Soil Science and Technology
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Lecture - 23
Sources of Charges in Soil

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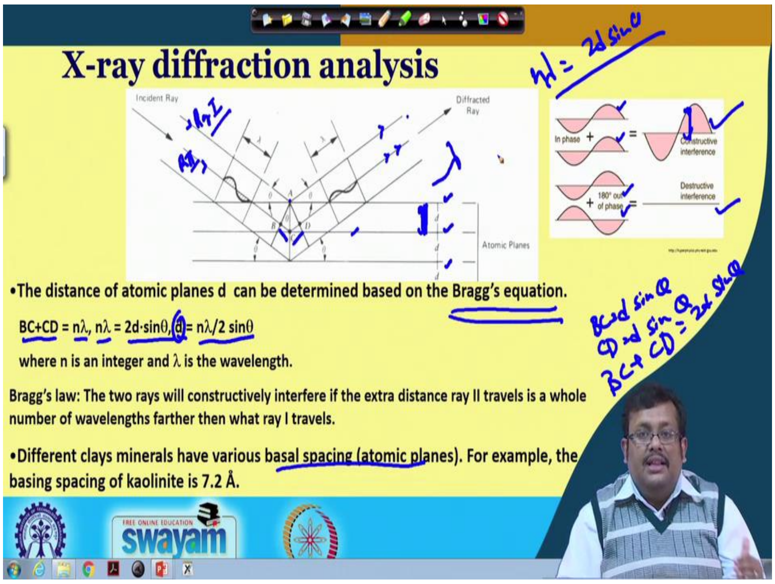

X-ray diffraction analysis

- The distance of atomic planes d can be determined based on the Bragg's equation.

  $BC+CD = n\lambda$, $n\lambda = 2d\cdot\sin\theta$, $d = n\lambda/2\sin\theta$

  where n is an integer and λ is the wavelength.

Bragg's law: The two rays will constructively interfere if the extra distance ray II travels is a whole number of wavelengths farther then what ray I travels.

- Different clays minerals have various basal spacing (atomic planes). For example, the basing spacing of kaolinite is 7.2 Å.

Welcome friends to this new lecture of Soil Science and Technology. And in this lecture we will be finishing we will be finishing this silicate clays because, we have started the silicate clays. And we will be talking about X ray diffraction analysis and after we cover the X ray diffraction analysis, I will be going to the next topic that is different sources of charge development in the clay minerals. And so, let us talk about X ray diffraction analysis.

Now, as I have already told you that d axis spacing is very much important for the identification of the clay minerals because; one clay mineral differ from another clay mineral based on their d axis spacing. As you can remember the d axis spacing of kaolinite is the smallest that is 0.72 nanometre followed by you know illite which is also non expanding. Then we see 1.4 which is for nanometre for you know 0.14 nanometre for kaolin for chlorite.

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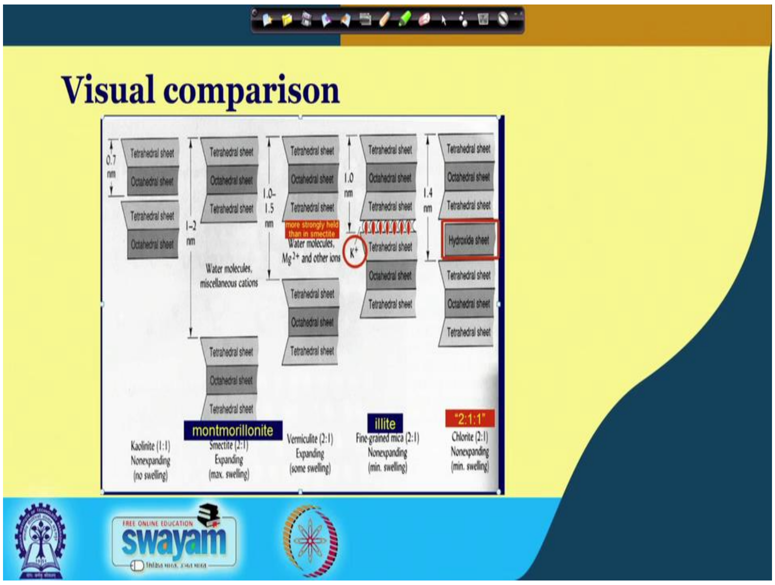

Visual comparison

If we go back and see there is 1.4 nanometre then 1 nanometre for illite 1 to 1.5 nanometre for the vermiculite 1 to 2 nanometre for smectite or montmorillonite. So, you can see there are differences in the d axis spacing and basically we use this structural difference for their identification using the X ray diffraction analysis. So, what is X ray diffraction? So, if you can see these are some parallel atomic planes; obviously, you know what are the parallel atomic planes and what is the d axis spacing I have already discussed this. So, the distance between these parallel you know distance within this parallel two lines of atoms is d axis spacing and suppose there are two different incidence X rays which are diffracting from the different planes.

So, let us considered this is the ray I and this is ray II. So, you can see the ray I is coming and ultimately it is getting diffracted from the first layer. So, this is the diffracted ray and in the and also in the IInd the ray also getting diffracted from the next parallel atomic planes from this plane. So, the distance of atomic planes D that is the distance of these atomic planes are D can be determined based on Bragg's equation which is given by scientist Bragg. The Bragg says that BC plus CD is or in other words Bragg's law says that the two rays will constructively interfere, if the extra distance ray II travels is a whole number of wavelength further then what ray I travels.

So, what is constructive interference first of all and what is destructive interference? So, let us consider this picture; obviously, we can see these two waves are in phase. And, when those two those two in phase waves combined they will form this constructive interference which will have higher amplitude than individual these individual you know waves. And here you can see these are these two waves are out of phase so, they are basically nullifying themselves. So, this is an example of constructive interference and this is an example of distractive interference.

So, the two rays here you can see this is the ray I and this is ray II. So, these two ray only can constructively interfere if the extra distance travel by this ray II will be an integer multiplier of the wavelength of this incident rays and the wavelength is lambda. So, you can see what is the distance this ray I travelling? The ray I is travelling A and from A to here. And, the ray II is travelling the extra distance ray II is travelling this BC plus CD, this is the extra distance that ray II is travelling. So, BC plus CD has to be an integer multiplier of the wavelength of incident ray. So, if the incident ray wavelength is lambda; obviously, n is the integer.

And or in another words n lambda is basically 2 d sin theta because BC equal to d sin theta, theta is the angle that it makes you know this is the angle theta and BC and also CD is another d sin theta. So, BC plus CD equal to 2 d sin theta or in other words n lambda will be 2 d sin theta which are or in other words d will be n lambda by 2 sin theta. So, this is the basic you know form of this Bragg’s law and different clay minerals now these d will vary from one clay mineral to another clay mineral.

