Transcriber's Name: Prabhavathi Environmental Soil Chemistry Prof. Somsubhra Chakraborty Agricultural and Food Engineering Department Indian Institute of Technology-Kharagpur

Lecture-10 Organic Soil Components (Contd.)

Welcome friends to this fifth lecture of module 2 of this environmental soil chemistry course. And in this lecture we will be talking about in details about different types of clay minerals especially the secondary clay minerals. We have already discuss about the major clay minerals like 1 is to 1 type of clay mineral like kaolinite, halloysite, and then we have talk about smectite, like montmorillonite, illite, vermiculite, chlorite.

And in today's lecture we will be talking about other types of clay minerals which are present in the soil. So, let us first start with the intergrade clay minerals. Now this intergrade clay minerals are basically intermediates between the vermiculite and smectite, you know vermiculite is a kind of an expanding clay mineral 2 is to 1 type of clay mineral and smectite or montmorillonite is a maximum swelling or maximum expansible clay mineral. And these integrate clay minerals are somewhat intermediate between these vermiculite and smectite.

And in this interlayers, in this mineral the interlayer space has exchangeable cataions and gibbsite like or brucite like Island but are not continuous like chloride. In case of chloride what happened in that in between in the interlayer space of 2 is to 1 type of layer there is a continuous you know hydroxy interlayer either it is a brucite or it is a gibbsite. So, here there is also a gibbsite or brucite like structure.

However the interlayer space as you know they do not have the continuous you know gibbsite or brucite like structure. So, this is the characteristic of this type integrate type of clay mineral. Now accordingly the interlayer space does not collapse or hitting as readily as with the smectite and vermiculite but it does collapse more easily than that of complete interlayer hydroxy sheet in chlorite. So, let us see how these interlayer space of this mineral basically looks like.

So, if we move ahead and see this is ok, so example is hydroxy interlayer vermiculite in acid soil. So, this is an example of hydroxy interlayer vermiculite you can see this is a vermiculite. In the vermiculite structure these are magnesium in the octahedral site so it is a 2 is to 1 type of mineral. In the interlayer space this is basically magnesium bound water as well as aluminum in the octahedral layer.

So, it is basically hydro you know here you can see the interlayer here is basically composed of the hydroxy aluminum layers. So, it is not a continuous layer it is you know somewhat in you know in discontinuous layer. So, basically you can see this is illite structure and when these illite you know interlayer potassium get replaced then it basically converts into the vermiculite. And you know that in the interlayer space of vermiculite magnesium bound water is present. And when these magnesium bound water is also having adjacent hydroxy aluminum interlayers aluminum hydroxy interlayer, then it is called hydroxy interlayer vermiculite. So, this is an example of interlayer clay mineral. Important source of aluminum in these soils and also in alkaline soil these intelligent materials are is basically hydroxy magnesium or magnesium hydroxy layer.

So if we move ahead and see another type of clay mineral called interstratified clay minerals. Now interstratified or mixed layer filer phyllosilicates are structures or phyllosilicates structure in which the layers have more than one type of clay minerals stack together within the crystal. So, they are usually metastable intermediate product and a sequence of reaction involving end member clay minerals.

So, when one clay mineral converge to another clay mineral due to different types of reaction, these are metastable variant or metastable intermediate products. Where you can see that different mix layers are present for example 2 is to 1 and 1 is to 1 type of clay mineral you know they have the strong interlayer bonding. But weak interlayer bonding they have strong inter intra layer bonding.

That means 2 is to 1 layer has the strong you know inter intra layer they have strong attraction. However, when the stack each other stack upon each other their bonding is relatively less. So, stacking as a result of that there is a stacking of different layers. So, example instantly interested you know interstratification of smectite with chlorite and this is known as the corrensite.

Also when there is a illite with smectite we call it rectorite also we can see kaolinite with smectite. So, these different types of clay minerals layer when they stack one of each other one above each other then we get this inter interstratified clay minerals. The reason again although within these 2 is to 1 type of layer the bond is strong however the interlayer bond is negligible. So, as a result of that there is occurrence of stacking.

