Transcriber's Name: DoneDoc07 Environmental Soil Chemistry Prof. Somsubhra Chakraborty Department of Agricultural and Food Engineering Indian Institute of Technology – Kharagpur Module # 05 Lecture # 25 Ion Exchange Processes (Contd.,)

Welcome friends to this fifth lecture of week 5 of this NPTEL onion certification course of environmental soil chemistry and in this week we are talking about an exchange processes in the soil. In the previous 4 lectures we have discussed different aspects of ion exchanges we have broadly defined what is ion exchange and then we have also discussed what is cation exchange capacity what is anion exchange capacity and why cation exchange capacity is important from the soil fertility point of view and also we have discussed why anion exchange capacity is also important from the soil fertility point of view.

Apart from that we have discussed how we can measure the cation exchange capacity in the soil and I have showed you different processes different protocols which we basically use in the laboratory for measurement of cation exchange capacity. I remember we have talked about the ammonia distillation method which we generally use for measuring the you know measuring the cation exchange capacity remember cation exchange capacities and early you know express in terms of centimole charge per kg of soil and cation exchange capacity and anion exchange capacity depends on soil pH.

If soil pH increases due to the variable charge the cation exchange capacity also increases and cation exchange capacity is also related to percent base saturation. Remember percent base saturation is the fraction of the cation exchange capacity.

Which is basically accounted for the calcium, magnesium, sodium and potassium and the 2 acidic anions such as acidic cations such as aluminium and H+ and not included in the cation exchange capacity. Now also percent base saturation in the last class in the last lecture we have talked about we have started the CEC numerical problems and we have discussed couple of very short CEC cation exchange capacity numerical problems.

Remember that I just want to give it you know very quick review of whatever we have discussed regarding the numerical problems. So remember that one mole of any substance that it could be either element molecular compound is the atomic mass of the element molecules and compound the mass of one mole of hydrogen is 1 gram and the muscle of one mole of calcium ion is 40 grams. Whereas one mole of nitrate is always 62 grams now in many chemical application a mole is basically a too large too big unit too easily manipulated so that is why we generally use centimoles which is basically 100th of a mole and millimole which is 1 thousands of a mole instead of a mole. So we use either centimole or millimole instead of mole and the mass of centimole of hydrogen you know for 0.01 gram and for millimole is obviously 1000 1/1000 of one gram that is 0.01 gram or 1 milligram.

So moles of charge is as the same as moles of anything else so 1 mole of charge is a charge either it is positive or negative of 1 mole of ion which is either +1 or -1 negative charge and ions such as calcium 2+ has 2 moles of charge each mole of calcium atoms because it has the 2 valency and a trivalent atoms such as you know trivalent atoms such as aluminium has 3 moles of charge per moles of aluminium.

And another major rule we have discussed that is one mole of charge of any ion will always be equivalent to one mole of charge of any other ion. So this makes the one mole of charge that is mole of charge a handy unit when discussing calcium, cation exchange capacity in soils. And remember that in the soil just like a mole the mole of charge is also too big number to easily manipulated so that is why we use centimole of charge which is actually 100th of mole of charge. And we express cation exchange capacity as the centimole charge per kg of soil.

So we started with this problem that is what is the mass of one mole, one centimole and one millimole of the following cations and anions? And I showed you know we have seen these cations like H^+ , Ca^{2+} , Na^+ , K^+ , SO_4^{-2-} , NO_3^{-1} and HCO_3^{-1} and we know that mass of one mole of these atoms are basically these ions are 1 gram, 40 grams,23 grams, 39 grams, 96 grams, 62 grams and 61 grams from that we calculated one centimole which is actually 100th of these mass of one mole and then we calculated mass of one millimole which is 1000th of this mass in one mole.

So, in the second problem we talked to our question was what is weight of one mole of charge that is mole of charge and one centimole charge of same cation and anions. So, in that problem we just basically divided the mole of charge, mole of mass with the number of valency so in case of H+ obviously it will be 1.