And different clay minerals have various basal spacing or atomic planes or in other words d axis spacing. For example, the basal spacing of kaolinite is 7.2 angstrom or 0.72 nanometre. So, based on this principle you can separate one clay mineral to another clay mineral. So, based on this d axis spacing you can separate one clay mineral to another clay mineral.

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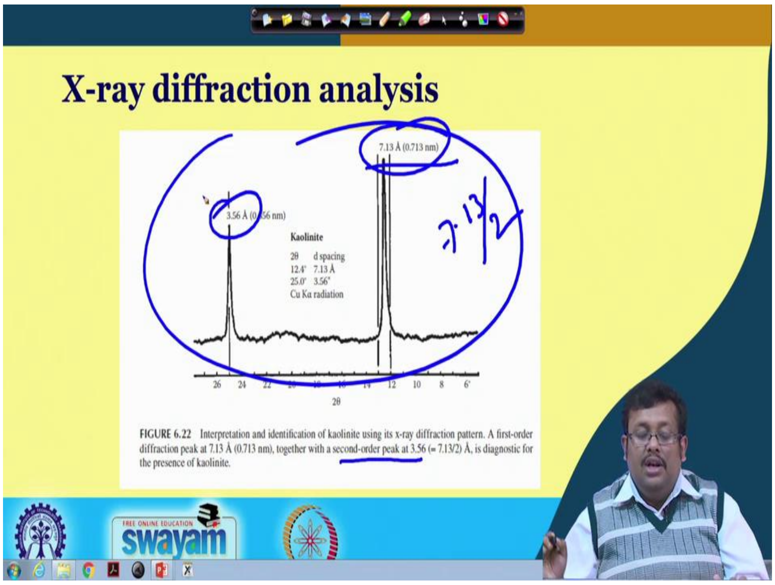

X-ray diffraction analysis

FIGURE 6.22 Interpretation and identification of kaolinite using its x-ray diffraction pattern. A first-order diffraction peak at 7.13 Å (0.713 nm), together with a second-order peak at 3.56 (= 7.13/2) Å, is diagnostic for the presence of kaolinite.

So, basically the technique we used for separating the clay minerals or identifying the clay minerals is called XRD technique or X ray diffraction technique. And basically you will in the X ray diffractions technique you will see some peaks like that and as you can see we are having the you know kaolinite peaks arising at 7.2 angstrom around 7.2 angstrom. And by changing the two theta value we can get the second order peak also at 3.56 angstrom which is basically 7.13 divided by 2.

So, you can see these d axis spacing can be exactly identified by using the X ray diffraction analysis and this using this effect X ray diffract by the way we call it X ray diffractograms using this effect X ray diffractograms you can identify the individual clay mineral. So, this is about the X ray diffraction analysis and there are also you know there are several details about X ray diffraction analysis now we are not going in details. However, if you are interested you can consult any book which deals with the X ray diffraction analysis to gain better understanding of the processes.

So, guys we have completed the silicate clays, you know I hope that you have learned something new in this silicate clays. This is very important and then in the next topic we will be sources of charges in the soil colloids.

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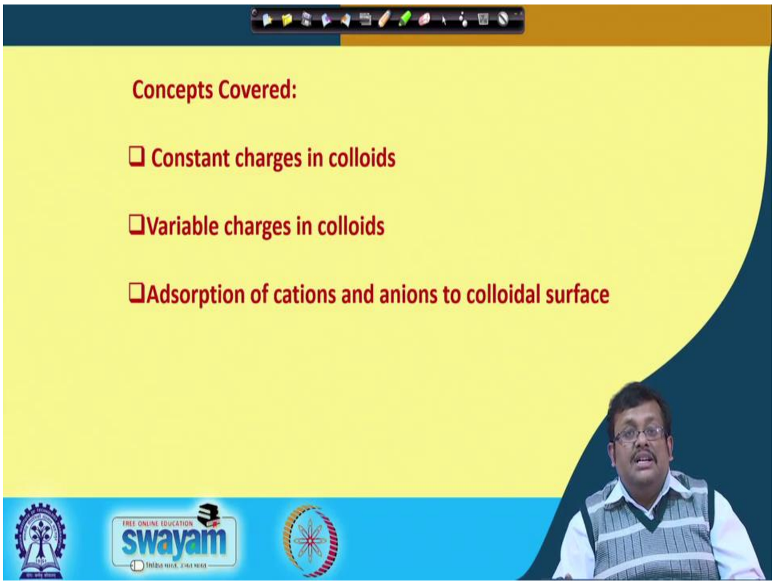

Concepts Covered:

❑ Constant charges in colloids

❑Variable charges in colloids

❑Adsorption of cations and anions to colloidal surface

So, let us start and in this lecture we will be covering in this topic we will basically covering these following concepts we will be covering the constant charges in colloids. Then we will be covering variable charges in colloids and then we will be talking about adsorption of cations and anions to colloidal surface.

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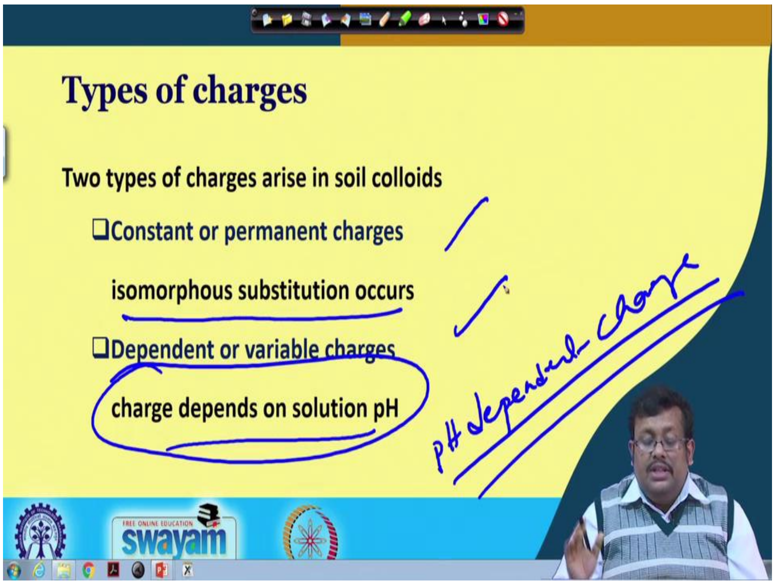

Types of charges

Two types of charges arise in soil colloids

❑Constant or permanent charges

isomorphous substitution occurs

❑Dependent or variable charges

charge depends on solution pH

pH dependent charge

So, let us talk about types of charges. Two types of charges arise in soil colloids; one is called constant or permanent charge and these you know this another charge is called dependent or variables dependent and variable charges. Now, constant or permanent chargers occurs, because of isomorphous substitution I have already talked about isomorphous substitution in our previous lecture and we will be talking about this pH dependent charge variable dependent charge.

Now, remember that this variable charge depends on the solution ph that is why it is also called pH dependent charge. So, these are two major sources of charge that develop within the soil colloid. So, we will discuss them one by one.

