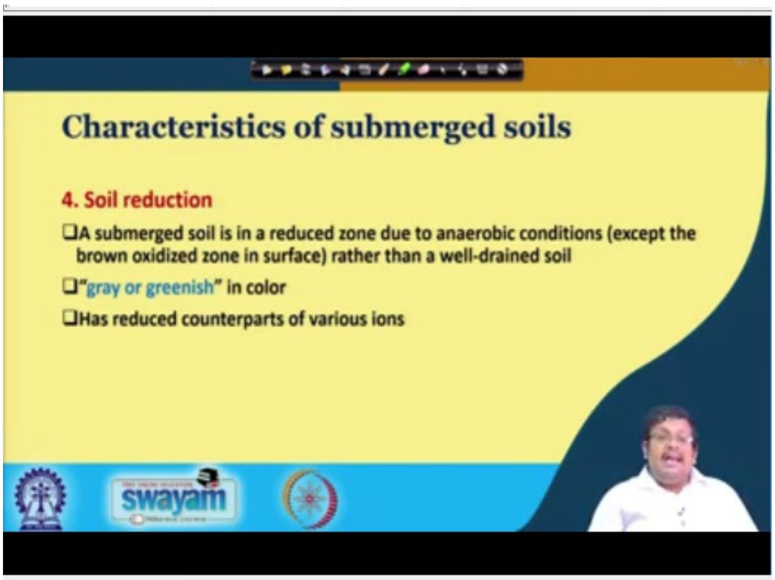

The fourth condition, the fourth characteristics of submerged soil is soil reduction. So, you will see that a submerged soil is you know in a reduced zone due to anaerobic condition which is except for the brown oxidized zone in the surface rather than a well drained soil. So, basically they, they show a grey or greenish in color and they have reduced the counterparts of various ions. So, again submerged soils is in reduced zone due to the high anaerobic condition and as a result, they will produce a bluish green colour or grey colour and they have a reduced counterparts of various, you know, of various ions.

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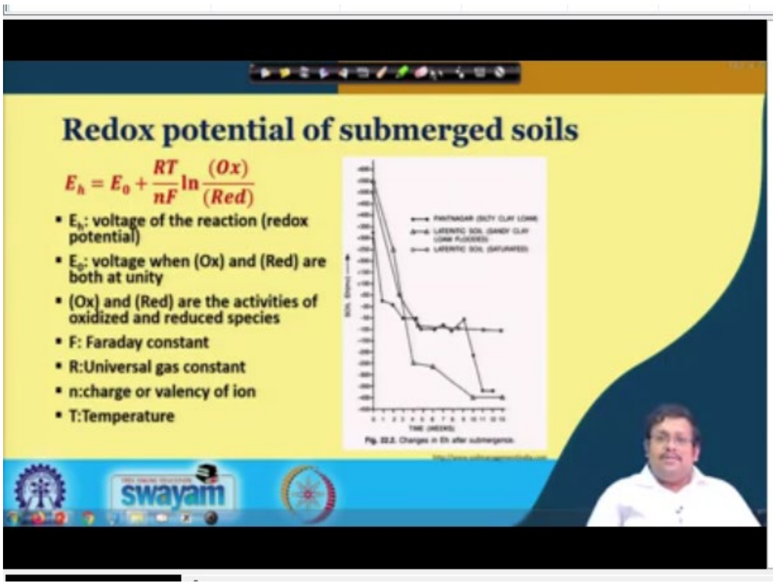

So, this is a general form of redox potential in terms of this, you know, in terms of this voltage when E 0 and these RT nF ln was oxidized by reduced species, we have seen these in details, I am not going to discuss it further, but the reason I am showing you this plot is how the soil Eh can change after certain weeks of you know submergence. This is a data from an Indian soil. You can see that for all different types of soil based whether it is a silty clay loam.

Whether it is a sandy clay loam, flooded or it is a saturated soil, you can see that as the time progresses all the soils are basically you know these silty clay loam soil basically, their Eh value reduced and also for other two soils also their Eh value reduce. So, as submergence progress, the Eh value of soil basically reduce okay. And then reaches a stability after certain weeks of submergence. So, these are the some characteristics of you know submerged soils.

We have seen different types of submerged soil, what are their characteristics, we have discussed different physical features of the submerged soil, their mottle zone, their color development bluish green colour development and all these. So, let us wrap up our lecture here and in the next lecture of the final lecture of week 7, we will see more details about these redox potential in the submerged soils and their implication in submerged soil chemical dynamics. Thank you very much.