In case of Ca^{2+} the valency is 2 so we are getting a mass of mole of charge of 20. Similarly, 23 for sodium, 39 for potassium, 48 for sulphate and then 62 for nitrate and 61 for bicarbonate and from there we calculated the centimole of charge which is 100th of the mole of charge. In the third example we talked about what is the weight of the calcium chloride you would require to replace 4 moles of charge calcium in the soil.

So, you need to replace 4 mole of charge of calcium so you need at you know 4 mole of charge of you know you need to sorry you need to remove 4 mole of charge of potassium. So, you need to apply 4 mole of charge of calcium. So, from the equation from the formula of CaCl₂ you know that one mole of calcium ion produced 2 mole of charge. So basically, to supply 4 mole of charge we require 2 moles of calcium, calcium chloride which basically weights 2 into multiply by 111 that is mole of weight.

So, basically 222 grams of calcium chloride to supply 4 moles of charge of calcium which will further replace 4 moles of charge of potassium from the soil. And fourth question was how many moles of mole of charge of potassium does it take to replace 12 mole of charge of calcium? So for 12 mole of charge of calcium we require 12 mole of charge of potassium we remember that one mole of charge of any element any atom any ion can be replaced by the one mole of charge of any irrespective of their valency.

The fifth question we have talked about that what weight of a potassium is required potassium ion is required to replace 12 mole of charge of calcium ion. So we have calculated 12 mole of charge of potassium will be required to replace 12 mole of charge of calcium. So we basically have to just calculate what is the weight of 12 mole of charge of potassium and from the table which you have shown already we know that it is 468 grams.

In the sixth problem which we solve last what weight of calcium 2+ is required to replace 12 mole of K+. So, we know that to replace 12 mole of K+ we require 12 mole of Ca²⁺ and 12 moles of Ca²⁺ is basically coming from 6 moles of calcium chloride. So basically or 6 moles of calcium chloride and 6 moles of calcium. So 6 multiplied by 20, 6 multiplied by 40 is basically the 240 grams because we know that one moles of calcium ion equals to 40 grams.

So 6 moles of calcium ion will be required will be 240 grams. So these 240 grams of calcium 2+ ion will be required to replace 12 moles of potassium. So the next problem says the what weight of calcium carbonate is required to replace to 12 molecular charger potassium ion. So in the previous problem we have already determined that to replace a 12 molecule charge of potassium we require 12 molecular charge of calcium ion.

So, 12 molecular charge of calcium ions is equal to 6 molecular 6 molecules of 6 moles of calcium 2+ ion and so each if we if we consider that you know each mole and that each mole of calcium is coming from the calcium carbonate. So each mole of calcium carbonate is basically equals to 100 grams we know that the molar mass of calcium carbonate is 10 grams.

So 6 moles will be equal to 6 into multiply by 100 that is 600 grams. So that is why we need a total of 600 grams of calcium carbonate to replace 12 molar charge of potassium. Now the eight question was what is the cation exchange capacity of a soil that has 6 mole of charge of H+, 6 mole of charge per kg of calcium 2+ ion then mole of charge of per kg of magnesium ion and one centimole of charge of K+ ion and sodium ion each.

So basically we have to calculate the cation exchange capacity it is very simple. So if you assume that you have removed 100% of ions from the exchange complex of the soil then you need to sum the all the centimole charge which we are seeing here. So basically if we sum up all these 6 centimole charge plus 6 centimole charge plus 2 centimole charge and 1 plus 1 centimole charge we will get the answer is 10 centimole charge per kg of cation exchange capacity. So these are very relatively very short and simple question. Now the 9th numerical problem is what is the weight of H^+ , Ca^{2+} and Mg^{2+} , K^+ and sodium plus on the exchange complex in question 8. Now we know that to determine the mass we need to multiply the number of centimole of charge by the mass per centimole of charge. So, we need you know the units at centimoles and not in the moles.

So from the answer in problem 2 which you have already shown you we know that what is the mass per centimole of charge. So basically we have to multiply it so we know that centimole charge per kg on exchange complex is 6 centimole charge per kg for hydrogen. In case of $Ca^{2+} 6$ centimole of charge per kg and in case of Mg^{2+} it is 2 centimole of charge per kg.