Now let us move ahead and see some amorphous mineral which are present in the soil, examples are allophane and imogolite. So, these are basically clay sized minerals commonly associated with the volcanic ash type of soils where there is sufficient moisture for silica to leach. It also occurs in some non volcanic regions but mostly it they are basically occur in the volcanic region.

Three major type of alkane allophane is there, aluminum rich soil allophone, silicon rich you know soil allophone and you know steam stream deposit allophanes. So, these are 3 major variants of allophanes which we can see in the soil. So, this is the you know how this allophane looks like, basically in this allophone, silica and alumina ratio is basically 0.82 to 2 it varies from 0.84 to 2.

It is also similar to kaolinite, aluminum is present in both tetrahedral and octahedral coordination and exhibit spherical particles with 30 to 50

nanometer diameter. In soils with allophane have significant organic matter and also allow low bulk densities due to high organic matter. Now another amorphous mineral is imogolite where the silica alumina rate ratio is 1 and aluminum is present only in octahedral coordination, it exhibits thread like particles that are parallel tubes of 20 nanometer diameter. And it has the capacity to absorb monovalent patterns like halloysite.

Another type of clay mineral we can see in the soil are fibrous clay minerals just like here you can see it is palygorskite it is a special type of fibrous clay mineral. Now it has been why it is fibrous clay minerals because they have fibrous morphology and it is composed of ribbons of 2 is to 1 one type of phyllosilicates and it does not have continuous octahedral sheet. So, these are the reason that is why it looks like fibrous.

And the ribbons are basically link to each other by inversion of silica tetrahedral along a set of silica oxygen silica bonds, we will see in the next slide. And basically the required alkaline condition and have and they basically have high silica and magnesium activity for stability. So, basically they require alkaline condition for the stability in the acidic condition they will degrade. So, as I am telling you these ribbons are linked to each other by inversion of silica tetrahedral along the set of Si-O-Si bond let us see.

So, as you can see there are different models of these palygorskite as you can see these is a 2 is to 1 type of layer, this is another 2 is to 1 type of layer. However, in this 2 is to 1 type of layer when these you know this is basically a silica tetrahedral layer and this blue is basically aluminum octahedral sheet. So, aluminum octahedral sheet is sandwiched between 2 tetrahedral sheet and when the 2 tetrahedral sheet in the adjacent layer are joined together by sharing their you know sharing their epic sharing their oxygen.

As you can see here is just a Si-O-Si bond, as a result of that we will see this fibrous like structure. Now depending upon their distance they are of different variants, for example you can see here the different b axis spacing is 1.806 nanometer. However according to the gard-follett model it is also a 1.806 nanometer. However the c axis spacing is 1.27 nanometer. This is another clay mineral called sepiolite. As You can see here the distance is 2.68 nanometer whether c axis is spacing is 1.34 nanometer, so this is how these fibrous mineral basically composed.

Other important minerals which are present in the soil as a result of high weathering, high amount of chemical weathering or different oxide, hydroxide and oxy hydroxides. So, oxides refers to the metal hydroxide, oxy hydroxides and hydrous oxides. And they have you can see here the gibbsite structure that means it is dominated by aluminum. They have high specific surface area and reactivity and they may exist as discrete crystals.

As coatings on phyllosilicates and humic substances and mixtures, so these are basically the end product of the intensive chemical weathering. Let us start with 1, aluminum oxides or gibbsites, now the gibbsite you can see it is basically most common gibbsite is most common sorry yes yeah it is a most common aluminum hydroxide mineral, it is found in highly weathered soils like oxysols and ultisols. And it has 2 planes of closely packed hydroxyls with aluminum in between them. So, you can see here these are closely packed hydroxyl with aluminum in between them.

So, it is a basically di octahedral kind of structure and the d axis spacing is 0.48 nanometer ok. And in the interior obviously these aluminum as you can see they are sharing their they are they are basically sharing with 6 hydroxyl ions in the interlayer. However, those aluminums which are present in the edge they will basically share with only 4 hydroxyl ions. So, this is the shape of this structure of aluminum hydroxide or gibbsite.

