Environmental Engineering: Chemical Processes
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Lecture - 34
Carbonate and Non-Carbonate Alkalinity

Hello everyone so welcome back to our latest lecture session right. So we have been discussing the practical applications of you know acid bases and you know how to look at employing or deploying VMINTEQ to be able to make your life easier, right and I believe in the last lecture session we discussed problems with respect to mixing 2 solutions of different characteristics and we saw that we need to balance conservative quantities right.

For example, when I think the example we looked at was looking at solution of pH 6 and pH 8 and if you mix them together what would be the pH given that you have different alkalinities present and so on. So you cannot obviously just take the average neither can you just take the average of H+ concentration. So you need to take the, what do we say, you need to look at the total component balance or balance on conservative quantities.

So component balance is something that we are aware of and conservative quantities are alkalinity, acidity and so on, right. So today we are going to move on to probably the last aspect with respect to acids and bases. So here again we are going to consider mixing problem. So first we are going to discuss the theoretical basis for this or how to solve or approach these kinds of scenarios and then we are going to look at practical example and how to use VMINTEQ or solve by hand.

You know to analyze that particular situation let us see right.

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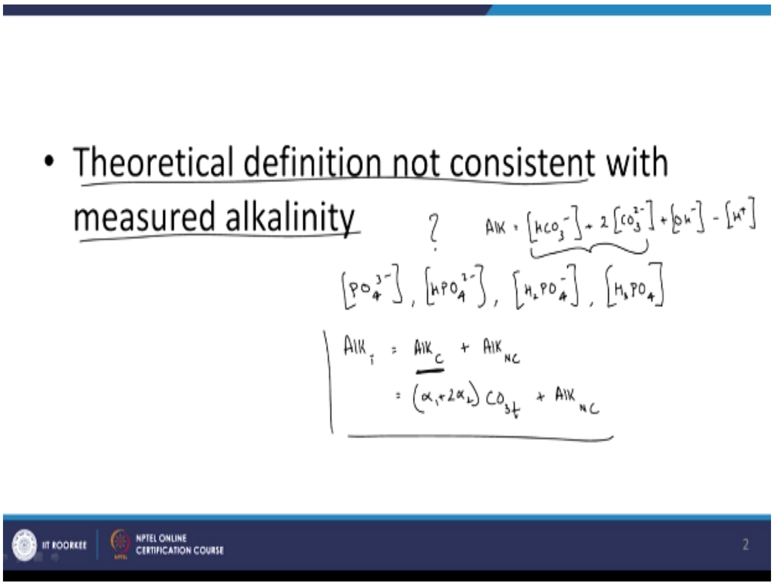

So let us move further and so the aspect that we are going to look at is when the theoretical definition of alkalinity is not consistent with the measured alkalinity right. So and when is this the case right and as we know alkalinity, the theoretical definition what is that, I think what are the bases here in the carbonate system HCo3- + 2 times Co3 2- + OH- - H+ right. So this is considering when we have only the carbonate system and that is what we look at with respect to the theoretical definition of alkalinity anyway right.

So obviously when would this particular definition of alkalinity not be consistent with the measured alkalinity and how do we measure this particular alkalinity. You know in your lab how do you do so. So I think we looked at titration end point or we consider a titration end point of 4.5 as mandated by the standard methods right and then we take an acid of known concentration and we titrate until we reach that particular end point pH 4.5.

And we calculate the amount of acid right or equivalent amount of acid that we had to consume or the solution consumed before reaching that 4.5. So obviously if only the carbonate system was predominant this particular theoretical definition would more or less be you know similar to what you would calculate or measure practically, but when would that not be consistent. So we looked at this case, so let us not go into it in great detail, but let us look at this case.

When we also have the species of Po4 phosphate let us say, you know, HPo4 2- right, H2Po4- and H3Po4. So let us say when you have the phosphate acid base or conjugate acid base species in your particular solution too then they are going to obviously interfere with your particular practical measurement because let us say depending on the pH HPO_4^- or $H_2PO_4^-$ and what is it now PO_4 3-2 can interfere with your particular measurement.

Why is that they can consume the proton right. For example, $H_2PO_4^-$ can consume one proton depending on your particular what is it now pH right and HPO_4 2-2 and so on right. Again we looked at how to calculate that based on the reference we take and the reference should be such that you know it is PKA is nearer to the 4.5 value and I think the reference we took was $H_2PO_4^-$ if I am not wrong the last time.

