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Environmental Soil Chemistry
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Lecture # 24
Ion Exchange Processes (Contd.,)

Welcome friends to this fourth lecture of week 5 and in this week, we are talking about Ion exchange process. In the last lecture we have talked about the percent base saturation and in this fourth lecture we will be talking about how what is the formula of calculating percent base saturation and we will also solve different numerical problems related to cation capacity. Now you know what is percent base saturation we have discussed acidic in our last class.

The percent base saturation is basically the percentage of CEC which is occupied by basic cations like calcium, magnesium, sodium and potassium and they do not consider the acidic cations like H+ and Al^{3+} and because aluminium is very toxic in the acidic condition for the plant and also they with the with the increasing soil acidity the aluminium concentration or aluminium toxicity increases in the soil

Now we have also discussed what are the reasons of high soil fertility in a soil with high percent base saturation. There are three reasons one is they have little or no acidic cations like Al^{3+} which can show toxicity for the plant growth. Secondly, they have the soils with high percent base saturation also have high pH they are more buffered against the acidic cations and also different acid forming process like nitrification, acid rain etc., and thirdly they contain greater amounts of essential plant nutrients which plant nutrient cations like potassium, calcium, magnesium for the use of the plants.

Now let us see how to calculate the percent base saturation. So the formula percent is saturation is basically with you know you have to sum up the concentration of calcium, magnesium, sodium and potassium and then you have to divide it with the CEC total cation exchange capacity multiplied by 100. So, this is basically the percentage of the total cation exchange of initial capacity that is basically occupied by these 4 cations now depending on soil pH the soil base saturation maybe a fraction of CEC or approximately equal to CEC based on different soil pH condition.

So, in case of acidic condition, in case of alkaline condition, in case of some neutral condition the percentage varies. So, in general if the soil is below 7 that is acidic in nature the base saturation is less than the CEC. Obviously because the CEC will calculate both H+ and you know Al^{3+} also in the calculation of the total CEC we incorporate H+ and Al^{3+}. So, in the acidic condition which contain high amount of H+ as well as Al^{3+} the percent base saturation will be less than the CEC.

Now at pH 7 or higher soil clay minerals and organic matter surfaces are occupied by basically because the alkaline condition the CEC will be more dominated by the basic cations. Thus the best saturation is equal to the cation exchange capacity. Obviously in this picture you can see in the acidic condition they exchange complexes is occupied by Al3 as well as H+ ions and for calculating the CEC we calculate not only the Al^{3+} and H+ not only this calcium, magnesium, potassium sodium which is present in very minute amount in this high acidic condition.

So, obviously the percent base saturation will be very low in this condition as the pH increases from 3.5 to 5.3 you can see that the exchange complex is now more comparatively more dominated by these positive cations and also however there are still presents of these Al^{3+} acidic cations. So, as the pH further increases you can see all the exchange complex are occupied by these positive basic cations and as a result of that you know the CEC you know the percent base saturation is almost equal to the cation exchange capacity in the alkaline condition.

Now obviously this picture is also self-explanatory. So in the x axis we are plotting percent with saturation the Y axis this is soil pH. Obviously as the percent base saturation increases soil pH will also increase and it is quite evident because percent base saturation means when the exchange complex is saturated by more and more basic cations. When it is occupied by more and more basic cations obviously the soil pH will also increase.

So, this is the practical implication of percent base saturation. Percent base saturation is an indicator of soil fertility remember it is basically a fraction of the CEC which is counting for the calcium, magnesium, sodium and potassium and it does not include the aluminium and H+ ions which are also a part of easy calculation okay.

So, now effect of colloid types. Let us see what are the effects of different colloid types in the cation exchange capacity. Now differences exist in the tenacity with which the several types of colloids will specific cations obviously. Now at a given percentage of base saturation smectites which have a high charge density per unit of colloid surface hold calcium much more strongly than does kaolinite it is quite evident.

Because of high amount of isomorphous substitution the negative charge develop in this smectite is quite higher than that of kaolinite and as a result the charge density is also higher in case of smectite. So due to the higher charge density the they can attract these calcium you know cation more strongly than does kaolinite because they have limited amount of cation exchange capacity.

So calcium percent will have to be increase up to a certain percent to satisfy the need of plants in case of smectite. Obviously, we have to apply calcium more in case of a soil which is dominated by smectite but because smectite has more attracting power for the calcium than that of other soil. Now kaolinite can supply calcium at a relatively lower percent base saturation. So obviously the calcium can be available to the plant with relatively easier way in case of kaolinite than that of smectite.