In case of K+ it is 1 centimole of charge per kg and in case of sodium it is 1 centimole of charge. Now we already know from table 2 or from problem 2 that the mass per centimole of charge is 0.01 grams for hydrogen 0.20 grams for calcium for magnesium it is 0.24 gram for potassium it is 0.39 gram and for sodium it is 0.23 grams. So basically we have to multiply for each you know for each cations to get ultimately the mass per in grams per kg of soil. So, this is our basically our answer for this question 8. So if we move question 9 so if we go to question 10 question 10 says that if the cation exchange capacity of soil is 30 centimole charge per how many centimole charge of H⁺, Ca²⁺, Mg²⁺, K⁺, Na⁺ are on the exchange complex if the exchange complex has 5% H+ 50% Ca²⁺ 20% magnesium 2+ 23% K+ and 2% sodium plus.

So basically what is the weight of each of these cations on the exchange complex. So we know that percentage of each ion on exchange complex is 5 in case of H+, 50 in case of Ca^{2+} , 20 in case of Mg^{2+} , 23 in case of K⁺ and 2% in case of sodium plus. Now we already know that the cation exchange capacity of the soil is 30 centimole of charge per kg of soil.

So basically if we multiply the CEC with the percentage of ion in the exchange complex we will get the centimole charge per kg of soil for each of the ion that means in the 30 centimole of charge of per kg of soil so that is in the total CEC what is the contribution of individual? And we can get by multiplying the total CEC with the fraction of individual ion.

So in this fashion we are getting this value for H+ we are getting 1.5 centimoles charge per kg in case of calcium we are getting 15 centimole of charge per kg. In case of magnesium we are getting 6 centimole of charge per kg in case of potassium we are getting 6.9 centimole of charge

per kg. sodium we are getting 0.6 centimole of charge per kg of soil.

Now what is the weight of these ions on the exchange complex? Now we know that the mass of centimole charge for so basically if we multiply the mass of centimole charge with this centimole charge per kg. So basically we get the weight of this cation so in case of H+ we are getting 0. 015 in case of calcium we are getting 3 gram per kg in case of magnesium ion we are getting 0.72 grams per kg in case of sodium we are getting 2.69 gram per kg. In case of sodium we are getting 0.138 grams per kg so this is how we solve a question 10.

So let us move to the last question so the last question says that if a soil as a CEC of 25 centimole. So if a soil has a CEC of 25 centimoles per kg and 12% of the exchange capacity is saturated with sodium what weight of calcium sulphate must be added to 1 kg of soil to remove one half of the sodium from the exchange complex when you are assuming 100% efficiency.

Now here one thing is important we need to first calculate that what is the CEC which is basically contributed by sodium and then half of the CEC is basically replaced by calcium in the form of calcium sulphate. So if we remember this thing if we if we can so if you can sort these things out of this thing the answer will be very easy. So first we have to find out how much sodium is in the exchange complex.

Now we know that the 12% of CEC if occupied by sodium then 0.12 multiply by 25 centimoles charge per kg because this is the total CEC. So basically the sodium is accounting for 3 centimole of charge per kg. So this is the basically the centimole of charge per kg contributed by the sodium. Now the problem is to replace that is one half of the sodium with calcium from gypsum.

So we need to replace half of 3 centimole of charge per kg that is 1.5 centimole of charge per kg of sodium with the same number of centimole of charge of calcium because we know that according to the thumb rule that one centimole of charge of any cation can replace one centimole of charge of any other cation. So similarly 1.5 centimole of charge per kg of sodium will be replaced by 1.5 centimole of charge per kg of calcium.

So basically we need to add 1.5 centimole of charge of calcium in the form of gypsum. Now we know that each centimole of gypsum basically carries 1 centimole of calcium and 2 centimole of you know 2 centimole charge of calcium. So basically we have to supply 1.5 centimole of charge of calcium.