Anyway we are not going to discuss this again, but we are going to look at the applications here let us see. So again here let us understand that you know if I write down the particular equation in this case you know the total alkalinity will be equal to alkalinity due to the carbonate species and alkalinity due to the non-carbonate species right. So that is what we are trying to understand here. So what are the contributing species here.

And they are this and what would that be alpha 1 + 2 alpha 2 * CO_3 total right + alkalinity due to the non-carbonated species right. So this is the key aspect that you need to understand that you know we are going to specify alkalinity due to carbonate and non-carbonate species independently and from our understanding of alkalinity we know that you know alkalinity due to the carbonate species would be = HCO_3^- + $2CO_3^{2-}$.

And which we are representing obviously as alpha 1 + 2 alpha 2 times CO_3 total using the ionization fractions right. So again once we have this particular case so how do we go further let us see right. So let us say you know we consider 2 cases.

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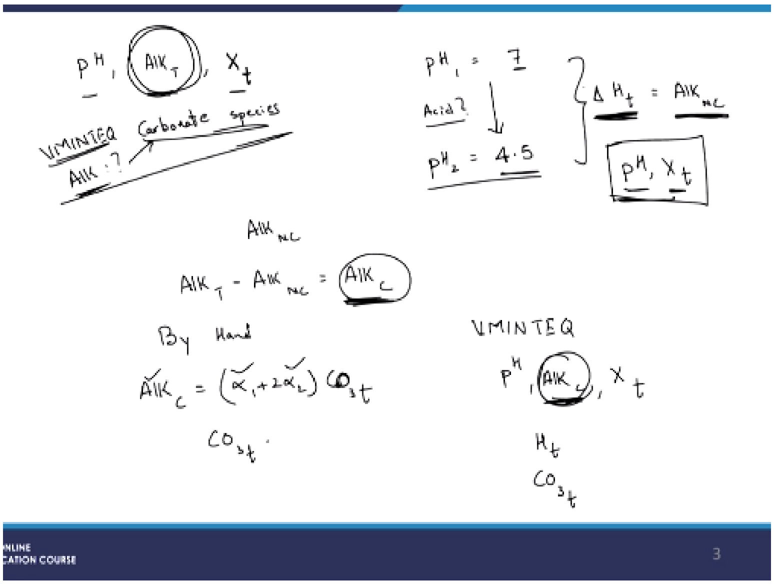

So we look at the example later on in greater detail. So initially let us say we have pH and we have alkalinity, total alkalinity and let us say we also have Po4 total, so which I will you know approximate by or use the variable X to approximate it I guess right. Since the Po4 total I am having representing it as X total. So pH alkalinity total and X total. So let us say how can I calculate H total or Co3 total now.

So either by hand or by VMINTEQ let us see. So we will look at the fundamental basis here. So again as we just discussed we need to identify the 2 aspects independently what are they the carbonate alkalinity and the non-carbonate alkalinity, right. So how can we do this let us say you know. So for example let us say this is pH at pH 1 initially right and after your titration what do you know that the pH is going to be the, pH 2 you know is going to be = 4.5 right.

This is from your practical measurement, the standard method value right. So what is your end point for alkalinity measurement. You add enough acid such that the pH falls down to 4.5 right that is how you end up measuring the alkalinity. So let us say this is the key that we are going to look at. So we are going to measure let us say pH 1 is for example 7 let us say. Initial pH is 7. So I am going to use VMINTEQ to measure the H total required to bring down the pH from 7 to 4.5.

As in when would the pH fall from 7 to 4.5 when I add an acid right or H total increases right. So I am going to look at the delta H total right and what will that give me an idea about that delta H total is nothing but going to be the case of alkalinity due to the non-carbonate species and when is that the case when I only enter pH and X total. So this is the key here. Let us just look at what we are up to.

So I want to be able to calculate alkalinity due to the non-carbonate species right. So I am going to consider the case where I have no carbonate in the system and I am going to use VMINTEQ to approximate that and how can I measure that now. You know that practically right we measure it by adding enough acids such that the pH falls down to 4.5, which is our end point for alkalinity titrations.

