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Environmental Soil Chemistry

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Lecture-18

Soil Solution-Solid Phase Equilibria and Sorption in Soils (Contd.)

Welcome friends to this NPTEL online certification course of environmental soil chemistry and we are currently going through our week 4 of lectures and our topic in this week 4 is soil solution, solid phase equilibria and sorption in soils and today we will be, you know, today will be the third lecture of this week and but before discussing the materials in the third lecture.

I will just, you know, want to, you know, go for a quick recap of whatever we have discussed so far. So, so far we have covered the measurement of soil solution. And then we have covered the speciation of the soil solution. Then we have covered the ionic activity and activity coefficients, dissolution and solubility processes, surface complexes and so so basically we have covered up to dissolution and solubility process. And we have covered up to the stability diagram.

And so just to give you a quick recap of whatever we have covered so far we have discussed about the soil solution. And what is, you know, we have talked about briefly about the inner and outer sphere complexes. And then we have discussed about the dynamic equilibria reaction in soil and in other words, how the free ions as well as the complex forms of ions can move from soil solution to different pools and when, you know, all these movements are reversible.

So, they also can come back to the soil solution, how this process occurs. There is, you know, we have we have seen that. There are total 12 process through which these ion can move from soil solution to different pools and then come back to the soil solution again. So, then we have talked about the intensity factor and capacity factor.

And we have covered the main types of technique which we use for extracting the soil solution. Remember that it is the displacement techniques. We have talked about the centrifugation and saturation pastes. So, this is the column displacement we have talked about in our previous lectures. Then we have talked about how centrifugation can remove the soil solution for subsequent measurement.

And what are the other, you know, aspects of centrifugation we have talked about. And then we have talked about the saturation paste or saturation extract and how we can extract that soil solution to measure the ionic concentration in the saturated extract. Obviously, we have also talked about the speciation of the soil solution which is very important.

We have talked about the hydrolysis, how hydrolysis process occurs. And how these general complexation reaction between a hydrated metal and ligand and how it, you know, to form an outer sphere complex we have we have discussed this reaction. And then, we have talked about details about the speciation that means a mass balance equation for total concentration of metal ion in the soil solution can be given as a, you know, as a as a as a summation of the concentration of free hydrated metal ion species as well as concentration of metal ion associated with the remaining metal ligand complexes.

And then we have talked about some important stability constants, like conditional stability constant. And then, you know, thermodynamic equilibrium constant and what are the properties of thermodynamic equilibrium constant.

We have shown one reaction from there we have talked about the thermodynamic equilibrium constant. And then we establish a relationship between the conditional, we establish a relationship between the activity and concentration with the help of activity coeff, activity coefficient for a particular species.

And using that, we have established the relationship between the conditional equilibrium constant or conditional stability constant and thermodynamic equilibrium constant. And from there we have seen that thermodynamic equilibrium constant is related to the conditional equilibrium constant, where conditional equilibrium constant multiplied by ionic activity ratios, you know, multiple, you know, ionic activity coefficients, you know, they, when we when you multiply the conditional probability conditional active conditional stability constant with the ionic activity ratio.

Then we can get the thermodynamic equilibrium constant. Then we have we have discussed one numerical problem where we can calculate the concentration of different calcium species present in the soil solution from a basic soils. And then we have seen, you know, how how we can do that I have I have discussed in details. So, I am not going through in details again.

So, from there. So, we have already covered these things. Then we have talked about the ion activity and the activity coefficients, how we can calculate the ionic activity. What is the formula of the ionic activity, how we can calculate the ionic strength.

And how this ionic strength of different monovalent and divalent cation changes. And trivalant cation changes. And depending upon the concentration and when the concentration is higher, then how it form, it follows the Debye's equation. And then we have shown you the calculation of, you know, shown sample problems for measurement of I by for different different, different compounds like potassium nitrate as well as potassium sulfate.