Now the need to add limestone to the two soil will be somewhat different you know partly because of this factor. Obviously you know in case of a when we add limestone we add basically limestone to reclaim the soil acidity. So in case of smectite soil it will we need to apply more lime than that of kaolinite because in case of smectite the attraction for the calcium ion is more than that of kaolinite.

So another important point is this graph yeah this graph you can see in the x axis we are plotting the soil pH, the y axis we are basically plotting the effective cation exchange capacity for different types of clay minerals as well as organic matter. So you can see here it is showing the kaolinite this graph is for kaolinite and this graph is for humus and this is for smectite type of clay.

Now in case of smectite the cation exchange capacity is almost constant up to pH 5.52 you know 6. Because the negative charge which is responsible for cation exchange capacity in case of smectite type of clay mineral is basically generated from the isomorphic substitution and isomorphic substitution does not depend on soil pH. When the soil is basically having more pH that means more than 6 then some amount of pH dependent are generated in the smectite.

So you can see from their mole you know slight increase in their cation exchange capacity or effective cation exchange capacity. However, in case of kaolinite clay and humus which is an organic colloid or their effective cation exchange capacity is almost dependent on the soil pH. So that is why you can see it is highly variable. In case of organic colloid obviously as the pH increases there is a high increase in effective cation exchange capacity.

Because the functional groups aromatic functional groups which are present in organic colloid like carboxylic group as well as the phenolic groups they basically a deep they basically dissociates and produce the negative charge and these negative charge is responsible for attracting more cations.

We have discussed this in detail during our organic you know organic colloid discussion. Now in case of kaolinite you can see they produce both positive both you know positive charge with the increase of pH because they are depending on the pH dependent charge however when the pH is negative or in the I am sorry when the pH is low that means soil is acidic then you can see the effective CEC is somewhat negative.

So basically in this case also they are producing instead of you know negative charge they are producing positive charge so they are by decreasing the get initial capacity. So this graph shows what are the effects of different types of clay minerals as well as the organic colloid and what is the relationship of effective CEC and soil pH in this for these three different fractions.

Now let us see another important thing that is implications of cation exchange capacity. Now if you see the implications of cation exchange capacity the higher the cation exchange capacity the more clay or organic matter present in the soil. This usually means that high CEC of clay that soils have a greater water holding capacity then low CEC. In other words, again the higher the CEC the more clay and organic matter because the CEC basically are you know in the soil the CEC is basically contributed by either clay mineral or the organic matter.

So obviously when a soil having more CEC it is understood that the soil have more clay as a well as organic matter. So obviously as a result of that the water holding capacity will increase as compared to the soil with low CEC or sandy soils. Now in case of low CEC soils these low CEC soils are more likely to develop potassium and magnesium and other cations deficiency.

So the low CEC souls are more likely to develop potassium magnesium deficiency we have discussed this you know while discussing the percent base saturation while high CEC are less susceptible to leaching losses of these cation. So obviously because high CEC means high cation exchange capacity higher affinity so low leaching loss of the cation so for sandy soil large one-time addition of cation that is potassium can lead to larger leaching losses because soil is not able to hold to the excess potassium.

So more frequent the addition of smaller amounts are better obviously the soil with low cation exchange capacity is more susceptible for leaching loss of those cations because they cannot attract them but in case of high canonization capacity soil they can attract them. So you can apply one time. However, in case of soil with low cation exchange capacity frequent addition of smaller amounts of a particular you know cations are particular nutrients are important

So the lower the CEC the faster the soil pH will decrease with time. So sandy soil need to be limed more often than clay soil. So, when the soil is having lower CEC the faster the soil pH will decrease with them obviously because they are positive basic cations are less when the basic cations you know are very limited obviously the pH will decrease. So the sandy soils need to be limed more often than that of clay soils to increase the soil pH.

Now the higher the CEC the larger the quantity of lime that must be added to increase the soil pH we have discussed just this you know just in the last slide because in case of smectite which has more cation exchange capacity we have to add more lime to increase the to increase the CEC. Sandy soils needs less line then clay soils to increase the pH to desired levels. So these are some practical implications of cation exchange capacity.