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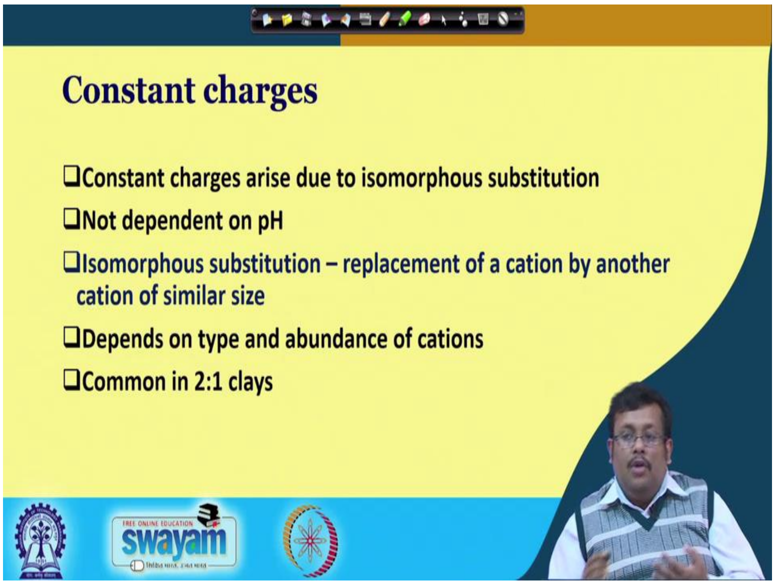

Constant charges

- ❑Constant charges arise due to isomorphous substitution
- ❑Not dependent on pH
- ❑Isomorphous substitution – replacement of a cation by another cation of similar size
- ❑Depends on type and abundance of cations
- ❑Common in 2:1 clays

Let us start with the constant charge; the constant charge arise due to the isomorphous substitution and it is called constant or permanent because it does not depends on the variable pH, it is constant it depends on the internal structure of the clay mineral. So, it is not dependent on pH it only depends on isomorphous substitution which is basically replacement of cation by another cation of similar size and depends only the type and abundance of the cations.

And; obviously, this type of isomorphous substitution basically you can see you know in 2 is to 1 type of clays like montmorillonite like vermiculite and you know like illite I have already discussed them in our last lecture.

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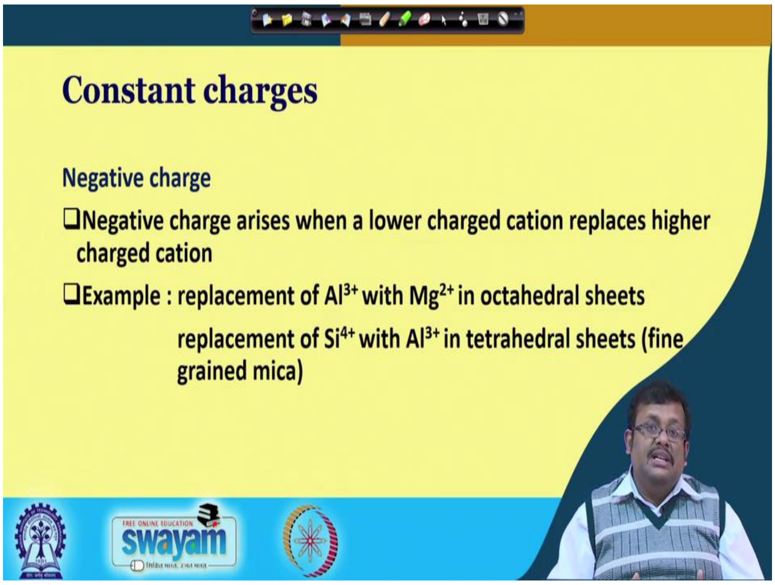

Constant charges

Negative charge

- ❑Negative charge arises when a lower charged cation replaces higher charged cation
- ❑Example : replacement of Al^{3+} with Mg^{2+} in octahedral sheets
  replacement of Si^{4+} with Al^{3+} in tetrahedral sheets (fine grained mica)

So, this negative charge arise basically when a lower charge of cation replace higher charge cation you know we have discuss about that replacement of alumina with Al^3 plus with Mg^2 plus octahedral sheet. And also replacement of Si^4 plus with Al^3 plus tetrahedral sheet in case of fine grained mica if you remember. So, these are some examples of isomorphous substitution and as a result of this isomorphous substitution there is a development of constant or negative permanent charge.

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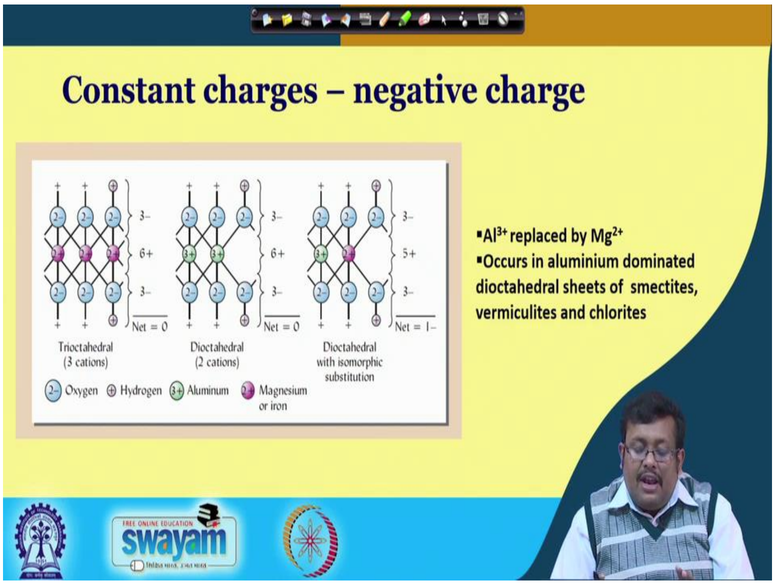

Constant charges – negative charge

- ▪Al^{3+} replaced by Mg^{2+}
- ▪Occurs in aluminium dominated dioctahedral sheets of smectites, vermiculites and chlorites

I have discuss already this picture in our last this diagram in our last lecture. So, I am not going to in details, but just to give you know just to you know brief idea you can see aluminium 3 here is replaced by magnesium and; obviously, occurs in an this type of thing occurs in aluminium dominated dioctahedral sheets of smectite vermiculite and chlorite.