And also we have identify, we I have shown you how to calculate the activity coefficient for a, you know, for cadmium ions at a particular temperature and with a particular ionic strength. Then we have talked about the dissolution and solubility. Remember the dissolution and solubility depends on the, you know, basically controls the weathering, soil formation and contaminant mobility.

And, you know, for different soil like calcareous minerals like gypsum dissolve relatively rapidly and congruently. And what is the incongruent reaction, we have talked. Then we have talked about the dissolution of the silicate minerals. And from there we have shown you how to use. You know, the solubility, how to calculate the thermodynamic dissolution constant, which is denoted by this K0 dis for and for a particular reaction when this gibbsite is reacting with a proton to produce the aluminum ion as well as water, how this thermodynamic dissolution constant can be calculated.

And based on this thermodynamic dissolution constant how we can calculate the thermodynamic solubility product constant. And what is the relation between the, you know, ion activity product and solubility ion activity product and the solubility product constant, and how it changes and how it can governs the solubility or, you know, precipitation of different mineral phases.

And then we have talked about the stability diagram, the stability diagram, gives us the answer for how whether a solid phase control the, how a solid phase control the concentration of an element in the soil solution and if it does what is the solid is. And then we have talked about this standard free energy formation how this standard free energy of formation can form can can be used to calculate the free energy accompanying the reaction.

And from there, considering the considering the, you know, considering the reaction of gibbsite with, with the proton. How we can calculate these delta G 0 r. And from there, how we can get the stability diagram. Remember, the stability diagram can be calculated based on these 2 that is log of aluminium for and as well as log of aluminium is in the y axis. Whereas, pH in the x axis.

And then I showed you how this stability diagram can be made for different aluminum and iron oxides or hydroxides and how we can differentiate their solubility based on the solubility stability diagram. So, similar diagram can be done in case of, I have showed you in case of kaolinite, you know, has a dissolution reaction of this where the kaolinite can be reacted with the 6 protons to produce aluminum, and silicic acid and water and this associated dissolution constant can be calculated as 5.45.

And from there, we can get this reaction simplified reaction as you can see here, log aluminum + plus 3 pH equal to 2.73 - log of H4 SiO4, this log of H 4 SiO 4, also known as the pH for SiO 4 or it is a negative logarithm of pH for SiO 4 basically negative logarithm of silicic acid concentration.

So, if we plot the logarithm of silicic acid and the logarithm of Al 3 plus pH in the y axis and logarithmic of a logarithm of silicic acid in the x axis, we can see the stability of different, you know, clay minerals, for example the vertical lines as you can see here, they are basically producing the silica quartz. Because they are straight line because in their structure there is no aluminum and, you know, their dissolution reaction is independent of this aluminum. So, they are basically the straight line.

However, the stability diagram are very useful predicting the other, you know, stable solid phases. For example 2 is to 1 minerals like montmorillonite are stable only when the concentration of silicic acid in solution is controlled by solid phases more soluble than quartz.

And you can see here that here as the, you know, pH decreases as the pH decreases from 11 10 to 9, and you know, this condition that is log of aluminum + 3 pH as it decreases, we are getting from illite to montmorillonite to ultimately kaolinite, if you remember the stability of different clay minerals which I have discussed in our week 2 of lectures, obviously the illite and montmorillonite are the earliest stages of weathering weather at the advanced stages of weathering we get this kaolinite.

And one important observation is that, this is consistent as kaolinite is the most dominant phyllosilicates mineral observed in acid soil, that means more acidic the soil, you will see the dominance of kaolinite that receives a substantial amount of rainfall. So, this kaolinite is present in the soils which, which goes through extensive leaching or substantial amount of rainfall, under more extreme leaching condition, you can see under more extreme leaching condition that means, when the, you know, you know, H 4 SiO 4 is less than 5, is less than 5.3.