So, if we move ahead and see iron oxide, iron oxide the most prevalent iron oxide is basically composed of iron and oxygen, octahedron is the basic structure of all the iron oxides can be either alpha phase that is hexagonal close packing or you know gamma phase which is cubic close packing. And so I some isomorphous substitutions some time basically replace iron you know Fe3+ with Al3+ and Mn3+ with Cr3+ ok. So, Fe3+ some time get replaced by either Al3+ or Mn3+ or Cr3+, so isomorphous substitution occurs in this iron oxides also.

So, Goethite as I have told you it is a one of the most common and thermodynamically stable iron oxides, it is found in humid as well as in semi arid regions, it is thermodynamically stable, it you know it is basically needle shape crystals with edge and grooves as you can see from this structure. It is an shape with a you know with the edges and the grooves has double bands of a FeOH octahedral sharing edges and corners. As you can see in this structure and also bands bonded partially by hydrogen bonding, so this is the structure of goethite.

So, another important iron oxide which is present in the soil is hematite. The hematite has the formula of Fe2O3 and it is the second most prevalent or most common iron oxides mineral in the earth crust after a goethite. It is also responsible for red color of many soils, it is mainly found in highly weathered soils as you know. We have already discussed that these oxides are basically present in highly weathered soils because of chemical weathering.

And also has FeO6 octahedra connected edge by shape, so this is basically the structure of these hematite where this red dots are showing the oxygen whereas this blue dots are showing the iron. So, another important oxide is manganese oxides and in the manganese oxide are basically occurring as coatings on soil particles, in cracks and veins as well as nodules. One example you know major sources of you know manganese in the soil, manganese as you know it is one of the major plant micronutrient. And these manganese oxides are the one of the major source of manganese in the soil.

Act as oxidant for metals like either arsenic or chromium and it is mostly amorphous and examples are birnessite site as well as pyrolusite. So, this is an example of pyrolusite which is one of the most prevalent manganese oxide in the earth crust. So, apart from these all these oxide, integrate minerals, interstratified minerals, prime mini you know 1 is to 1 type of mineral, 2 is to 1 type of mineral, 2 is to 2 type of mineral.

We also see carbonates and sulfate minerals in the soils. So, they are basically most you know prevalent in arid and semi arid regions and they are highly soluble compared to silica minerals. And they are unstable you know unstable carbonate minerals are examples are calcite as well as magnesite.

And stable carbonate minerals are example you know dolomite and siderite, where dolomite is basically calcium magnesium carbonate whereas siderite is iron carbonate. And sulfate minerals. you know as per as the sulfate minerals are concerned the most important one is gypsum which is basically calcium sulfate di hydrate. So, these are some of the important carbonates and sulfate minerals which are present in the soil.

So, let us discuss another very important thing that is specific surface of minerals. Now specific surface area is a property of solid define as the total surface area of a material per unit of mass and it is basically expressed in terms of meter square square meter per kg of solid. So, secondary minerals remember they have high surface area because their size is very small. There the end product of weathering, that the end product of all type of weathering with physical and chemical weathering.

So, basically they have very small size and the total surface area of the secondary minerals are basically given by the SE + SI where ST is basically the total surface area in square meter per gram whereas the SI is basically the internal surface area square meter per gram and SE is the external surface area that is square meter in gram.

So, so the external surface area is determined by measuring the amount of nitrogen gas adsorbed by a surface at temperature near the boiling point of liquid nitrogen which is 77 Kelvin. Now surface analysis is the you know surface area analysis is done based on the BET equation. Now BET equation basically given by this name of these 3 important 3 scientists Bruner, Emmett and Taylor.

So, it is a BET equation, BET theory we will just learn in the next slide. So, depending on the surface area we use different types of adsorbent. For example if the surface area is greater than 10 square meter per gram will use the nitrogen. If it is between 1 to 0.1 to 10 then we will be using krypton gas, if it is less than 0.1 meter square square meter per gram we will be using ethylene. So, let us see how this BET theory explains this calculation of the surface area.

