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Environmental Soil Chemistry

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Lecture-16

Soil Solution-Solid Phase Equilibria and Sorption in Soils

Welcome friends to this NPTEL online certification course of environmental soil chemistry and today we are going to start our week 4 or module 4 lectures, and the topic of this module 4 is soil solution-solid phase equilibria and sorption in soils. So, in this week, we will be covering very important aspects of different, different soil chemistry aspects. And we will be talking about different solubility.

And then we will be talking about different adsorption processes, adsorption isotherms and we have will be also talking about different diffused, diffuse double layer models and different, you know, electro kinetic phenomenons. For example, we will be talking about zeta potential. So, this week is very important as far as the soil electrochemistry as well as soil, you know, solutions and dynamics are concerned.

So, in this week, we will be basically talking about these concepts, we will be covering this concept, first of all we will be talking about measurement of soil solution, how we generally measure the soil solution, then we will be talking about the speciation of the soil solution and then, we will be talking about ion activity and activity coefficients and then we will be talking about dissolution and solubility process.

Then we will be talking about surface complexes, what type of complex is generally, you know, different metal forms with the soil surface, with the soil with the soil particles and then we will be talking about adsorption isotherms, then equilibrium based adsorption models, then we will be talking about sorption of metal cations and sorption of anions and then surface precipitation we will be talking about. And finally, we will be talking about speciation of metal contaminated soils. In this first lecture basically we will be covering the measurement of soil solution. And we will try to cover the speciation of the soil solution. So, let us start.

So, what is basically soil solution? Soil solution is the aqueous liquid phase of soil and its solutes and it is basically, you know, in case of soil, you can see the major solutes are, are the ions which are present in the soil solution, they may be cations, they may be anions okay. So, these ions occur either as free hydrated ions, like aluminium 3+ or as various complexes with organic and inorganic ligands.

So, what are the ligands we have already covered in our previous week lecture, when we are talking about, when you talked about the chemistry of soil organic matter. So, you have a basic idea about the ligands and how they form. And these ions either occur as the free hydrated ions like aluminum which we also discussed in our last lecture and as various complexes with organic inorganic ligands, you know, the ligands could be either organic or inorganic.

So, total ion concentration in soil solution thus can be considered as a cumulative, you know, it is basically some of the free ions and as well as the complexed ion and various complex chemical reaction interact with each other, you know, reactions interact with each other through the soil solution. So, these are just some basic points about the soil solution.

So, let us talk about the inner and outer sphere complex. Now, inner sphere complex is basically when no water molecules are present in between the metal ions and the ligand and they interact directly in the solution. As we can see here, you know, basically and they are also tightly bound. So, this is the inner sphere complex and you can see that here these, you know, this iron atom is basically directly linked with or this metal ion or iron ion is basically linked with these ligands and without the presence of water molecules in between these.

So, although you can see the water molecules that present surrounding the iron, but in the link which is directly linking with the ligand, there is no presence of water molecule. And now, outer sphere complex is water molecule, when water molecules formed bridge between the metal ligand metal ion and the ligand. So, as you can see here, this is again the metal ion which is surrounded by 1 2 3 4 5 6 water molecules.

And these water molecules basically forming the hydrogen bond with these ligands. So, due to the presence of these, you know, water molecules, you know, as a bridge between the metal ion and the ligand, they are called as outer sphere complex. So, this is inner sphere complex and this is the outer sphere complex. Remember, the outer sphere complex are not tightly bound, as the inner sphere complexes.

Because the inner sphere complex, the bond is directly between the, between the iron as well as the ligand. However, here the water is acting as a bridge. So, obviously the strength of the, you know, strength of the binding strength varies from inner sphere complex to outer sphere complex.

So, so in case of inner sphere complex and outer sphere complex remember that an uncharged outer sphere complex is referred to as an ion pair, for example, in case of calcium and sulfate ions are known as to form an ion sphere, ion pair of calcium sulfate. So, soil solution consists of a variety of ion species either in complex or noncomplex forms.

Now, what is the dynamics of equilibrium, you know, equilibria reaction in the soil. It will be very clear if you see in this, in this diagram. And one thing is clear that the solution, in the soil solution we have already discussed, it is basically the free ions as well as the complexed ion. And these free ion and complexed ion can move in different pools and different, you know, different, different pools and these are basically mentioned here.