That means, when it is it is less than 5.3 that means in this region, obviously you will see that only this gibbsite is more stable than that of kaolinite. So, as the silicic acid potential, as the silicic acid concentration is going down and pH is going down, then we can see the, you know, the predominance of gibbsite, instead of kaolinite. So, this shows that this is the basis through which we can develop the the presence of different, you know, clay minerals at different stages of weathering.

Whether it is an advanced level of weathering when there is an extensive leaching, we will see kaolinite in the early stages of weathering. We will see illite and the intermediate stages of weathering we will see the montmorillonite. Now we will go through the, we will go to the adsorption. Now adsorption can be defined as the accumulation of the substance accumulation of a substance or material at an interface between the solid surface and the bathing solution.

Remember that absorption affects the electrostatic properties example, for example coagulation and setting of suspended particles and colloids. Now both physical and chemical forces are involved in adsorption of solutes from solution. Remember adsorption is a surface phenomena, whether absorption ab absorption is an internal phenomena, where as adsorption is a surface phenomena, and it can be governed through both physical forces as well as chemical forces in the physical forces

Vander Waals forces and electrostatic outer sphere complexes are important. However, in case of chemical forces ligand exchange mechanism, covalent bonding and hydrogen bonding are important. As you can see in this picture you see it is a physical adsorption and physical adsorption basically occurs through these either physical process or chemical process, however, the chemical absorption the physical adsorption you can see that it basically goes, you know, mediated through either Vander Waals forces or electrostatic outer sphere complex as you can see it is electrostatic outer sphere complexes.

Outer sphere complexes where, where there is a presence of internal water molecule. However, in case of chemical adsorption, you can see either formation of covalent bonding or hydrogen bonding or ligand exchange reaction. So, although they are adsorption but depending on the nature of adsorption, we can differentiate either it is a physical type of adsorption or chemical type of adsorption.

Now surface complexes, what are the surface complexes? When the interaction of a surface functional groups with an ion or molecule present in the soil solution creates a stable molecular entity. It is called a surface complex and the overall reaction is referred to as a surface complex system. Remember, in the surface complexes can be, you know, there are 2 types of surface complexes we have already covered them briefly. They are outer sphere complexes and inner sphere complexes.

Now these shows a clear, more clear picture of outer sphere complexes and inner sphere complexes. The first picture shows the inner sphere complex where the potassium is, you know, it is placed in the interlayer space of vermiculite, it is producing a lock structure. Now you can see in this potassium, you know, these are these are inner inner inner surface complex.

However, this is the outer surface complex can be found in case of montmorillonite whereas the calcium is present surrounded by water molecules. So, these are 2 different complexes, one is the inner sphere complexes, and in case of outer sphere complex. In case of inner sphere complex, you will not see there is an intermediate water molecule. However, in case, I am sorry, this is an inner sphere complex there is no intermediate water molecule.

However, there is an outer sphere complex where the outer, you know, intermediate water molecule. So, these are the examples of inner sphere complexes and outer sphere complexes formed between metal cations and siloxane ditrigonal cavities on 2 is to 1 type of clay mineral.

We will see these cavities. Now, now talking about the outer sphere complexes we all know that if you have water molecules present between the surface functional groups and the bound ion of the molecule the surface complexes term is outer sphere. Now remember in these outer sphere complex it involves electrostatic columbic interactions. Now, these outer sphere complexes are weak, as compared to the inner sphere complexes.

And complexes is a, complexation is rapid process that is reversible and binding is basically it is basically covalent or ionic bonding. Now adsorption occurs only on surface of opposite charges to the adsorbate. Obviously, this type of adsorption can occur in between the opposite charges, now I am showing you one inner sphere surface complex, now inner sphere surface complex if there is no water molecule present between the ion and molecule and the surface functional groups to which it is bound, then it is known as the inner sphere complex.

Now remember the inner sphere complex can be, you know, can be monodentate. By monodentate, it means that the metal is bounded to only one oxygen, and can be bidentate, where the metal is bounded to 2 oxygen and can be mono nuclear and bi nuclear are, you know, slower and also they are not reversible. So, inner sphere complexes are not reversible, they are slower as compared to the outer sphere complex, they can form either monodentate complex or bidentate complex. So, you can see here, these are schematics illustration of the surface structure of arsenic.