So even here I am going to try to approximate that so here for a practical what to say for an example I am assuming that the pH is initially 7. So let us say I am going to use VMINTEQ to mimic and calculate the amount of acid required to bring down the pH from 7 to 4.5 right. So that is what we are talking about how much acid is required to bring down the pH from 7 to 4.5 right.

And I can look at that with respect to delta H total right and as we know that you know if there is no carbonate system present it will be equal to the alkalinity due to the non-carbonate species. So thus when inputting the relevant variables in VMINTEQ what do we need to input only the pH and X total certainly not alkalinity because alkalinity in VMINTEQ only considers the carbonate system right.

So VMINTEQ when you look at alkalinity what does it consider, it considers that the system is predominate by the carbonate species right so we are going to try to mimic the case where we add enough acid to bring down the particular pH to 4.5 and calculate the amount of acid required right. So from that I can calculate what is it now, the alkalinity due to the non-carbonate species and I know let us say from my initial case alkalinity due to the total alkalinity.

So alkalinity total – alkalinity due to the non-carbonate species would give me the alkalinity due to the carbonate species this is something I can calculate right. So then I can either calculate by hand or by VMINTEQ, the other total components and how can I calculate it by hand. We just looked at this in the previous slide what is alkalinity due to the carbonate species.

It is alpha 1 + 2 alpha 2 times Co3 total right. So this is the known value which you are calculating out here right and alpha 1 and alpha 2 are fixed for the carbonate system for a particular pH and so you can end up calculating Co3 total right and how do I do that in VMINTEQ let us say. So now I can plug in pH alkalinity due to the carbonate species that is what I can calculate right and then X total right.

And from this plugging this in what can I calculate I can calculate H total and Co3 total. Again you know people might ask why cannot you just plug in alkalinity due to the total, alkalinity total here right well because VMINTEQ only considers carbonate species when it calculates alkalinity. So you are going to end up with an erroneous value right. So let us look at in particular example.

So I believe you are going to look at an example with respect to anaerobic digester. So anaerobic digester I think people have enough background in that particular aspect so I am not going to go in to that in detail, yes. So let us look at where we are. So let us go through this particular question once.

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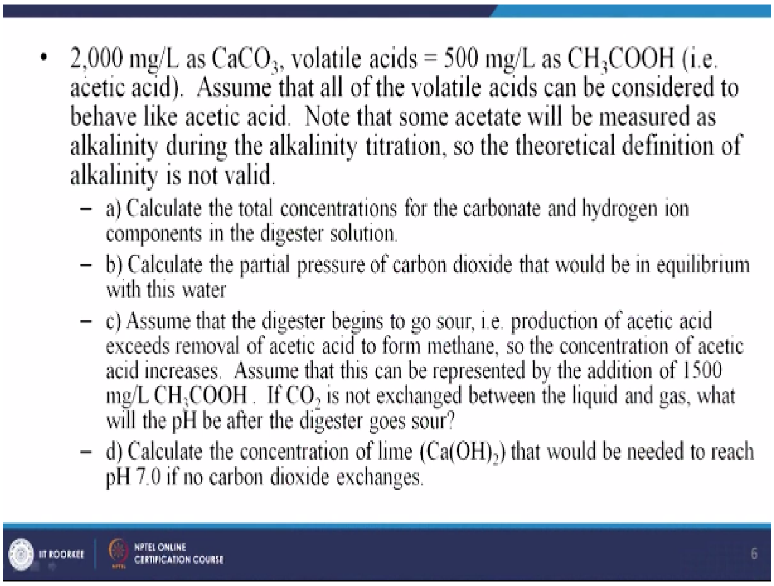

So looks like 2000 mg/L as CaCO3 right and that is the alkalinity I believe right and we have volatile acids as 500 mg/L as acetic acid and this is alkalinity total right. Assume that all the volatile acids can be considered to behave like acetic acid right. So obviously you are going to have formation of volatile acids in your particular anaerobic digester and so here we are going to consider that all these volatile acids are going to behave as acetic acid let us say, okay.

You know that is valid assumption here and so obviously this is what we just talked about right that some acetate will be measured as alkalinity during the alkalinity titration. So the key is that the theoretical definition of alkalinity is not valid right. So here what do we have here please we have that the alkalinity total = 2000 mg/L as CaCO3 and volatile acids in the form of equivalent to 500 mg/L as acetic acid right.