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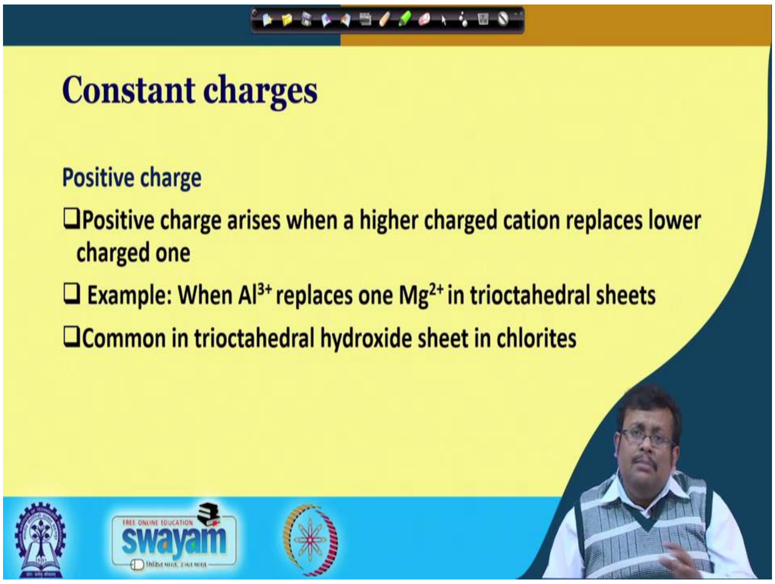

Constant charges

Positive charge

☐ Positive charge arises when a higher charged cation replaces lower charged one

☐ Example: When Al^{3+} replaces one Mg^{2+} in trioctahedral sheets

☐ Common in trioctahedral hydroxide sheet in chlorites

So, we talked about constant charge they are basically negative, but sometime positive constant charge also develop. So, how they develop? Remember that positive charge arises when a high charge cation replace lower charge ion it is for example, when Al^3 plus replace as Mg^2 plus in trioctahedral sheets and it is a common in trioctahedral hydroxide sheets in chlorites. So, this is an example where positive constant or permanent charge also can develop within clay.

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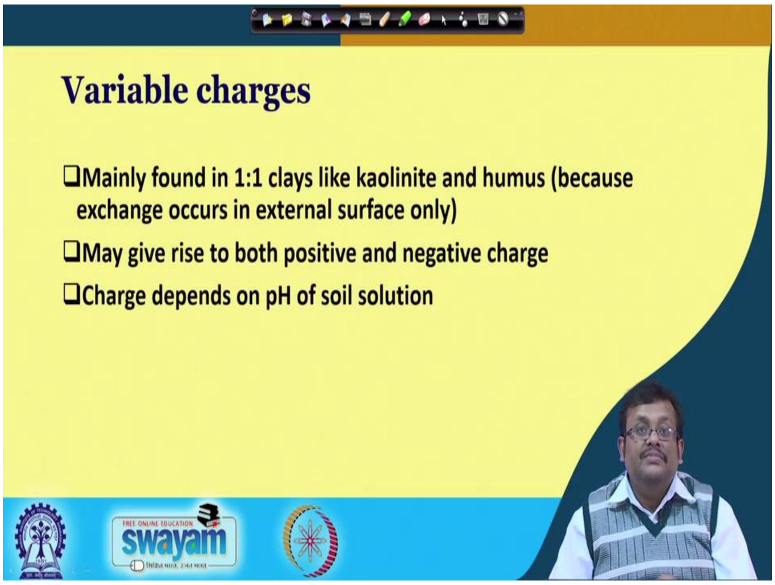

Variable charges

- ☐Mainly found in 1:1 clays like kaolinite and humus (because exchange occurs in external surface only)
- ☐May give rise to both positive and negative charge
- ☐Charge depends on pH of soil solution

Now, what is variable charge or pH dependent charge? The pH dependent charge or variable charge is mainly found within 1 is to 1 type of clay like kaolinite and humus. Remember that humus is the one of the humus is the organic colloid and it is one of the major component of soil. And remember that this 1 is to 1 type of clay and kaolinite you know and humus basically shows variable charge because, exchange occurs in the external surfaces only.

I remember that they may give rise to both positive and negative charge that is why we are calling it variable charge because they can generate either positive charge or negative charge. However, in case of constant charge it is mostly negative charge. So, in case of variable charge or pH dependent charge is depends on pH of the soil solution.

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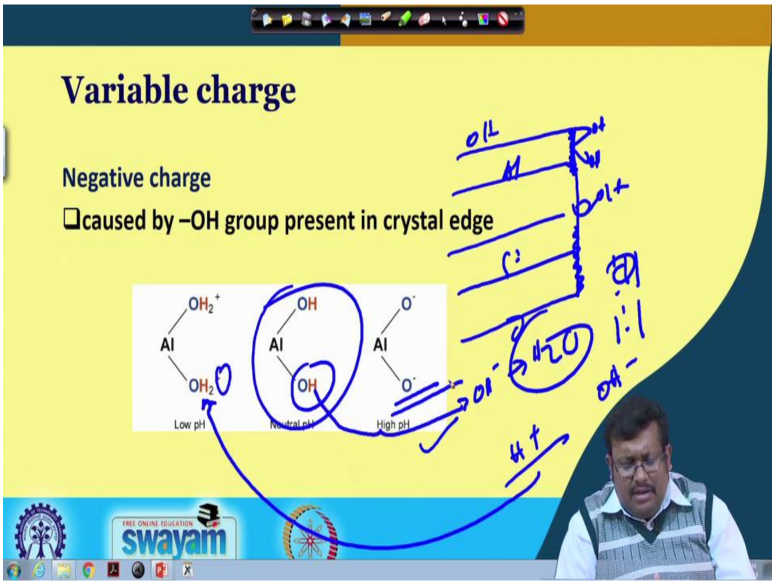

Variable charge

Negative charge

❑caused by –OH group present in crystal edge

Now so, what is variable charge variable charge I mean you can see here this is the neutral pH. Now you know that clay mineral contains different layers of atoms like hydroxyl followed by aluminium, then followed by oxygen hydroxyl, then followed by silica, then followed by you know oxygen in case of 1 is to 1 type of layer; obviously, 1 is to 1 type of layer.

So, these are some edges so, when this type of edges are present; obviously, you will see that there will be hydroxyl group which are present at the edges broken edges of aluminium. And in case of lower pH; that means, when there will be lower pH when there will be high dominance of protons you know that. So, this proton will go and attach to these hydroxyl to form this positive charge. And so, you can see at the at acidic condition.

In acidic condition this 1 is to 1 type of clay or edges of the 1 is to 1 type of clay they can produce the positive charge. However, in case of high pH condition; that means, in alkaline conditions there will be dominance of OH minus and this H will react with OH minus to produce H_2O and ultimately living these O minus. So, they are ultimately creating negative charge.

So, you can see based on different pH the charge distribution is also changing in case of lower pH here getting positive you know there will be development of positive charge and in case of higher pH there will be development of negative charge. So, that is why we call it variable charge all right.