So, let us start with the first, first of all, the plants can take up the nutrients or ions from the soil solution which we already see here by pathway 1, and at the same time, plant exudates a substance secreted by the plant. So, basically they reside into the soil and from there, there will be movement of ion in the soil solution, second, third is ion can move, ion from the soil solution are sorbed on the organic and inorganic components of the soil.

So, sorption means, it is basically either there are 2 types of sorption either adsorption or absorption. Though in both these conditions absorption is an internal phenomena, however adsorption is a surface phenomena. So, the ions in the soil solution gets sorbed on different organic and inorganic components of the soil and however, this sorbed ions are released back into the soil solution also. Now, the So, these are the first 2, you know, first 4 pathways through which the ions can move from this soil solution to different pools.

Now, also, if the soil solution is super saturated, let us considered the soil solution is super saturated. Then with mineral in the soil, that mineral basically precipitates. So, this fifth pathway is basically showing the precipitation of the ions in the forms of solid phases and minerals and reversibly if the soil solution is under saturated with any minerals in the soil, the mineral dissolves and then go back to the soil solution to maintain an equilibrium until this equilibrium is reached.

So, you can see this is how these, you know, ions move to the solid, you know, precipitates and further, you know, dissolves to maintain, dissolves to go to the soil solution to maintain the equilibrium. Now, so first 6 pathway we have discussed. Now 7 says that ions in the soil solution can be transported through the soil into groundwater removed by surface runoff.

So, the ions can move directly to the, you know, to the groundwater through solute transport and then from there they will, you know, they can and also they can be removed through surface runoff and in the reverse simply through evaporation and drying the, you know, upward movement of ions into the soil solution may also happens through this pathway 8.

Now, pathway 9 says that microorganisms can remove ions from the soil solution, because you know, microorganisms are known for different chemical conversion of ions. So, they basically takes up different ions and then convert them. Now when the microorganism die, organic matter decomposes and ions are released into the soil in the form of mineralization. So, it can be either immobilization, you know, 9th pathway is showing basically the, basically showing the immobilization in the plant under the organic matter and microorganisms body.

And when they die, there will be mineralization, so that these mineral further goes to the soil solution, and 11th pathway is basically showing that the gases may be released to the soil atmosphere and gases maybe dissolved in the soil solution. So, this is another way through which the, you know, the ions can move from soil solution to the atmosphere and vice versa. So, this is basically giving an idea about the movement of different free and complexed ions from the soil solution to different pools and their movement and their reversible movement directly back to the soil solution.

Now, when we talk about the measurement of soil solution, there are 2 factors we need to consider. One is called the intensity factor, another is the capacity factor. Now what is the intensity factor? Intensity factor basically says the concentration of a particular ion in this soil solution, whereas the capacity factor, basically denotes the ability of solid components in the soil to resupply an ion that is depleted from the soil solution.

Now we have already seen the capacity factor in the last diagram, wherever we have seen that the concentration of a particular soil solution, particular ion goes down into the soil solution to maintain an equilibrium from the precipitate or solid phase precipitate minerals or solid phase, the minerals can dissolve and then they basically supply that ion back to the soil solution to maintain an equilibrium.

So, that is the capacity factor. Now intensity factor measurement is very important in predicting and understanding various reaction in the soil environment. However, measurement of intensity factor in situ is very difficult, obviously, the intensity factor, talks about the concentration of a particular ion which is intact is very difficult to measure in situ depends on site. So, the actual constant, so also the actual concentration of an ion species in the soil solution varies with changes in soil moisture content. So, these are some of the factors which basically says that intensity factor calculation is little bit problematic.

So, the main, 3 main types of techniques we generally follow to extract the soil solution at as far as, you know, Adam and Wolt, who have given, you know, different process. First of all is called the displacement technique. Second is called the centrifugation and so, the first one is displacement technique. Second one is centrifugation. And the third one is called the saturation process or saturation extract. So, we will see them one by one.

So, let us first concentrate on the displacement process. So, displacement process basically we, you know, as is, as a soil scientist we generally use column displacement to make, to measure the concentration of ions, or intensity factor. For example, a field moist soil as you can see in this picture, a field moist soil is packed into the glass column and displacing solution is added. So, you can see it is a leaching solution or displacing solution.

So, we are adding this displacing solution at the top of the packed column, packed soil column through peristaltic pump and this leaching solution or displacing solution, which is basically essentially water is collected, I mean, basically, you know, when the, when when we are passing this leaching solution, this leaching solution will pass through this soil column and then will be collected at the bottom.