And then obviously you know we are so again you have in your anaerobic digester certain alkalinity total right and you also have volatile acids being formed which are equivalent to let us say 500 mg/L of acetic acid and I believe the first aspect of this question you know looks for fundamentals what are they, the total concentration of carbonate and hydrogen ion as in what is Co3 total and what is H total right.

So again you know this is the practical application but we obviously need to know the total components to be able to calculate any other variables right. So the first aspect or key aspect is to be able to approximate what is the total carbonate concentration and also the H total right. So how do we go about this we are going to obviously look at what we just discussed earlier right. So let us move on.

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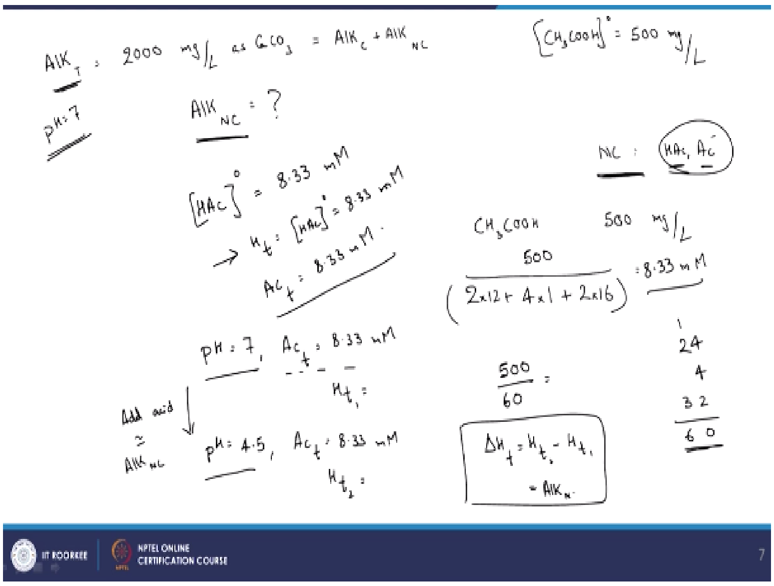

So we have 2000 mg/L as CaCo3 right and that is our alkalinity total and as we know alkalinity total has 2 components why is that because we have acetic acid let us write CH3 COOH initial and what was that equal to I think it is 500 mg/L let me just confirm that, right that is 500 mg of acetic acid per liter of the solution right and here as we know alkalinity total and the contribution is going to be due to alkalinity due to the carbonate species and also alkalinity due to the non-carbonate species here.

So they are non-carbonated species what are they here obviously right you have HAc and Ac – acetic acid right. HAc and the acetate ion yes, we have these 2 particular variables that are going to affect your non carbonate alkalinity. So the first key aspect as we discussed earlier was to be able to come up with calculating alkalinity due to the non-carbonated species right. So how do I do so right, I am going to mimic the particular case so I am going to use VMINTEQ.

So what is the initial pH here do we have an initial pH here I believe it should be pH 7. So let us plug that down so the pH 7 right and total alkalinity was 2000 milligram per liter so looks like I missed putting that in the question. So we have pH of 7 right, alkalinity total and thus, so how can I calculate or end up calculating alkalinity due to the non-carbonate species.

So again as we discussed earlier we are going to use VMINTEQ to calculate the amount of acid required to bring down the pH from the current value to the alkalinity end point, titration end point what is that 4.5 right. So how do we do that let us go through I guess, right, so let us switch over to VMINTEQ and obviously what do I have.

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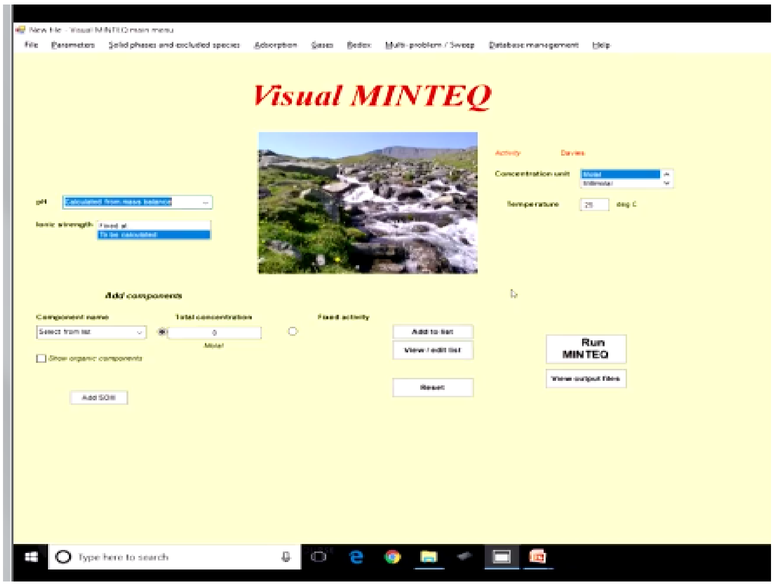