So if we simplify it we will basically get that you know we need to apply 1.02 grams of calcium sulphate in this fashion to basically supply the required amount of calcium to replace half of the exchange half of the sodium in the exchange complex. So this is how you can solve it now you can know you know that how we how we get these 1.02 grams so we know that the mass of 1 gram 1 centimole of gypsum is basically 1.36 grams.

So 1.36 gram basically contains 0.40 gram of calcium and 0.960 gram of sulphate. So weight of 1 centimole charge of calcium from the gypsum is 1.36 grams calcium sulphate per centimole of gypsum divided by 2 centimoles charge because here the calcium has you know 2 valency. So we need to add basically 0.68 gram of gypsum per centimole charge replaced. So right now when you were when we are when we want to replace 1.5 centimole charge basically we have to multiply 0.68 into 1.5.

So basically that will gives you 1.02 grams so that amount of you know calcium sulphate need to be applied to the soil to replace that half of that sodium in from that exchange complex. So this is how we solve these different types of cation exchange capacity related numerical problems.

Now let us go to a new topic that is cation exchange equilibrium constant and selectivity coefficients. Now many attempts to define the equilibrium exchange constant have been made since such a parameter would be useful for determining the state of ionic equilibrium at different ionic concentration.

Now some of the better-known equations which we are going to discuss today are Kerr's equation, Vanselow equation and Gapon equation. So, these three are major equations which basically use for calculating the cation exchange equilibrium constants. So, in many studies it has been shown that equilibrium exchange constants you know derive from this equation and not constant as the composition of the exchanger phase or solid phase or solid surface changes.

So, if we remove if we basically consider that soil is a solid and which is basically an equilibrium with the surrounding a solution then based on the composition change of the solid surface the equilibrium exchange constants also varies. So, this has been reported by several studies thus it is often better to refer to them as a selectivity constant instead of you know equilibrium exchange constants, we generally prefer to use this selectivity coefficients rather than exchange constants.

So let us first discuss the Kerr's equation okay now according to Kerr in 1928 he proposed a equilibrium

constant in soil. Now the soil was a solid solution as I have told you because it is basically a macroscopically homogeneous mixture with a variable composition you know the soil is very heterogeneous mixture so it has a variable composition. So for a binary reaction so what is the binary reaction? Binary reaction means same reaction involving 2 ions so here you can see this is a binary reaction where these A is basically A and these B are basically exchanging cations and x represent the exchanger

In case of this reaction it is basically solid okay now this aq represent basically the aqueous phase and s represents a solid phase. So basically what happens in the aqueous phase these A ion and in the solid phase this B ion is basically absorbed. So during the ion exchange process this B from the exchange exchanger solid exchanger will be replaced by these A. So ultimately these B will be coming to the aqueous phase and A will get absorbed into that solid phase. So this is a basically binary reaction.

So based on this binary reaction Kerr has proposed a constant. So Kerr expressed the equilibrium constant or more correctly is selectivity coefficient for that equation. And he denoted that equilibrium constant a selectivity coefficient as Kk where basically it is taking this formula. Now in this formula these brackets basically indicates the concentration of the aqueous phase and these braces

basically represents the concentration in that solid exchanger phase.

So one thing is clear basically this is a ratio between the you know the concentration of the ion in the aqueous phase as well as the concentration of the ion in the you know multiplied by the concentration of the ions in the solid phase. So this is called equilibrium constant by Kerr.

Now Kerr studied a typical exchange system that is calcium and magnesium exchange system and found that this Kk or this constant value remained relatively constant as exchanger composition changed. So, although the exchanger complex changes or composition changes that means although the soil composition changes this constant Kk remains same. Now this indicated that system behaves ideally that is the exchanger phase activity coefficient for 2 cations were each equal to 1.

Now he was kind of a you know he was fortunate because calcium magnesium exchange is one of the few binary exchange system where ideality is observed in most of the cases this ideality is not present. So what will be the cation exchange constant in those situation or non-ideal situation.