Now let us see some specific CEC numerical problems and how we how we can solve them these are very easy but before solving them we need to review a couple of things. Now you know that one element of any substance that is element either it could be element or molecule or compound etc is the basically atomic mass of the element or molecules or compound. So the mass of one mole of hydrazine is 1 gram you know that the mass of one mole of calcium is 40 gram.

And the mass of one mole of nitrate is 62 which you calculate it by you know 62 grams of nitrogen that is 62 gram of coming from this 14 gram of nitrogen plus 3 oxygen that is 3 multiplied by 16 that is 48 + 14. So, 48 + 14 we are getting 62. So, in many chemical applications a mole is too big unit to be easily manipulated. So in those cases we generally use this a unit called centimoles that is a you know 100th of a mole that is 0.01 moles or sometimes we use the millimole also so that is 0.001 moles.

So basic chemical you know in case of CEC based chemical equations and applications also that is why we apply centimoles instead of moles. So the mass of a centimoles of hydrogen is 0.01 gram because we know that one mole is one gram so obviously the one centimoles hydrogen will weigh around 0.01 gram and one millimole is 0.001 gram or one milligram. So the moles of charge are same as moles of anything else remember this is a very important point moles of charge are the same as moles of anything else.

So one mole of charge is the charge either it is positive or negative have one mole of ion with either positive or negative charge. For example, an ion such as calcium has two moles of charge for each mole of calcium atoms so it is basically the valency so for each mole of calcium atom it has two mole charges because it has valency of +2 it has two positive charges so two fewer electrons and protons. So similarly, a trivalent atom such as aluminium has three moles of charge per mole of aluminium atoms okay. So, this is how we can calculate it the mole charge.

Now the most important thumb rule for calculating the cation exchange capacities is one mole charge of any ion will always be equivalent to one mole charge of any other ion. So, one mole charge for example one mole charge of calcium will be always equal to the one mole charge of aluminium. Remember I am talking about one mole charge not one mole so one mole charge of any ion will always be equivalent to one mole charge of any other ion irrespective of their valency.

So, this makes the mole of charge that is mole of charge a handy unit when discussing the cation exchange capacity in the soil. So, this equivalent baseline that is the mole charge gives the equivalent baseline for calculating the

CEC in the soil with more easier way. So in soil is mole of anions and cations is too big number to be easily manipulated. So the most common unit when CEC of soil clay minerals or organic method is basically centimole of charge per kg of soil.

Now you have understood why we are using this term centimole of charge per kg of soil earlier it was milliequivalent per hundred grams of soil now it is centimole of charge per kg of soil. Again these mole of charge concept is it is basically charged of one mole of substance. So in case of one mole of calcium ions the mole of charge will be 2 because this is valency of 2.

Similarly, for tri valent ion the mole of charge will be +3 remember one mole of charge of any ion will be equivalent to one mole charge of any other ion and that is why it produced a common baseline for calculation or CEC in any in soils and since these mole is a bigger concept for easy you know and it is difficult to manipulate this bigger unit while calculating the cation exchange capacity in the soil that is why the most common unit is the centimoles at which is 100th of mole charge okay.

So, let us see one example so here first question is what is the mass of one mole one centimole and one milli mole of the following cations and anions that is H+, Ca2+, Na+, K+, sulphate nitrate and bicarbonate. so one mole is the atomic mass or molecular weight per litre for each cations and anions we know that so from the periodic table we can easily see what is the weight or mass in gram of one mole of these different grams.

For example, in the case of H+ we know it is 1 gram in case of calcium it is 40, sodium 23, potassium 39, sulphate 96, nitrate 62, bicarbonate 61. So obviously mass of 1 centimole will be 100 of this mole of charge weight. So basically we are getting 0.01 grams 0.4, 0.23, 0.39, 0.96, 0.62 to 0.61 and mass 1 millimole will be when we are converting now it is 2 millimole obviously we will be getting 1 mg 40 mg, 23 ,39,96,62, 61.

So basically, we were converting gram to milligram and then that is basically mass of 1 millimole. So, this answer is pretty much simple we just have to see the mass of 1 mole of these ions and from there we have to calculate the centimass of 1 centimole and mass of 1 millimole.

Now the second question is what is the weight of 1 mole of charge? Now we are converting into now we are going into the mole of charge. So what is the weight of 1 mole of charge and one centimole of charge of the same cations and anions. Now it is an atomic mass or molecular weight divided by the charge.