I have acetic acid right I need to plug that in so it is an organic compound so I am going to use that here show organic compounds yes, and acetic acid or acetate so before I go through I guess here the units are in molar, okay, I do have milligram per liter units to so I guess I can use that or if not I can obviously you know let us calculate the concentration in molar units right so CH3, COOH the concentration is 500 milligram per liter.

So molecular weight what is that going to be 2 carbon 2 * 12 + 4 hydrogen + 2 oxygen, right, so hopefully dividing this 500 by you know this I am going to end up with a concentration in millimolar right. So that is going to make my concentration in millimolar so we can get that done with VMINTEQ I guess so let me open up VMINTEQ okay later on and but for now I am going to use a state as in the units of milligram per liter right and that is going to be equal to any way I think it is better that I calculate the concentration.

So let us see how this going to be I guess. So let us look at what this molecular weight of acetic acid is so that is 2 * 12 = 24 + 4 and 32 right. So that is 60 grams per mole and so we need to calculate what is it now 500/60 and that and told is coming out to be 8.33 millimolar right. So let us just plug this in so that we can switch over seamlessly to VMINTEQ later on so HAc 0 = 8.33 millimolar units right so let us say H total is also going to be = HAc 0 right.

That is going to be = 8.33 millimolar or rather I am not going to look at this right now right because I am going to specify pH I do not need to specify this now anyway acetate total is going to be equal to 8.33 millimolar right. So what are we going to do now, we are going to specify pH = 7 and acetate total = 8.33 millimolar and we are going to end up calculating H total and then we are going to specify pH = 4.5 which is our end point and keep acetate total the same 8.33 millimolar and now I am going to get a new H total, H total 2 right, H total 1.

So what is delta H total this is going to be a higher value is it I am going to add an acid. So H total 2- H total 1. So what is this now how can the pH go from pH 7 to pH 4.5 only when you add in acid right. Add acid that is when the pH is going to fall down and the equivalent amount of acid is going to be nothing but equal to the alkalinity due to the non-carbonate species which is acetic acid here. So that is how we are going to end up calculating our alkalinity due to the non-carbonate species right.

So let us plug this in first and calculate H total here. So pH 7 and acetate total of 8.33 millimolar right. So let us switch to VMINTEQ here and we are going to have now millimolar units hopefully we have that yes. So we now need to go to key 8.33. I will add that to the list and as we know pH is fixed at 7 okay. So view edit list just to be on the safer side back to main menu and run MINTEQ working, so now we should calculate H total.

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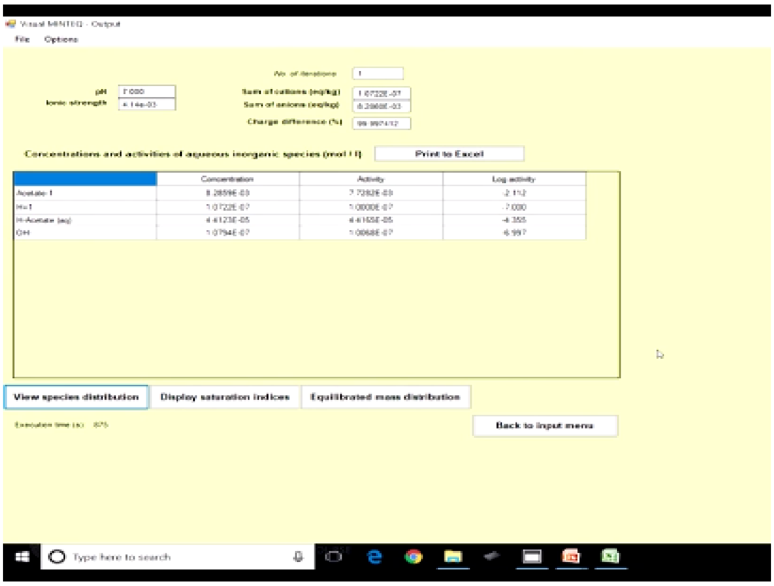

So that is going to be equal to what now. How do I calculate H total please? How do I calculate H total?