So, this called the displace solution, which is essentially water. So, basically they collect at the bottom of the, of the glass column and analyze for its concentration. And this is the most reliable method however tedious and time consuming. So, here you can see basically we are adding a leaching solution. This leaching solution is leaching down all the elements or all the ions which are present in the soil, and before that, the soil is packed inside this glass column.

And then these ions are moved down or leach down and basically collected at the bottom and then further we are measuring. So, this is the most reliable method however they are tedious and time consuming. The second method is called the centrifugation method. So, centrifugation involves the application of centrifugal force to separate particles based on their size, shape, density, viscosity and rotor speed.

Generally we apply more than 1 mega Pascal of pressure from, you know, from 30 minutes to around 2 hours, so more dense components move away from the axis of the centrifuge, and vice versa. And the larger the size and density of the particles, the faster they are separated from the mixture as you can see, before centrifugation you can see the particles are suspended.

However, after suspend after the centrifugation, you can see the particles has settled down and forming the pellets and obviously more dense components as you can see, they will move away from the axis, and then they will form the pellets. So, in this way we can separate out different, you know, different particles, based on their size, shape, density, viscosity and rotor speed.

So, the centrifuge, also in case of centrifuge, you know, there is a term called immiscible liquids. So, when 2 liquids are completely insoluble in each other, they are known as immiscible liquids. So, though it is a mixture, 2 different phases are present in the liquid separately. So, during centrifugation an immiscible liquid such as carbon tetrachloride or ethyl benzo benzoylacetate is added to the soil to physically remove the soil solution.

As you can see, basically, in case of centrifugation we apply these liquids such as carbon tetrachloride or benzoylacetate or ethyl benzoylacetate to the soil to physically remove the soil solution without being mixed into the soil solution that is essentially water. So, the immiscible liquid passes through the soil and then the soil solution is displaced upward. Since these two, you know, so, this is these two liquids are immiscible to each other, they will not mix they will not be mixed with each other.

And as a result they will displace each other. So, when we are passing this immiscible liquid that passes through the soil and displace the soil solution. So, the displaced soil solution is collected and filtered through a phase separating filter to remove the traces of immiscible liquid. And further it is filtered through a 0.2 micron membrane to remove the suspended clay minerals. So, you can see in this way by adding a displacing liquid or adding an immiscible liquid, we are basically replacing the soil solution, not only the replacing soil solution then by filtering, we are removing the traces of the displacing solution. And also, we are removing the suspended clay particles. And this is basically relatively simple and equipments are also easily available in most of the chemistry labs.

Now the third one is called the saturation extract. So, distilled water is added to the soil in a beaker and stirring with a spatula, as you can see here, and beaker is tapped occasionally to consolidate the soil water mixture and saturation is achieved when the soil glisten and as you can see in this picture. The soil is glistening, so you can see that the soil is saturated that means all the pore spaces are filled by water.

And then from the, you know, And also during the saturation soil drops freely, you know, soil drops freely from the spatula and the soil flows together with the separated with the, you know, with the spatula, and then it is then allowed to stand for 4 to 16 hours prior extraction to basically to, to basically homogenize, and also to equilibrate, and then the soil paste is then transferred to the funnel containing the filter paper.

And then the funnel is connected to a flask, generally we have, you know, then this funnel is connected to the flask, and we apply the vacuum, then the filtrate is basically collected. So, what happens again step by step we are basically adding the water, making a saturated paste, keep it for the equilibration for 14 to 16 hours, after that we are putting into the funnel, and then applying the pressure to suck out the, you know, dissolved ions through the leaching solution or through the solution which is basically filtered.

And then, we are basically measuring the concentration of ions in that filtrate. So, this is how the saturation extract basically occurs. Now average ion composition of soil solution, obviously we have seen that calcium is the most predominant metal cation in the soil solution, however, nitrates, chlorides, sulfates are the most common anions or ligands in acidic soil. And also remember that the carbonate is the most predominant anion in the basic soils. And basically in the basic soil you will see the precipitation of calcium carbonate.

Now, the speciation of soil solution, it basically refers to the determining of the, determining the distribution of the ion in their various chemical forms. So, when we can determine okay, these are the ions and these are their forms, which are present in the soil solution we can tell that we have made the speciation of the soil solution. Now ions in the soil solution can form a number of species due to the hydrolysis, complexation and redox reactions. You have already know what is hydrolysis, what is complexation and redox reaction. Let us see.

Now let us first with the, let us first discuss the hydrolysis process. Now hydrolysis involves the splitting of an H + ion or a proton from a water molecule which forms an inner sphere complex with a metal ion. So, the general hydrolysis reaction from a hydrated metal ion is given as M H 2 O x n+ and from there we can get these 2 species where this is basically the hydrated metal ion. This is the hydrated metal ion.