To solve that problem Albert Vanselow another scientist was you know he first introduced the ion exchange in thermodynamical context. So considering the binary cation exchange reaction in equation 1 we have already seen this equation so he described the thermo dynamic equilibrium constant as Keq okay thermo dynamic equilibrium constant as Keq.

So basically this parentheses basically indicates the thermodynamic activities so instead of concentration it is basically thermodynamic activities.

Now we know that it is not difficult to determine the activity of solution components. Since the activity we already know from our previous chapter or previous week discussion that activity of solution components is the activity would equal to the product of equilibrium molar concentration cation multiplied by its solution activity coefficient. So basically if we basically multiply for example in case of this Cation A if we multiply the you know the equilibrium molar concentration with their solution activity coefficient for both the cations for A and B we will get there basically the activity of the solution component.

So CA and CB here are the equilibrium concentration so CA and CB are the equilibrium concentration of A and B respectively and these terms are basically solution activity coefficient of this two cations. So, solution phase activity coefficient calculation activity calculation is not problematic the problem comes when calculating the activity of the exchanger phase it is not that simple. Now Vanselow now defined that the exchanger phase activity in terms of mole fractions he basically expressed these exchanger phase activity in terms of mole fraction that is NA and NB for ions for A and B.

So thus according to Vanselow equation it could be rewritten as you can see this is the equation 3 we know and basically this is so these exchanger phase is basically represented by this mole fraction okay where this mole fraction can be represented by these 2 equation. So we can basically simplify this as this Vanselow coefficient and you can see this term is basically multiplication of this solution activity coefficient of that particular ion with the equilibrium molar concentration and multiplied by mole of fraction of that particular ion. Okay so this is how this ratio will calculate this Vanselow coefficient.

He assumed that this Kv was equal to Keq however he failed to realize one very important point the activity of component of a homogeneous mixture is equal to its mole fraction only if the mixture is ideal. So if the mixture is ideal then fA = fB = 1 where fA and fB are the exchanger phase activity coefficients for cations A and B respectively. Now if the mixture is not ideal then the activity basically will be a product of mole of fraction and

this if which is where f is exchange phase activity coefficients.

So, for this Keq will know then this form so you know this was previously there it is basically now we are basically multiplying this fA and fB with these smaller fraction to express this Keq in terms of Kv and the ration of the exchanger phase activity coefficients. So this is how you can simplify Keq = Kv multiplied by the ratio of exchanger phase activity coefficients.

So, where these basically fA and FB we know that this will take these two forms so basically f we ultimately see the Vanselow coefficient Kv = K eq multiplied by fB/fA okay so Kv is an apparent Kv now it is called an apparent equilibrium exchange constant or cation exchange selectivity constant.

So basically by rearranging that we get this final form in the form of equation 8. So this is called an apparent equilibrium exchange complex. So basically Kv = Keq or equilibrium constants when it is multiplied by the ratio of this fB and fA.

Now other empirical exchange equations of Krishnamurthi and Overstreet they basically use the statistical mechanical approach and include a factor of valence of the ions to obtain a selectivity coefficient that is Kk0 for monovalent ion they have got this value of 1 for divalent ion they got this value of 1.5 and for trivalent ions they got this value of 2.

Now another equation was given by Gaines and Thomas and also Gapon and other scientists also given exchange equations other empirical equations. Also they introduced exchange equations that yielded selectivity coefficient in case of Gaines and Thomas we know it is KGT and in case of Gapon it is KG respectively.

So, for KCA exchange on a soil the gap and convention would be written as Ca 1/2 soil + K+ then K+ half of Ca2. So here you can see that here the exchange is going on with chemically equivalent quantities it is very important it is chemical equivalent quantities of the exchanger phase and that exchangeable cation. So, this is the special characteristics of Gapon's equation.

So the gap on selectivity constant for KCa exchange will be equal to this it is very simple this is where brackets express their concentration in the aqueous phase and these braces represents the concentration in the exchange complex or in case of soil. Now the selectivity coefficient obtained from this Gapon equation has been most widely used in soil and appears to vary the least as exchanger phase composition changes.