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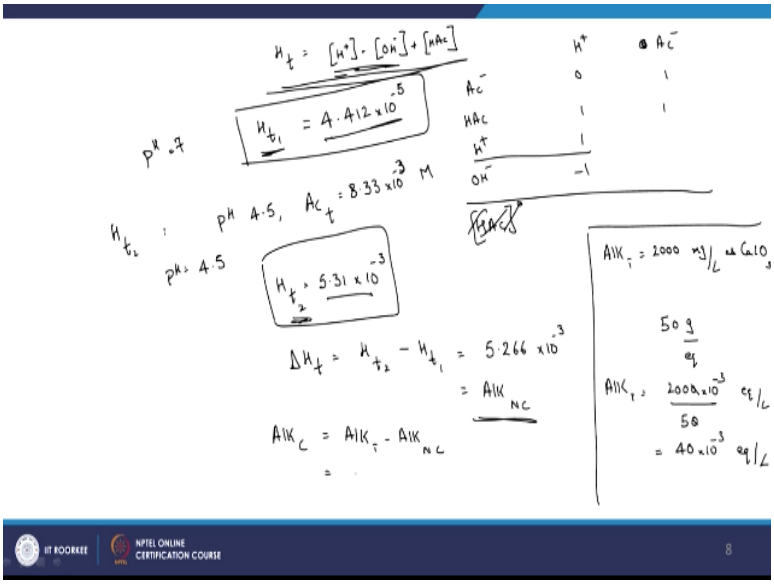

H total as we know is nothing but H + - OH- right and what else here. So we have H + and OH pardon me AC – here and what are all species there, AC- HAc H+ and OH-. So what is the contribution here. So it is 1 and 0, 1 and 1, H+ is 1 and -1 and right and this is nothing but what is the recipe species HAc 0 that we looked at earlier right. So anyway we do not need to plug this in now because we are fixing the pH at 7, but anyhow H total = H+ which we just plugged in here.

Oh- - Oh– which we plugged in and + HAc right. So this is what I was trying to elaborate here. So we need to use XL now to be able to calculate this particular set of variables or HT1 right. So let us first go back to VMINTEQ output right. So let us say print to XL and now I need to be able to calculate = H+ concentration is this, - OH- + HAc and that is going to be = 4.4122 * 10 to the power -5 molar right.

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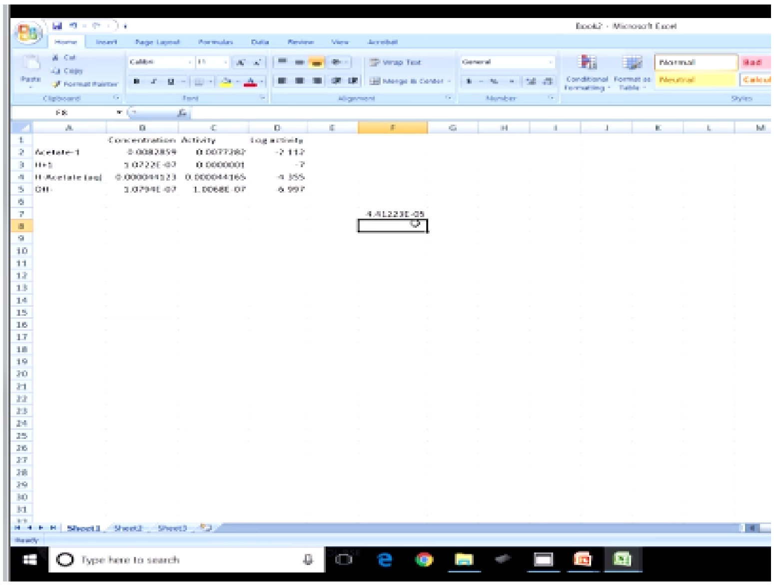

So let us go back to this particular case and plug that in so just we can remind ourselves later on. So right what did we just get please, 4.412 * 10 to the power -5. It is 4.412 * 10 to the power -5 molar units right. So this is Ht1. Now I need to calculate Ht 2 and what is the case when the pH is 4.5, but obviously I state total is the same as what we had earlier I think we had 8.33 * 10 to the power -3 molar units right.