So, this is the formula of BET equation as you can see P by V PO - P where this P is basically the pressure of gas at equilibrium with the solid you know with the with the solid in Pascal. And PO is the basically gas pressure require for saturation at the temperature of the experiment that is also measured in Pascal. V is the volume of adsorbed gas absorbed at pressure P in cubic meter. Vm is the volume of gas required for mono layer coverage over the complete adsorbent surface. And C is a constant which you basically calculate by using this formula whereas E1 basically shows the heat up adsorption of the first layer of adsorbent. And E2 is basically heat of liquification of the gas whereas R you know there is a gas constant and T is the absolute temperature. So, by using this formula of BET equation we can calculate the mono layer adsorb adsorption of nitrogen how let us see. So, if we once, so we know this formula, so once V m is determined by the linear plot between P V versus P by P0 because we know if we. So if we go back to our previous slide it will be clear that.

So, if we put a if we draw a graph using these 2 then this is basically the if it is the dependent and this is if this is the dependent and this is an independent variable, if we consider this, this is basically slope and this is the offset. So, basically while drawing a graph we can basically calculate these 2 terms and from there we can calculate the V m. So, once VM is determined by linear plot between these 2 terms P v P by V into PO - P and P by PO.

Then the specific surface can be calculated according to this formula given by Hiemenz that E = N a sigma multiplied by Vm by VO where the E is the specific surface area of the adsorbent measured in square meter. And N is basically Avogadro's number you know which is 6.02 into 10 to the power 23 molecules per mole and sigma is the cross sectional area of the adsorbent in square meter. VO is the molar volume in cubic meter and Vm is the volume of gas required for mono layer coverage over the complete adsorbent surface. So, this is how once we calculate Vm we can calculate the specific surface area ok.

Now the specific surface area of different minerals as you can see it varies from one clay mineral to another clay mineral. In case of kaolinite you can see it is from various from 7 to 30 meter square square meter per gram. Whereas in case of trioctahedral vermiculite and also montmorillonite you can see it is varying from 600 to 800 square meter per gram because of their high accessibility of the interlayers.

Remember in case of Kaolinite at the accessibility of the interlayer is very less, there is no interlayer because the structure is collapsed and there is no space interlayer space. However in case of montmorillonite in case of vermiculite there is huge interlayer space as a result that the specific area is also higher in case of montmorillonite and vermiculite as compared to kaolinite.

Now how to measure the total surface area, we also use the ethylene glycol monethyl ether which you know also known as EGME. Also they we use it commonly as an adsorbent for total surface area measurement. Now excess of EGME is applied what how we measured that, we basically apply excess of EGME to the adsorbent which has been dried over the P2O5 desiccant in a vacuum desiccator.

So, basically put the absorbent and then dry it in the vacuum desiccate in the presence of P2O5 desiccant and then we put excess amount of ethylene glycol monoethyl ether or EGME. Then all except the mono layer is removed using a vacuum desiccator containing calcium chloride as a desiccant. So when we remove the layers of this EGME then we can plot the weight of EGME retained on the solid on the solid as a function of time.

Because as the time will pass obviously the weight of the EGME which is written on the surface will go down and we can then determine when the weight of the EGME become constant. So, the mono layer coverage is assumed to be attain at this point when the weight of this EGME becomes constant. When it is reducing along with the time and becomes constant at a particular time then we can assume that we are getting the monolayer coverage.

Then the surface area is calculated according to this formula given by the scientist Carter et al. Where A is the specific area specific surface area in square meter per gram, Wg is basically the weight of the EGME retain by the sample after monolayer equilibrium, Ws is basically weight of P2O5 desiccant which we use to dry the samples before putting the excess amount of EGME.

And basically we know that 2.86 into 10 to the - 4 grams of EGME is required to form a mono layer on 1 square meter of surface. So, to once we get the total surface area from that surface area we can also calculate the internal surface area by just subtracting the you know the external surface area. So, this is how we can calculate internal surface area, external surface area and the total surface area.

The type of charges in the soil you have also already know there are 2 types of charges, already occur in the soil one is called the permanent charge another is variable charge. In case of permanent charge it is always occurred to isomorphous substitution as a result of isomorphous substitution excess of negative charge developed. And these negative charge is known as permanent charge this is a structural component you know this is a structural characteristics, so that is why it is called permanent charge.