So you can see the here different scientists have given different selectivity coefficients like Kerr, Vanselow ,Krishnamurthi, Overstreet, Gaines-thomas and Gapon. So, this basically a combination of different selectivity coefficients for homovalent exchange where in case of homovalent exchange the example is when the potassium sodium type of exchange that is called homovalent exchange and when there is a potassium calcium type of exchange then it is called hetrovalent exchange. So, for both types of exchange these selectivity coefficients are already given.

Thermodynamics of ion exchange also thermodynamics equation provides the relationship between the exchanger phase activity coefficient and exchanger phase composition and this equation basically demonstrated that calculation of an exchange of phase activity coefficient we already know that exchanger phase activity coefficient is basically a ration where a is the activity in the exchanger phase and N is the molar fraction we know that.

Now the standard state for the adsorbed phase is the homoiconic exchanger in equilibrium with a solution saturating you know cation at a constant ionic exchange. So we already know this formula which you saw in case of Vanselow equation. So assume that any change in this Kv with regard to exchanger phase composition occurred because of a variation of exchanger phase activity coefficient.

So if we simplify this equation by taking log so we will basically take the it will basically take this form off 11. Now after taking this log if you take differential this will again take this form of equation 12. So basically by taking these Vanselow coefficient we are taking the log and by simplifying the log we are getting these two different equations.

So once we get this differential equation remember that any change in the activity if Bx that is in the reactant phase in the reactance when there is an activity change in the solid exchanger phase that will be accompanied by a change in the activity of the you know product in the product also in the solid phase of activity of the product also such that the mass of the exchanger is conserved.

So this necessity is application of Gibbs- Duhem equation can be expressed in terms of this. So this is basically question 13 so equation 12 and equation 13 we can solve and basically we can get this equation 14 and equation 15. Now from this equation 14 and 15 another important thing is that these if you see this equation 14 one thing is clear N_B/N_A+N_B and N_A/N_A+N_B these two are basically this N_A+N_B is basically E_A which is an equivalent fraction of A_X and E_B is basically equivalent fraction of B_X .

So basically if we put these values will 1 finally get in terms of EA if we basically if we put the values of EA in equation 14 and 15 that will become basically this equation 14 will become equation 16 and equation 15 will become equation 17.

So basically we are basically inputting the value of EA into equation 14 and 15 to get equation 15 and 16. So integrating cushion 16 and 17 by parts finally we wil get this equation 18 and 19. S what is the need of saying all these things? We can see that these are the final two equation 18 and equation 19.

So substituting these equations of equation 18 and 19 to equation 11 basically equation 11 you know that this is equation 11 which you started by taking the logarithm of Vanselow equation. So by putting inputting all this value into this equally into that equation 11 we will basically give this final value which provides that for the calculation of thermodynamics equilibrium exchange constant. So thermodynamic equilibrium exchange constant so if we basically plot from this equation from this integral equation it is clear that by plotting this K_V and E_A and integrating under the curve from $E_A=0$ to $E_A=1$ one can calculate Keq. So basically if we plot this K_V versus E_A and integrate from EA values of 0 to 1 we will basically calculate Keq. So one can calculate Keq ion exchange studies Kex is the equilibrium exchange constant. So this is how the thermodynamic concept is highly integrated with the iron exchange process and using this thermodynamic principle we can calculate different types of equilibrium exchange constants.

So equilibrium exchange constant so I hope that guys you have learnt something news in this ion exchange processes lectures.

And these are two three references environmental soil chemistry by Donald Sparks , the nature and properties by soils by Nyle C.Brady and Ray Weil and principle of soil chemistry by Kim Tan. I know that I cannot cover all these things due to time constraint however if you are interested these books will be very much helpful to understand these processes in more details.

So, I hope that you have learned something new in the cation exchange process and cation exchange capacity and

anion exchange capacity is now more clear to you. So, let us wrap up this week five of lectures and let us meet in week six of lectures to discuss other aspects of environmental soil chemistry. Thank you very much.