We know that so here for example 1 mole of calcium atoms basically gives to moles of charge. So, to calculate it we have to divide the mass of molecular weight by the charge or the valency to get the 1 mole of charge. So for example the mass of 1 mole of calcium and so for example here we can see the mass of 1 mole of calcium is 40 grams for example okay. So, the mass of calcium ions required to supply 1 mole of charge of calcium ion.

So, mass of mole of charge will be 40 divided by valency or chart that is 40 divided by 2 that is 20. So when you calculate the mass of mole of charge obviously mass of centimole charge will be 100th of it. So similarly for each and every one so in case of H obviously says the valency is 1 we are having the similar mole of charge, mass of centimole charge is 0.01. In case of sodium, we are getting the same value in case of mass of mole of charge and mass of centimole charge K+ also same in case of sulphate it is 96/2 that is 48.

In case of nitrate that is 62, 62 same in case bicarbonate it is 61, 61 since however when we are converting into the centimole of charge we are basically taking the 100th of mass of molecular charge. So, this is also very simple solution

Now the third question is what weight of calcium chloride would do you need to replace 4 mole charge of calcium potassium in a soil? So, you have a soil with and you want to replace 4 mole of charge of potassium in its soil using the calcium chloride. So how what weight you need? Now we need to replace the potassium which is positively charged with positively charged calcium ions.

Now remember that each mole of calcium chloride has 2 mole of charge chats supplied by the calcium 2+ we know that. 1 mole of calcium chloride will supply 2 mole of charge of calcium. Now we need to replace 4 mole of charge of potassium and we know that 1 mole of charge of any ion is equivalent to 1 mole of charge of another ion irrespective of their valency.

So obviously to replace 4 moles of charge of potassium ion we need 4 mole of charge of calcium. So, to supply 4 mole of charge of calcium we need 2 molecules of calcium chloride because 1 molecule of calcium chloride gives you 2 molecular charge of calcium. So, to get 4 molecular charge of calcium you need 2 molecules of 2 moles of calcium chloride. So, 1 mole of now 1 mole of calcium chloride weighs 111 gram.

So 2 into that is 222 grams of calcium chloride will be needed to supply 4 mole charge to replace the potassium it is very simple. So we are starting you know the basic concept is to replace 4 mole charge of potassium you need 4 mole charge of calcium to supply this 4 mole charge of calcium you need 2 moles of calcium chloride and just you have to multiply the molecular weight using 2.

Now the 4th query is how many moles of potassium does it take to replace 12 mole of you know calcium it is also simple now so we need to replace 12 molecular charge of calcium. So obviously we need 12 molecular charger potassium so because it takes it always takes 1 molecular charge to replace 1 molecular charge regardless of ion carrying the charge

Now the 5th question is what weight of potassium is required to replace to 2 mole of charge of calcium. So what weight of potassium is required to replace 2 mole of charge of calcium so in the problem for that is in the previous problem it was determined that 12 molecular charge potassium 12 molecular potassium are required to replace these 12 molecules calcium. Now from the answer in the problem to that means that table where calculated the mass of mole of charge we know that one molecular potassium one molecular charge of potassium has a mass of 39 gram.

So, we need 12 multiply 13 and that is 468 grams of potassium ions to replace 14, 12 mole of calcium ions. So, this is again simple again we need to we need to have 12 molecular charge of potassium to replace 12 molecular charge of calcium. Now from the calculated value of mass of non-molecular charge of potassium we can just have to we just have to multiply it. So, 12 multiplied by 39 that is 468 grams of potassium. Now the 6th question is what weight of calcium ion is required to replace 12 mole of potassium.

Now we know that to replace 12 mole of potassium we require 12 mole charge I am sorry 12 mole charge of potassium we require 12 mole charge of calcium. But to supply the 12 mole charge of calcium we need only 6 moles of calcium because 1 mole of calcium can supply 2 mole of charge of calcium. So, from the answer of problem 2 we have already calculated these mole of charge we know that a mole of calcium is basically 40 grams and that a 1 molecule charge has a mass of 20 grams.

So, we can either solve it by multiplying these 40 into 6 or 20 into 12. So ultimately the answer is 240 grams okay so we know that a mole of calcium is 40 grams. So obviously for 6 moles it will be around it will be 240 grams okay so this is how we can calculate you know the or solve this problem okay. So guys I hope that you have you have learnt something new in this lecture.

And in the next lecture or the last lecture of week 5, we will be talking about some more numerical problems related to CEC and then we will be talking about thermodynamics principles as well as different equations to calculate the selectivity coefficients for exchange reaction.