It is also known as the constant charge and it does not vary why it is called a constant charge because it does not vary with the pH, it developed during the formation of the mineral. Another type of charge is there that is called variable charge or pH dependent charge. So, it is basically occur due to deep you know protonation and deprotonation of functional groups on inorganic soil minerals it basically and it basically changes with the pH.

So, basically at the edge of the mineral you know there are some you know hydroxyl groups are present. So, if the soil has high pH obviously the hydroxyl groups will be more prevalent. As a result of that one hydrozen or proton will go to meet with the excess of hydroxyl ions producing a negative charge in the pH. So, that will produce a negative charge, just opposite occurs in case of acidic soil.

In case of acidic soil there will be prevalence of H + ion, this H + will basically react with this OH and basically produce this positively charged OH2+. So, this is you can see it is variable from one pH to another pH condition, that is why it is called variable charge or pH dependent charge.

So, another important thing is known as the cation exchange capacities of secondary soil minerals. Cation exchange capacity the negative charge on the soil minerals is basically balanced by positive charge in the form of exchangeable cations. And cation exchange capacity is the total capacity of the solid soil to hold extendable cations, it is an inherent soil property and difficult to alter. And CEC determines the soil stability to hold nutrients and also provides a buffer against the acidification.

So, the soil which has more CEC will basically be considered as a nutrient rich soil because it can attract more cations. So, clear fractions and organic matter have more CEC than sandy soils obviously because of this negative charge development. So, if you see the difference of CEC for different clay minerals you can see kaolinite has the lowest CEC, talc has you know also the you know lowest CEC of less than one centi-mole per kg, kaolinite has also very low CEC and in case of trioctahedral vermiculite as well as montmorillonite you can see they have the CEC is varying from 100 to 200 or 80 to 150 centi-mole per kg of soil.

Because of huge amount of isomorphous substitution which is going on in the structure of these clay minerals. So, kaolinite basically CEC kaolinite varies depending on the impurity present in it, if few impurities present the CEC is as low as less than 2 centi-mole as pure kaolinite has various isomorphous substitution almost no isomorphous substitution, negative charge resulting from you know surface functional groups such as aluminum hydroxide. So, in case of kaolinite then whatever negative charge is present is due to the pH dependent charge because of the broken edges and the hydroxyl groups which are present in the broken edges.

So, in case of halloysite, pure halloysite has the little ionic substitution hence lower CEC it has association of halloysite with allophane also increases the it is CEC also exchangeable ammonium and potassium present in the interlayer is inflated CEC measurements. So, if you see the di you know vermiculite obviously di-octahedral vermiculite has more layer charge than smectite but less CEC due to presence of potassium, some amount of potassium present in the interlayer.

And K + as the smaller hydration radius and that fits snugly I have already told you it is a very small so it is fits very snugly in the interlayer space. And the attraction between the K + and clay's interlayer surface is more hence it is less available to exchange. And in case of trioctahedral vermiculite has calcium and magnesium in the interlayer. So, more CEC than that of di-octahedral vermiculite because they have no restriction for cation exchange.

If you see montmorillonite they have high CEC due to substantial isomorphic substitution and fully expanded interlayer. In case of mica they have more layer charge than vermiculite but lower CEC and also due to presence of potassium in the interlayer space, they have lower CEC. Although they have low you know more layer charge than vermiculite, they have low CEC because of the potassium ion in the layer space because of the lock structure. In case of chlorite although there are some substitution occurring in the in the layers. However due to the presence of the aluminum hydroxy or magnesium hydroxy layer lock structure the lesser CEC than expected can be found. In case of allophane aluminum substitute you know silicon So, lots of edge sites created therefore the CEC is very high like hallyosite adsorption of other salts also cause high CEC.

So, this is a reaction between this is a relationship between CEC and different types of clay minerals. One is one thing is very clear that as we go from mild weathering condition to intermediate weathering condition, so strong weathering condition cation exchange capacity goes down. And also the cation exchange capacity is highest increase of 2 is to 1 type of clay, intermediate in case of 1:1 type of clay and aluminum hydroxide and iron oxide they have the lowest cation exchange capacity.