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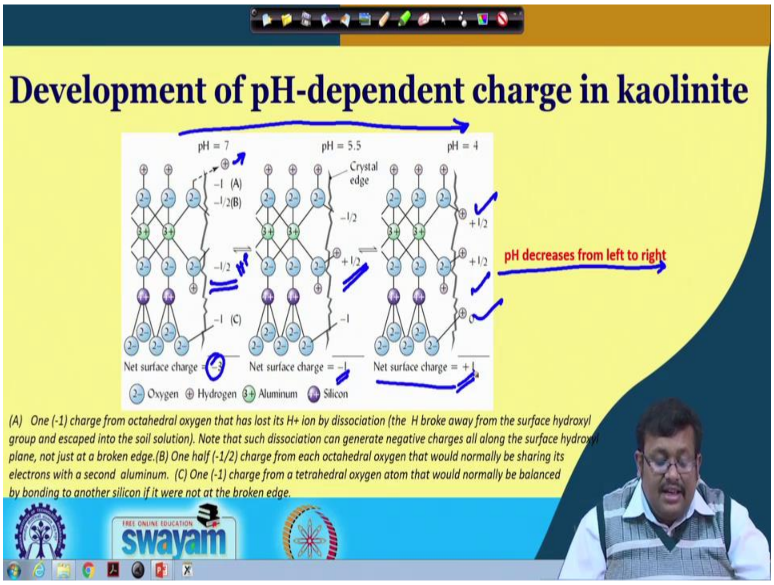

Development of pH-dependent charge in kaolinite

(A) One (-1) charge from octahedral oxygen that has lost its H+ ion by dissociation (the H broke away from the surface hydroxyl group and escaped into the soil solution). Note that such dissociation can generate negative charges all along the surface hydroxyl plane, not just at a broken edge.(B) One half (-1/2) charge from each octahedral oxygen that would normally be sharing its electrons with a second aluminum. (C) One (-1) charge from a tetrahedral oxygen atom that would normally be balanced by bonding to another silicon if it were not at the broken edge.

So, development of a pH dependent charge in kaolinite in this specific example; obviously, let me show you. So, this is a 1 is to 1 type of layer and is to in this one 1 is to 1 type of layer one charge from octahedral oxygen that has lost this hydroxyl. So, you can see one hydroxyl is getting lost from this from here and we are getting a net surface charge of minus 3 and the crystal edges of 1 hydroxyl will attached to this 1 sorry 1 proton will attached to this minus half to create positive half. So, here we are getting net negative charge edge I mean minus 1 and ultimately we are also getting net surface charge of plus 1.

So, you can see as pH decreases from left to right. So, here pH is decreasing from left to right so; that means, in lower pH condition there will be higher dominance of H plus, higher dominance of H plus will produce more positive charges at the edges. So, you can see with the increase of the pH the net surface charge is getting positive from minus 3 to plus 1. And; obviously, you can see here how these protons are getting attached to this edge I mean this hydroxyl groups which are present at the edges or broken edges.

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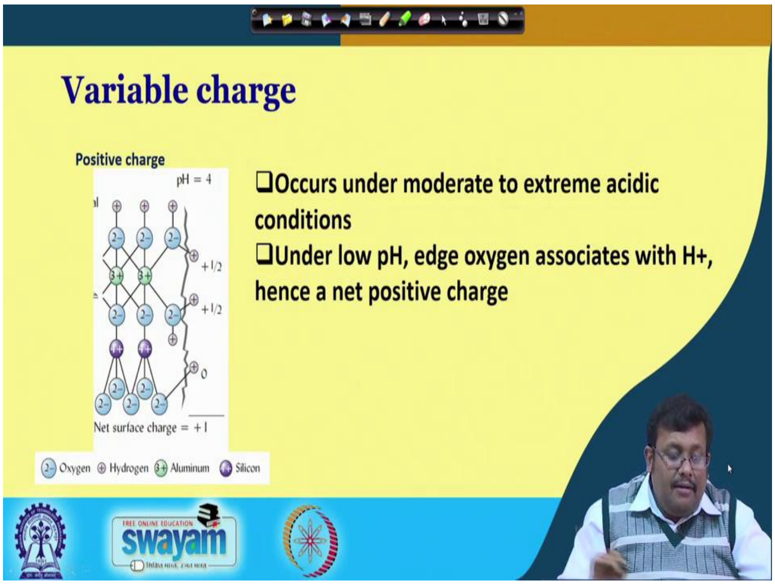

Variable charge

Positive charge

- ❑Occurs under moderate to extreme acidic conditions
- ❑Under low pH, edge oxygen associates with H+, hence a net positive charge

So, I hope it is now clear to you. So, let us go and see you know variable charge ok, we have discussed about the negative charge; obviously, this positive charge occurs under moderate to you know extreme acidic condition and; obviously, under low pH edge oxygen associate with H plus hence a net positive charge I have already told you that.

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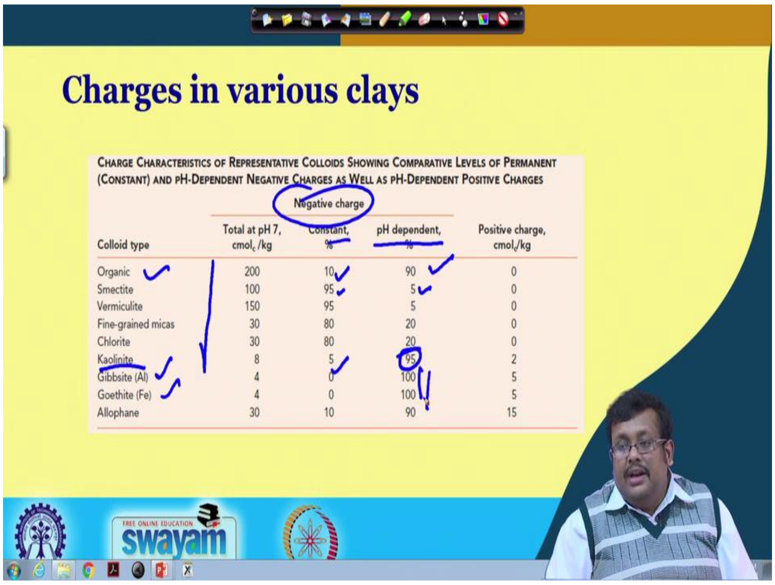

Charges in various clays

CHARGE CHARACTERISTICS OF REPRESENTATIVE COLLOIDS SHOWING COMPARATIVE LEVELS OF PERMANENT (CONSTANT) AND PH-DEPENDENT NEGATIVE CHARGES AS WELL AS PH-DEPENDENT POSITIVE CHARGES

	Negative charge			
Colloid type	Total at pH 7, cmol$_c$/kg	Constant, %	pH dependent, %	Positive charge, cmol$_c$/kg
Organic	200	10	90	0
Smectite	100	95	5	0
Vermiculite	150	95	5	0
Fine-grained micas	30	80	20	0
Chlorite	30	80	20	0
Kaolinite	8	5	95	2
Gibbsite (Al)	4	0	100	5
Goethite (Fe)	4	0	100	5
Allophane	30	10	90	15

So, let us see there these are charge characteristics of representative colloids showing comparative levels of permanent and pH dependent negative charge. You can see one thing that in case of organic the constant charge is percentage of negative in the total negative charge; obviously, the percentage of constant charge is only 10 percent; however, the pH dependent charge is 90 percent.