You can see here, it is a monodentate complex, and in the monodentate complex this arsenic is basically bounded with this iron atom with a single oxygen. So, this is a monodentate complex, in case of bidentate complex you can see arsenic is bounded to 2 oxygen and this is a mono bidentate complex. However, this is a mono nuclear. However, this is also binuclear bidentate complex where arsenic, is is linked with 2 oxygen, which is basically coming from 2, you know, 2 iron atom which is also in terms of linked with the 2 different iron atoms .

So, it is bidentate binuclear complex. Now it is a monodentate complex you can see chromium, which is bounded to the single oxygen, which is also in terms bounded with the iron to form inner sphere complex. So, it is a monodentate complex. This is a bidentate complex you can see, it is a mono nuclear bidentate complex for chromium and also this is a bidentate binuclear complex of chromium, where the chromium is attached to 2 oxygen which are in turn, attach to 2 different iron atoms.

So, this is the example of different types of inner sphere surface complexes. Now apart from these monodentate and bidentate complexation, we can also define these surface complexes by assuming a polyhedral approach. Now, a polyhedral approach can be used to determine the molecular configuration of ions sorbed on mineral surfaces. Now possible configuration include these 4 types of possible configuration you can see, one is a single corner monodentate, mononuclear.

We call it single corner monodentate mononuclear complex, in which a given octahedron shares only 1 oxygen with another octahedron. So, 2 octahedron are basically complexed by sharing 1 oxygen. Second is the double corner bidentate binuclear complex in which a given octahedron shared 2 nearest oxygen with 2 different octahedron. So, you can see, 1 octahedron sharing 2 nearest oxygen to 2 different octahedron. So, we call it double corner bidentate binuclear.

Because they are using that they are attaching with the 2 oxygen and with the 2 different octahedrons. Third is an edge bidentate mononuclear complex in which and octahedron shares 2 nearest oxygen with another octahedron. So, it is called it is bidentate because it is sharing the 2 oxygen, and it is a it is called the edge, because it shares 2 oxy nearest oxygen with another octahedron.

And the fourth one is a face tridentate mononuclear complex in which an octahedron share 3 nearest, you know, 3 nearest neighbors with another octahedron. So, that is why it is called tridentate mononuclear.

Now, it will give you a more detailed picture of this polyhedral approach, you can see there is a finite number here, we have seen an example of characteristic iron element, you know, aluminium lead separation for Pb II adsorb to AlO 6 octahedra, AlO 6 octahedra, now here we are assuming that these lead ions are, you know, having a trigonal pyramidal coordination geometry. As you can see, these are trigonal pyramidal coordination geometry.

So, here you can see corner sharing mono nucleate mononuclear monodentate. So, here this is a monodentate and this is a mononuclear and also corner sharing bridging binuclear bidentate you can see bridging bidentate and binuclear since it is attaching which 2 Al OH, Al O 6 octahedron. Third one is edge sharing mononuclear bidentate. So, here you can see it is sharing the edge, but it is bidentate because they are attached to 2 oxygen.

And this is a mononuclear octahedron, and also face sharing mononuclear tridentate so you can see it is share, it is linked with 3 oxygen, you know, 3 oxygen atoms which are basically attached to 3 corners of a face of an octahedra. So, basically it shows the mononuclear tridentate octahedral coordination. So, apart from that one another thing is important, you can see that each linkage resulting in a characteristic lead aluminium distance.

So, lead ions could absorb either in monodentate bidentate or tridentate fashion, we are clear from this polyhedral approach representation of the surface complexes.

Now remember that the sorption mechanism of metals and soil minerals are, you know, they have, you know, you know, each and every metal can have multiple sorption mechanism on soil minerals.