And n basically, generally n basically says the charge on the metal ion, where x is basically the coordination number. And here, y is basically the number of protons released into the solution. And so basically and this is the intensity factor. So, let us see some important based on this.

If you see the complexation, the another process. In general, the complexation reaction between a hydrated metal, this is the hydrated metal and the ligand which is termed as, L 1- to form an outer sphere complex is.

This is the outer sphere complex. So, basically this is the hydrated metal + ligand, forming outer sphere complex where a, b, c, and basically a and b, now there is no c and d, a and b are the stoichiometric coefficient. We have already discussed stoichiometric coefficient. These are the degree to which the chemically, you know, chemical species participate in a reaction.

So, this is a complexation. And in case of speciation this soil solution analytical it is little possible to determine all the individual ion species that can occur into the soil solution, I have already told you that measurement of in situ, you know, measurement of intensity factor is somewhat difficult. So, to identify the species ion association or speciation model must be applied using the total concentration data for each metal and ligand in the soil solution.

So, let us see how we do that. So, a mass balance equation, let us consider a mass balance equation for total concentration of a metal ion. Let us consider this metal ion, this is the metal ion in the soil solution phase is given by, this is the mass balance equation, where this M n+ is basically concentration of the, this M n+ is basically concentration of free hydrated metal ion species, and this M ML is basically concentration of metal ion associated with the remaining metal ligand complexes.

So, when we combine these two forms. One is the hydrated metal ion species, another is the concentration of metal ion associated with the remaining metal ligand complexes, we will get basically the total ion, which is present in the total of that particular ion which is present in the soil solution. So, the ligands can be inorganic anions or humic substances like humic acid and fulvic acid we have already seen that previously.

Now, so similar mass balance equation can be formulated for total concentration of each metal ligand in the soil solution. So if we consider, there are several elements or several metals which are present in the soil solution, we can develop this mass balance equation for individual metals, so each metal ligand complexes and associated conditional stability constant, which you have already seen during our discussion during the organic chelates.

So, the conditional block, you know conditional stability constant varies with electrolyte concentration we have also seen that. However, these conditionals stability constant of inorganic complexes can be related to thermodynamic equilibrium constant K 0. Now, this K 0 is independent of electrolyte composition at a particular temperature and pressure. So, although this conditional stability constant varies with electrolyte concentration, this K 0 or thermodynamic equilibrium concentration constant, you know, K is basically independent of electrolyte composition at particular temperature and pressure.

So, what is the relationship between these two constant, one is K condition that is conditional stability constant, and then thermodynamic equilibrium constant. So, basically for any reaction if you see that is a b c d are basically the stoichiometric coefficients. So, at thermodynamic equilibrium, a thermodynamic equilibrium constant K 0 is basically given by this, this formula where this a b c d as, you know, these are the stoichiometric coefficients.

And these a b c d are chemical species whereas this parenthesis refers to the chemical activity of the species. So, chemical activity of c to the stoichiometric coefficients power, and then the chemical activity of d to the power, stoichiometric coefficients corresponding stoichiometric coefficients by the, you know, concentrate, or the chemical activity of a power, to the power of their corresponding stoichiometric coefficients at the chemical activity of b with to the power of their corresponding stoichiometric coefficients. So, this is the relationship. However, so, how to get the relationship between K 0 and K condition.

So, the thermodynamic equilibrium constants are, excuse me, let me just just go back last slide so. So, the thermodynamic equilibrium constants are independent of concentration of the electrolyte. We have already seen, because they, because they are expressed in terms of activities, rather than concentration, since they are expressed in terms of activities as you can see, rather than concentration.

So, they are independent, they are basically are independent of concentration of the electrolyte. Unfortunately, the activities of the ions in the solution cannot be measured directly, which we have already, already discussed. So, fortunately the activity and concentration of an ion in a solution has a relationship and this relationship is basically, this one.

So, if you see that the activity of a particular ionic species is basically the multiplication of the concentration of that ionic species in the soil solution in mole per liter into their single ion activity coefficient for species B. So, if we multiply the, the concentration of specific ion in the soil solution with their corresponding ion activity coefficient, then we can get their, we know, their activity of that particular specific ion.