So, in case of smectite also the constant charge is 95 percent because of isomorphous substitution; however, there is only 5 percent you know you know pH dependent charge because, you know they do not show this type of broken you know there is no such you know positive charge development at the or negative charge development at the edges.

As you can go from organic then to you know smectite, vermiculite to kaolinite now you can see 95 percent of the negative charge is based on pH independent charge. Because, the constant charges is only 5 percent why it is that because, if you remember they have almost lock structure due to the presence of hydrogen bonding in the adjacent in between the adjacent layers.

As a result no cations or another you know moreover there is no isomorphous substitution in case of kaolinite as a result of less isomorphous substitution in the kaolinite; obviously, there will be no constant charge or negative charge development only they rely upon the pH dependent charge. However, in case of gibbsite and you know goethite their extreme condition; obviously, there will be 100 percent pH dependent charge. There will be no constant or permanent negative charge.

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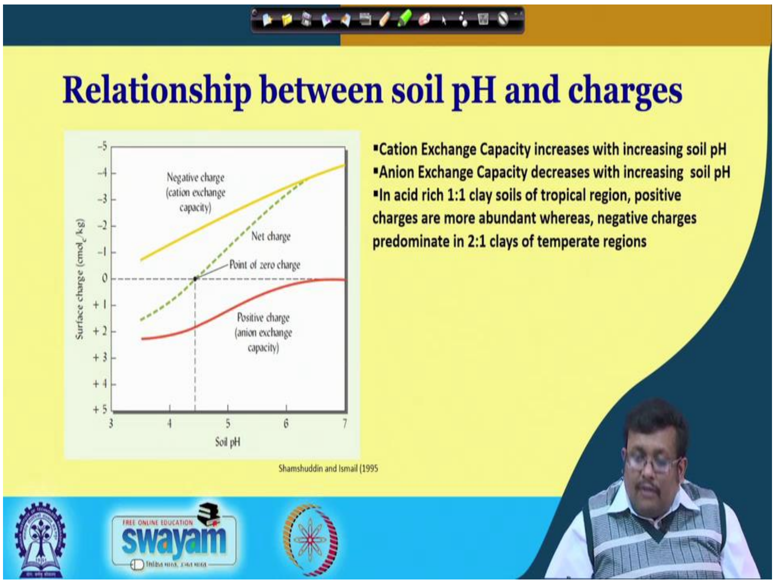

Relationship between soil pH and charges

- Cation Exchange Capacity increases with increasing soil pH
- Anion Exchange Capacity decreases with increasing soil pH
- In acid rich 1:1 clay soils of tropical region, positive charges are more abundant whereas, negative charges predominate in 2:1 clays of temperate regions

Shamshuddin and Ismail (1995

So, what is the relationship between pH and charges? Obviously, cation exchange capacity increases with increasing soil pH it is quite obvious because you can see here the relationship between soil pH and surface charge. So, as we can see if the soil pH is increasing the you know negative charge increasing or in other words cation exchange capacity is increasing or another word as the soil pH is increasing the negative charge increases because, of pH dependent charge. And, as a result of that there will be more cation exchange capacity or in other words there will be more ability for the soil to absorb more positive cations.

So, that is why cation exchange capacity increases with increasing soil pH; however, anion exchange capacity decreases with increasing soil pH as we can see the soil pH is increasing from 3 to 4 to 5 to 6 and 7. And positive you know anion exchange capacity is getting decreased here from 0.3 almost 0.2 point plus 2.5 to around 0, at around 7, at around 7, soil pH because of that I mean anion you know why is that because as we are increasing the soil pH you know negative charge further develops. And as a result of the negative charge develops that will that will create the repulsion of the negatively charged anions and as a result of that anion exchange capacity will decrease.

Now, what is cation exchange capacity? So, before discussing this: what is cation exchange capacity and anion exchange capacity? Cation exchange capacity is the soil to absorb the cations adsorb the cations from the nearby environment. Whereas, anion exchange capacity is basically the ability of soil to adsorb anions from the nearby environment; remember that since cations are positive negative charge has to be developed over the soil surface for their attraction and electrostatic attraction forms between these cations as and this negatively charged surface of the clay minerals.

So, and in case of anions; obviously, this is because of pH dependent charge and pH dependent charge in the low in the low pH condition in the low pH condition or acidic condition; obviously, there will be positive charge development. And this positive charge will attract the negative charge anions like nitrate and sulphates and they will attached to the soil surface. So, this is anion exchange capacity and cation exchange capacity.

So, I hope that now it is clear why cation exchange capacity increases with increasing soil pH and anion exchange capacity decreases with increasing soil pH. Now in acid rich 1 is to 1 type of in acid rich 1 is 1 is 1 type of clay soils tropic tropical regions positive charges are more abundant whereas, negative charges predominant in two is one type of clays in temperate region it is quite obvious. Because, 1 is to 1 type of clays kaolinite and kaolinite can only generate the pH dependent charge not the permanent charge due to isomorphous substitution.

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A negatively charged clay

Clay attracted to positive terminal, demonstrating its negative charge

Weil., 2015

So; obviously, clays are negatively charged because this is a very good you know experiment and where they have you know scientists have plays to electrodes. And; obviously, you can see the clay attracted to the positive terminal and demonstrate it is negative charge. So, clay particles are negatively charged and this negatively charged develops this negative charge develops predominantly from the isomorphous substitution or constant charge.

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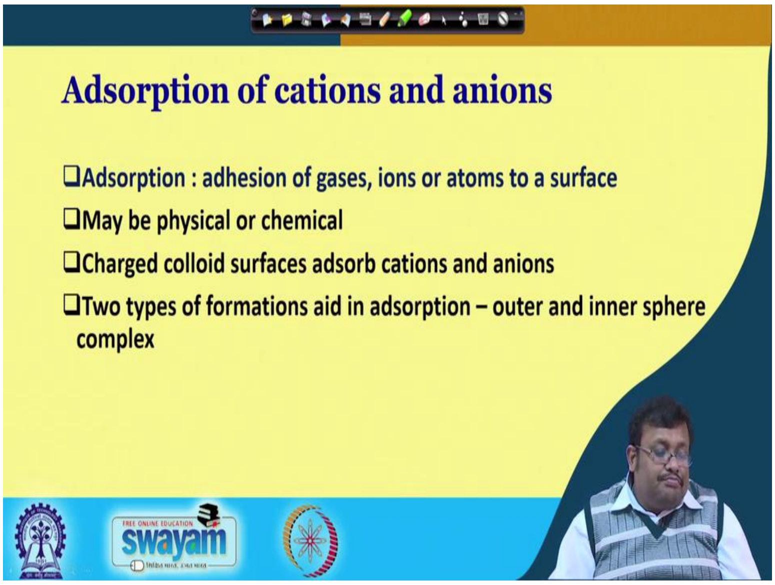

Adsorption of cations and anions

- ❑Adsorption : adhesion of gases, ions or atoms to a surface
- ❑May be physical or chemical
- ❑Charged colloid surfaces adsorb cations and anions
- ❑Two types of formations aid in adsorption – outer and inner sphere complex

Now adsorption of cations and anions adsorption remember that it is basically some examples are adhesion of gases ions or atoms to the surface. And it may be either physical or maybe chemical and charged colloid surface adsorbed cations and anions two types of formation aid in adsorption; one is outer sphere and inner sphere complex.