For example you can see here, in case of cadmium when it is when the sorbent is magnetite we can see inner sphere complex, in case of Al 2 O 3 we are getting multinuclear complexes. And in case of in case of silica we can get in cos, you know co-hydroxide precipitates cobalt hydroxide precipitates. And in case of rutile, you can see small multinuclear complexes, in case of kaolinite these cobalt produces cobalt aluminium hydroxide surface precipitates.

This chromium, when the adsorbent is goethite hydrous ferric oxide, it produces inner sphere chromium hydroxide surface precipitate, in case of silica it produce inner sphere monodentate. So, you can see, depending on the sorbent and depending on the metal, it varies in its sorption mechanism. So, for each metal we can get multiple sorption method mechanism for multiple different sorbents, and the sorption mechanisms are given here and this sorption mechanism have been well established by the research by the soil scientists.

Now, let us consider another important thing that is basic adsorption isotherms, when the process of adsorption adsorbate get absorbed in the on the adsorbent. So, if is consider this adsorbent is basically soil in our case and these adsorbate is basically the ions or metals which are present in the soil solution, then in the adsorption process these metal get absorbed into the soil surface and the opposite reaction is known as desorption reaction.

Where those adsorbed metal ions can, can come back, you know, come back to the soil solution from the from the soil surface, from the clay surface. So, this is the adsorption and desorption are opposite process. So, you can see here, it is represented by A + B going to formation the AB complex and then reversible to A + B again.

Now adsorption isotherm, what is called adsorption isotherm, the relation between the activity or equilibrium concentration of the adsorptive and the quantity of adsorbate on the surface at constant temperature is usually employed to describe adsorption. So, adsorption isotherm, why it is called isotherm, because this relationship is determined at a constant temperature, iso means constant and ther means temperature.

So that is why it is known as isotherms and we basically see the relation between the activity of the equilibrium concentration on the adsorptive. In other words the concentration of a particular ion in the solution and their quantity in the adsorbate on the surface. So, basically, the there. This, the partition or the concentration of a particular metal ion in the soil solution, as well as on the clay surface is basically denoted by adsorption isotherms at at a constant temperature.

So, basically we use this adsorption isotherms to describe the adsorption process. Now first solute adsorption isotherm was described by scientists Van Bemmelen in 1888 and in general the adsorption can be described by 4 general types of isotherm. One is called S-type, then L-type, then H-type and C-type, let us discuss them one by one. Now first of all, this S-type isotherm and we can see if we if we if we put the, the concentration of a particular species in the soil solution.

For example and their concentration on the clay surface and concentration of the concentration of their adsorb fraction in the clay surface. So, we will see that as the concentration in the soil solution increases we will see this S-type of curve. So, basically the slope initially increases with adsorptive concentration or in other words, concentration of a particular species in the solution, but eventually decreases and becomes 0 at vacant adsorbent sites are filled.

So, obviously you can see, initially it increases. So initially, it increases with adsorptive. So initially it increases with adsorptive concentration. So as we increase adsorptive concentration usually it increases. And then, after a certain period of time you will see decreased and ultimately goes to 0 as the vacant adsorbent sites are filled. So, at low concentration, the surface has a low affinity for the adsorptive, which increases at higher concentration.

So, in other words, at low concentration when we are seeing at low concentration, for example in this area the concept, the surface has a low affinity for the adsorptive or the species, which increases as the for with the higher concentration. So, as we are going through, you can see the steep slope here, so the concentration is getting high. So, this is called the S-type isotherm.

Now, another is called the L-shaped or Langmuir isotherm. Now Langmuir isotherm is basically showing the decreasing slope as concentration increases since vacant adsorption sites decreases as the absorbent becomes covered. So, you can see here as the concentration is increasing we are seeing, there is a, you know, there is a con, the slope is initially increasing and then it is decreasing.