So, rewriting the previous equation using concentration, rather than activities we can see that, we know, that this is the equation, so we can, we can just multiply, we can just rewrite this in terms of this, in terms of active this activity we can we can we can express this as a multiplication between the concentration and the activity coefficient concentration activity coefficient, concentration activity coefficient, concentration activity coefficient.

And from there we can simplify this. And now, we know that these term equals to the conditional stability constant. So, this is how this K 0 is basically conditional stability constant multiplied by this fraction. So, conditional probability stability constant is also known as conditional equilibrium constant. So, a thermodynamic equilibrium constant is equal to the conditional equilibrium constant multiplied by this fraction of intensity factor.

So, basically, the ratio of activity coefficients were as we have seen, relating the K condition to the K 0. So, as we have seen from here from this equation so the value of the activity coefficient and hence, the ratio of the activity coefficients which is this, changes with the changes in electrolyte composition. So, in very dilute solution, the activity coefficients approaches to 1. So, these total fraction will approaches to 1.

Hence, in that condition, the thermodynamic equilibrium constant will equal to the, to the conditional equilibrium constant. So, in case of very dilute solution, the activity coefficient approaches 1. So, this fraction becomes 1, then conditional stability constant and conditional equilibrium constant equals to the thermodynamic equilibrium constant.

So, if, you know, let us let us let us see, let us see an example, using the mass balance equation and the conditional equilibrium constant, we can speciate a metal ions in the soil solution. So, let us, you know, solve the problem, let us calculate the concentration of a different calcium species present in the soil solution from a basic soil.

So, assuming a pH of 7.9, the total calcium concentration is 3.715, multiplied by 10 to the power – 3 mole per liter. So, we assume that calcium occurs as free hydrated calcium ions as well as complexes with inorganic ligands like carbonates, sulfate and chloride, like calcium carbonate as you can see calcium bicarbonate, calcium sulfate and calcium chloride, let us assume this.

So, so using the mass balancing, you know, so calcium, the sum of all the complex forms, the sum Ca T if we consider CA T is the sum of free and complex forms, then we can we can we can express this in this through this equation, where Ca T equal to the free calcium + the complex form concentrations. So, where brackets indicates the concentration in mole per liter. So, each of these above 4 complex this 1 2 3 4, four complexes is a conditional stability constant given by this K 1 condition K 2 condition K 3 condition K 4 condition. We already know this from our discussion from the soil organic matter.

Now, if we take the calcium outside which is a common factor in this Ca T equation, then we can get this form. So, the Ca, if we consider Ca, then we can get this form. From there, we can have this simplification that is 1 + K1 condition, multiplied by CO 3 2- K2 condition, multiplied by bicarbonate concentration, K3 condition multiplied by sulfate concentration and K4 condition, condition multiplied by chloride concentration from the previous relationship from the, from the, from the equation of the stability constant. From the equation of the stability constraint we can get this relationship, by taking the calcium, ion income and or concentration of calcium in the common factor.

So, the mass balance equation are thus transformed into couple algebraic equations. So, we have seen that this is an algebraic equation. So, this mass balance equation are thus transformed into couple algebraic equation with the free ion concentration as unknowns by substitution for the complex concentrations. So, the algebraic equation can be solved iteratively using successive approximation to obtain the free ion concentration by using number of possible computer equilibrium models.

So, these algebraic equations can be solved by help of a number of computer equilibrium models which are present. Now this, we follow an iterative approach like Newton, you know, Newton-Raphson's approach or computers equilibrium model to solve these for free calcium ion concentration.

Now, speciation of the soil solution if you consider the computer models are thermodynamic database. The all these computer models have their thermodynamic database containing the equilibrium constants for aqueous complex species. So, the free ion concentration obtained from the iterative approach can be can be used to calculate the concentration of the metal ligand complexes.

For example, in this case the complex of calcium bicarbonate forms this reaction we can see that Ca 2+ H+ + CO 3 2-, we can see this is a calcium bicarbonate.

So, from there we can basically calculate, now we know this thermodynamic or, you know, equilibrium constant. This is the equilibrium constant or equilibrium stability constant, that is 9.33 into 10 to the power 10, we have know, we have, we have already know the value. From there we can get this equation. And from there we can solute, you know, we can solve the, you know, substituting this K2 condition into and solving this calcium bicarbonate concentration.

So, let us wrap up here. And the next in the next lecture, we will start from here and I will show you how we can use this computer models for inputting these different, you know, conditional stability constant to solve the or to gain or to or to basically calculate the total concentration of a particular element in the soil solution. Let us wrap up here and from the next in the next lecture, we will be discussing that, thank you.