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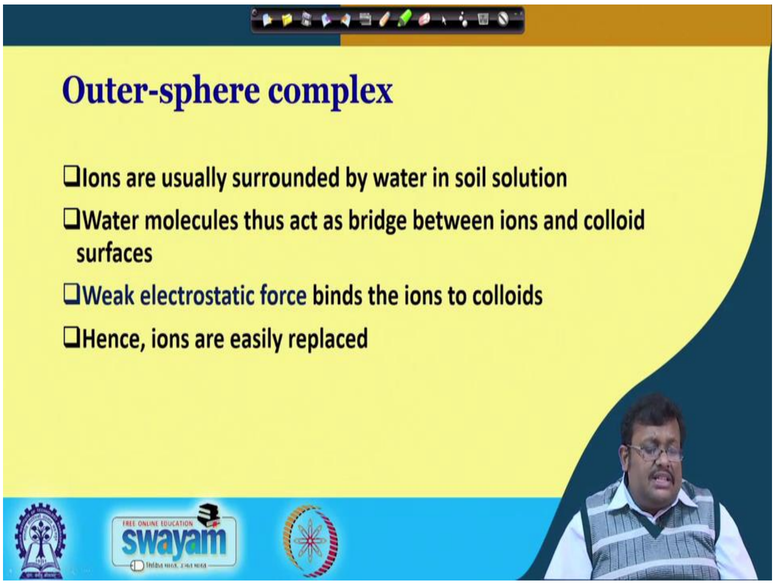

Outer-sphere complex

- ❑Ions are usually surrounded by water in soil solution
- ❑Water molecules thus act as bridge between ions and colloid surfaces
- ❑Weak electrostatic force binds the ions to colloids
- ❑Hence, ions are easily replaced

So, let us discuss what is outer sphere complex? Outer sphere complex is when ions are usually surrounded by water in soil solution and water molecules thus, acts as a bridge between the ions and colloid surfaces. And, these weak electrostatic force bind the two bind the ions and to the colloids and ions are easily replaceable.

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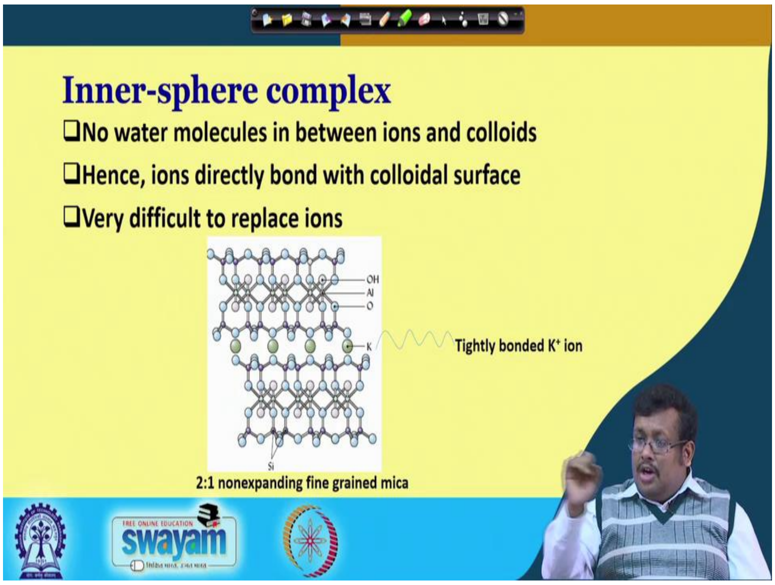

Inner-sphere complex

❑No water molecules in between ions and colloids

❑Hence, ions directly bond with colloidal surface

❑Very difficult to replace ions

2:1 nonexpanding fine grained mica

So, this outer sphere complex; what is inner sphere complex? Inner sphere complex is when no water molecule between the ions and colloids hence ions directly bound you know they are bond with colloidal surface as a very difficult to replace ion. So, here you can see tightly bonded K plus ions.

So, these are example of inner sphere complex this you know this is an example of fine grained mica or illite if you remember in case of illite there is only isomorphous substitution in the tetrahedral sheet. So, as a result of that the inner layer is occupied by the small potassium cations and these potassium cations forming this inner sphere complex they are not surrounded by you know water hulls. So, these are example of inner sphere complex.

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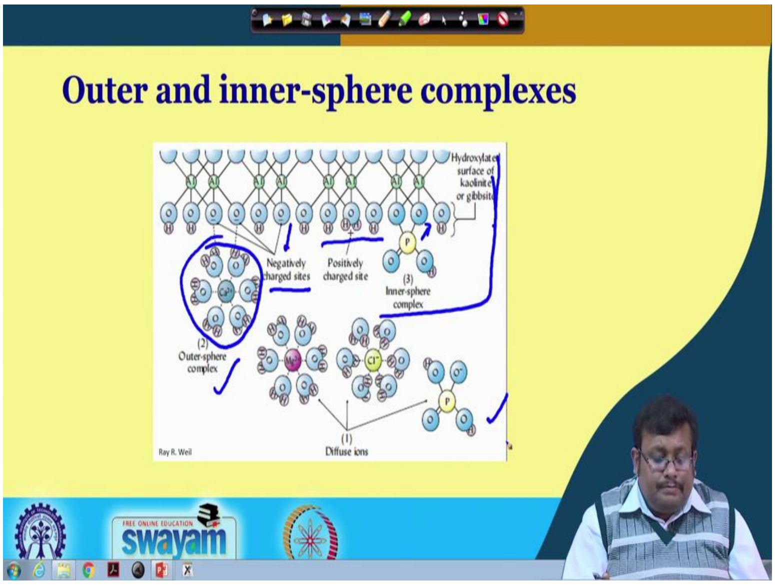

Outer and inner-sphere complexes

So, this picture shows in a nutshell what is inner sphere and outer sphere complex. So, you can see there are two types of surfaces; obviously, these negatively charged sites where we can see negative charge developed due to isomorphous substitution. And these are positively charged site which occurs due to variable pH and these negatively charged site are basically you know attracting different cations.