So, basically there is decreasing slope as concentration increasing by, you know, shows the vacant adsorption sites decreases as the adsorbent becomes covered. So, basically this Langmuir adoption isotherm is basically for monolayer adoption we will see in, we will see in details when we will discuss the Langmuir isothermal Langmuir equation in the details. So, basically it is for monolayer adsorption and as the adsorption site is become covered.

Then obviously there will be less adsorption and ultimately, the, the slope will be further decreased. So, basically, basically, this is basically explained by the high affinity of the adsorbent for the adsorptive at low concentration which then decreases as concentration increases. So, this is the example of L-shaped Langmuir isotherm.

The third one is called H type or high affinity isotherm. So, basically these H-type or high affinity isotherm shows strong adsorbate-adsorptive interaction such as inner sphere complex, we know that inner sphere complex is a highly stable and there is a strong bond. So, here you can see with the smallest increase in adsorptive concentration or in other words smallest increase in concentration of a particular ionic species, there is a steep increase of the adsorption.

And this is showing the strong adsorbate-adsorptive interaction. And this is an example, this is basically showing the high affinity of the inner sphere complexes. The fourth one is called the C-type isotherm and it basically showing the partitioning mechanism. Now here one thing is clear that adsorptive ions are partitioned between the interfacial phase and the bulk solution phase, without any specific bonding between the adsorbent and adsorbate. So, as it is increasing the concentration of the absorptive, we can see the adoption is linearly increasing.

And basically, adsorptive ions are partitioned here in the interfacial phase and the bulk solution phase, we will see these in details, while we will discuss the diffuse double layer okay. Now adsorption experiments, how we do adsorption experiments. Now in case of adsorption experiments are basic they are basically carried out by equilibrating, that means shaking or stirring an adsorptive solution of a known composition and volume with a known amount of adsorbent.

For example in case of soil we take a known amount of soil and then we shake or mix with a known volume of a particular solution containing a particular species of ions at a constant temperature. And pressure for a periodic for a period of time such that at equilibrium, such that an equilibrium is attained, so we basically stir or shake it for sufficient amount of time so that to attain an equilibrium.

However, adsorption reaches a at the equilibrium state the adsorption reaches a steady state or no longer changes after a period of time. So, at that time at that, at that time, we can see that the equilibrium has been attained. Now the pH and ionic strength are also controlled in most adsorption experiments. Now after equilibrium is reached. Then what you do, then the adsorptive solution is separated from the adsorbent by either centrifugation, either by settling or filtering and then analyze.

We know how to settle them, you know how to how to extract them, either we can do it by centrifugation, either we can do it by saturation extract. So, different ways we can extract that soil solution and then we measure the particular ion concentration and from there we can calculate the adsorption or amount of adsorption. So, the degree of adsorption can be calculated by using the following mass balance equation. So, here, C 0 V 0 – C f V f by m. So, here q equal to q.

So, q is basically amount of adsorption. In other words, it is adsorbate per unit mass of adsorbent or in other words, adsorbent means is the concentration of a particular species per unit mass of mass of soil in molecule per kg. Now C 0 and C f are basically the initial and final adsorptive concentration or the solution concentration in mole per liter. And V 0 and V f are basically initial and final adsorptive volumes, it later and m basically represents the mass of the absorbent in kilogram.

So, this is how we can do different types of adsorption experiment. So, guys you have learned in details about different types of inner sphere complexes and outer sphere complexes and how they form the surface complexes. What is the mononuclear and then what is the binuclear, bidentate, mononuclear, bidentate.

And then what is the tridentate coordination. Then we have seen the polyhedral approach for assuming these quad this, surface complexes.

And then we have discussed about the different, 4 different types of adsorption isotherms and I showed you how to do the adsorption experiment. So let us wrap up our lecture here. In the next lecture, we will be talking about specific adsorption isotherms or, you know, Langmuir equations. We will be talking about freundlich equations and so on so forth then what is their implication. And also we will be discussing about the diffuse double layer. Thank you very much. Let us meet in our fourth lecture. Thank you.