Similarly there is a negative you know inverse relationship between the cation exchange capacity and anion capacity. As the cation exchange capacity decreases anion exchange capacity increases because in those minerals which have low cation exchange capacity they have more pH dependent charge. So, as a result of more pH dependent charge they produce some anion capacity. So, this is the relationship between weathering CEC and AEC.

So, d axis spacing you can see that it is another important aspect of differentiating different types of clay minerals we will be discussing these in details in our future lecture in our in our lectures in the last week that is while we will discussing about the module 12, how we can use the X ray diffraction to calculate these d axis spacing. Now d axis spacing varies from one clay mineral to another clay mineral.

It is lowest in case of kaolinite however it is highest in case of smectite also it is high in case of vermiculite. So, the d axis spacing is the basis for differentiating one clay mineral to another clay mineral and we can use the X ray diffraction technique to differentiate different types of clay mineral.

So, this is the gist of X ray diffraction analysis . This X ray diffraction analysis shows that there are different layers of atoms. In these different layers of atoms at you know repeating layers of atoms the distance is called the d axis d spacing. So, if we use the X ray diffraction analysis, X ray diffraction analysis this is the one incident x-rays, this is another incident x-ray, this is another incident x-rays.

So, when the x-ray hit one plane it get diffracted, so, this is diffracted x-rays. So, there is a term called constructive interference and destructive interference. When 2 waves are in phase we call it when they create this constructive interference as you can see and when they had 180 degrees out of phase they are producing the destructive interference, this is the example of destructive interference.

So, one thing is clear that to create a constructive interference between these 2 rays diffracted rays the distance I mean we generally it generally follows the Bragg's equation. So, it shares the Bragg's law says the 2 rays, so if it is considered ray 1 and this is considered ray 2, the 2 rays will constructively interfere, so they will basically constructively interfere if the extra distance ray 1 travel is a number of wavelengths further than what ray 2 travels.

So, let us consider this is the ray 1 and this is ray 2, so, you can see the extra distance this ray 1 travel is this BC + CD as compared to the ray 2. So, this BC and CD can be calculated, so BC + CD is basically n lambda. So, basically it is a whole number of wavelength further, so if we consider the wavelength of the X ray is lambda and it is whole number multiple so whole number we can calculate by n lambda n is an integer.

So, the extra distance it is calculating BC + CD we can calculate that BC + = CD = D sine theta. So, BC + CD we can see here it will be 2d sine theta. So, n lambda = 2d sine theta so this is called the Bragg's equation and based on Bragg's this equation we can calculate. If we know this if we if we know this theta, if we know this n, if we know this lambda we can calculate this d axis spacing and from this d axis spacing we can identify ok this is the clay mineral.

For example different clay minerals or different types of d axis spacing, for example kaolinite has less than 7.2 angstrom or 0.72 nanometer. The you can see these are the X ray diffraction peaks of kaolinite at first order diffraction peak and this is a second order diffraction peak. So, this is how we can identify different types of clay minerals through X ray diffraction.

For a x-ray diffraction we do different types of pre processing of the soils, all those are mentioned here, what type of you know what type of pre processing we do here. Also we prepare different types of slides for processing and we process the glass we process these clays we orient this clays in the glass slides. And then we saturated them we either potassium or magnesium excess salt are removed with water and different types of different types of treatments are given.

So, you can see there are different types of treatments K potassium saturation, magnesium saturations and also different temperature and how these different temperature varies their d axis spacing. So, from there you will have an idea if we have this table in front of you and if you see those peaks from the X-ray diffraction you can identify ok, we are seeing this peak at this point, so obviously this will be the peak of either mica, either kaolinite, either montmorillonite.

So, guys this brings the end of this module 2 we have discuss in details about the different inorganic components And clay minerals different types of other secondary minerals how they can be differentiated. This is the reference of this chapter there is environmental soil chemistry by Donald L spark you can you can get more information from this book. And hopefully you have learned some new information from this lecture and please feel free to email if you have any questions I will be more than happy to answer your question, thank you.