And; obviously, this an outer sphere complex you know calcium ion surrounded by you know water molecules they are getting attached here and also this is an example of inner sphere complex where this H_2PO_4 is getting attached directly to the you know to the clay. So, it is hydroxylated surface of kaolinite and gibbsite this is an hydroxylated surface of kaolinite and gibbsite examples.

And so, basically both outer sphere complex and inner space complex are defused in the nearby soil solution. So, this is why this is called outer and inner sphere complexes and now I hope it is clear to you: what is the difference between outer sphere complex and inner sphere complex.

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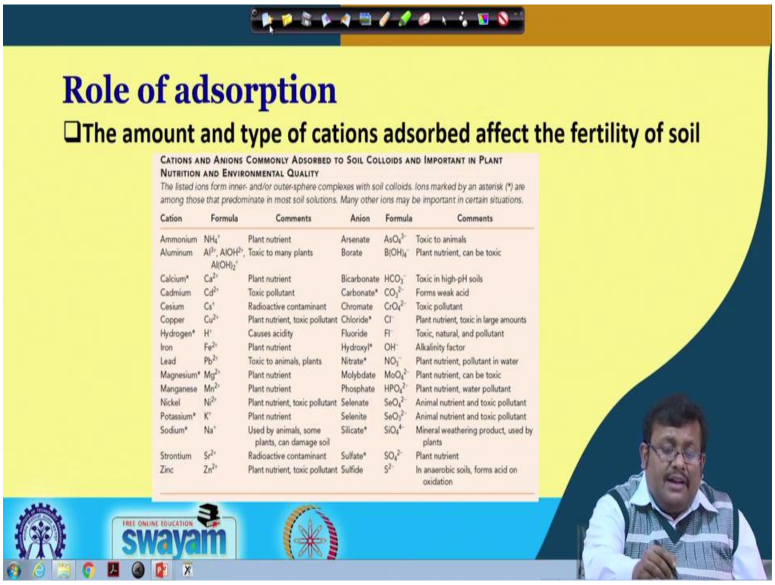

Role of adsorption

❑The amount and type of cations adsorbed affect the fertility of soil

CATIONS AND ANIONS COMMONLY ADSORBED TO SOIL COLLOIDS AND IMPORTANT IN PLANT NUTRITION AND ENVIRONMENTAL QUALITY

The listed ions form inner- and/or outer-sphere complexes with soil colloids. Ions marked by an asterisk (*) are among those that predominate in most soil solutions. Many other ions may be important in certain situations.

Cation	Formula	Comments	Anion	Formula	Comments
Ammonium	NH_4^+	Plant nutrient	Arsenate	AsO_4^{3-}	Toxic to animals
Aluminum	Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$	Toxic to many plants	Borate	$B(OH)_4^-$	Plant nutrient, can be toxic
Calcium*	Ca^{2+}	Plant nutrient	Bicarbonate	HCO_3^-	Toxic in high-pH soils
Cadmium	Cd^{2+}	Toxic pollutant	Carbonate*	CO_3^{2-}	Forms weak acid
Cesium	Cs^+	Radioactive contaminant	Chromate	CrO_4^{2-}	Toxic pollutant
Copper	Cu^{2+}	Plant nutrient, toxic pollutant	Chloride*	Cl^-	Plant nutrient, toxic in large amounts
Hydrogen*	H^+	Causes acidity	Fluoride	Fl^-	Toxic, natural, and pollutant
Iron	Fe^{2+}	Plant nutrient	Hydroxyl*	OH^-	Alkalinity factor
Lead	Pb^{2+}	Toxic to animals, plants	Nitrate*	NO_3^-	Plant nutrient, pollutant in water
Magnesium*	Mg^{2+}	Plant nutrient	Molybdate	MoO_4^{2-}	Plant nutrient, can be toxic
Manganese	Mn^{2+}	Plant nutrient	Phosphate	HPO_4^{2-}	Plant nutrient, water pollutant
Nickel	Ni^{2+}	Plant nutrient, toxic pollutant	Selenate	SeO_4^{2-}	Animal nutrient and toxic pollutant
Potassium*	K^+	Plant nutrient	Selenite	SeO_3^{2-}	Animal nutrient and toxic pollutant
Sodium*	Na^+	Used by animals, some plants, can damage soil	Silicate*	SiO_4^{4-}	Mineral weathering product, used by plants
Strontium	Sr^{2+}	Radioactive contaminant	Sulfate*	SO_4^{2-}	Plant nutrient
Zinc	Zn^{2+}	Plant nutrient, toxic pollutant	Sulfide	S^{2-}	In anaerobic soils, forms acid on oxidation

So, roles and adsorption; obviously, you know the amount and type of cation adsorbed affect the fertility of the soil here you can see a list of different cations and anions which are having different you know different roles for the growth of the plants. Obviously, ammonium is a plant nutrients there is a plant nutrient aluminium is toxic to the plants, calcium is a plant nutrient, cadmium is toxic pollutant so ones and so forth.

So, these roles of adsorption they are having high roles in adsorption because based on their dominance they can you know influence both you know soil fertility as well as plant growth.

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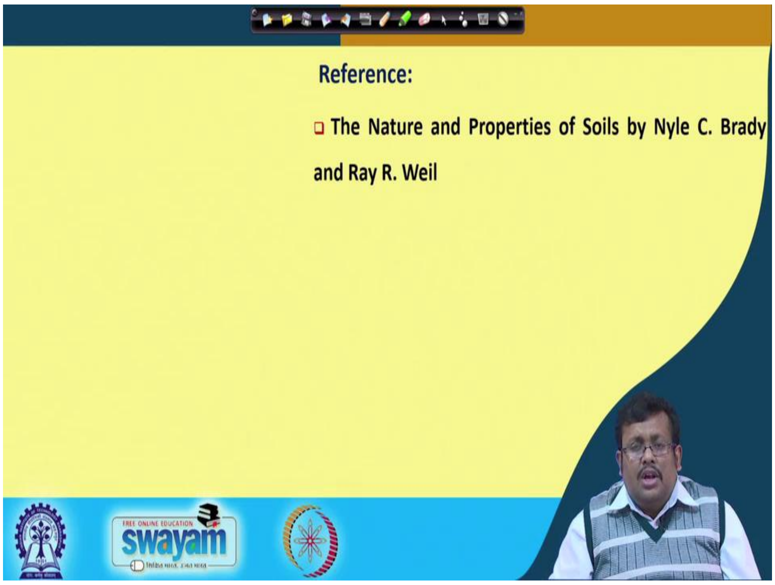

Reference:

- The Nature and Properties of Soils by Nyle C. Brady and Ray R. Weil

So, we have finish the different sources of different charges in the clay in the soil colloid. And I hope that this lecture was you know informative to you and you have learned something new and if you have any queries feel free to send me an emails and send the emails to my TAs. So, they will be more than happy to help you and let us wrap up here and in the next lecture we will be starting a new topic.

Thank you very much.