So now let us look at the second case. So now I am going to change the pH such that it is going to be at 4.5. So where do have this 4.5 right. So I am going to view edit list okay seems fine and I give the units here and now I am going to end up with running VMINTEQ and again let us print to XL and look at the new set of values here.

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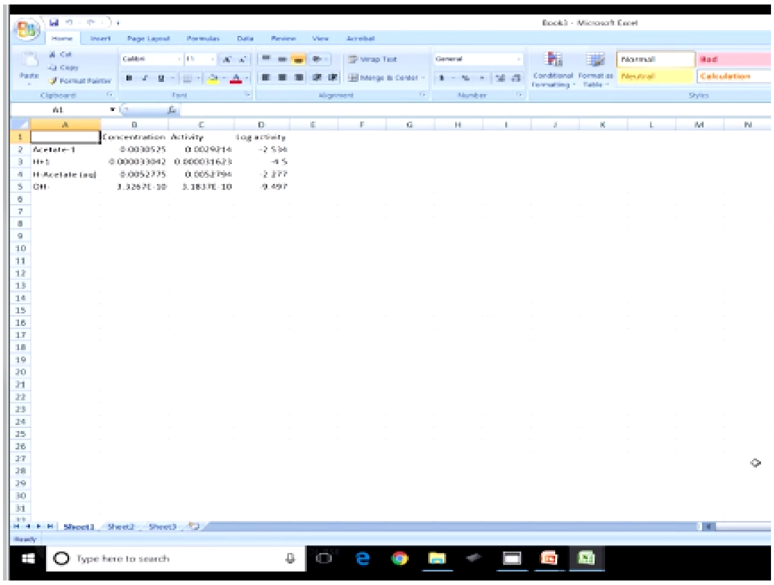

So again I need to calculate H total that is = H+ + acetate HAc acetic acid – OH- and that is going to be = 5.31 * 10 to the power -3 right. So let us plug that in somewhere here. H total 2 = 5.31 * 10 to the power -3. Let us just see if we are on the right track here, not right track pardon me, let us just look at our value this was the previous value and what is the current value here.

Okay 5.3 * 10 to the power -3, right so now we need to find the difference of these 2 values. So let us do that right here I guess, anyway so that is going to be = this particular value – and what was the valued from the previous case please. H total 1 that was = 4.412 E-5 and enter and so we end up with the value of 5.266 * 10 to the power -3. So let us plug that down here so H total or delta H total which is = H total 2 right –H total 1 = what was it equal to please 5.266 * 10 to the power -3 right.

So again how did this particular pH from 7 fall down to pH to 4.5 only when you increase our add in acid. So that is why you see that your H total is obvious increasing right. So what are we trying to do here. We are trying to mimic the case when we add an acid to bring down the you know mimic your titration case when you bring down the pH from 7 to your end point which is 4.5. So by calculating the difference in the H total you can calculate the equivalent amount of acid added right.

And what is that particular case equal to, not particular case, that number equal to that is nothing but equal to the amount of alkalinity due to the non-carbonate species right. So that is = alkalinity due to the non-carbonate species right. So obviously we need to now calculate alkalinity due to the carbonate species and that is = alkalinity total – alkalinity due to the non-carbonate species right.

So how do I get that here now. So where is our alkalinity total. I think we had alkalinity total as 2000 milligram per liter as CaCo3 right. So let us change the units here. So alkalinity total was = 2000 milligram per liter as CaCo3 right and we know that the equivalence, I guess 50 gram per equivalent for CaCo3 right. So we are going to have to divide that here. So the relevant units are going to be 2000 * 10 to the power -3/50 equivalence per liter. So that is going to be equal to 220/5 would be 4 right.

So 40 * 10 to the power -3 equivalence per liter, so right hopefully I am on the right track and so this is nothing but 0.04 – alkalinity due to the non-carbonate and that was equal to 5.266 * 10 to the power -3. So I am just going to subtract 40 - 5.266 in XL right. So let me switch to XL here. So that is = 40 - 5.266 and enter that gives you 4.734. So that is going to be = 34.734 * 10 power -3 right.

Again obviously equivalence per liter units, yes, so what is this now this the alkalinity due to the carbonate species. So let us move on to the next case.

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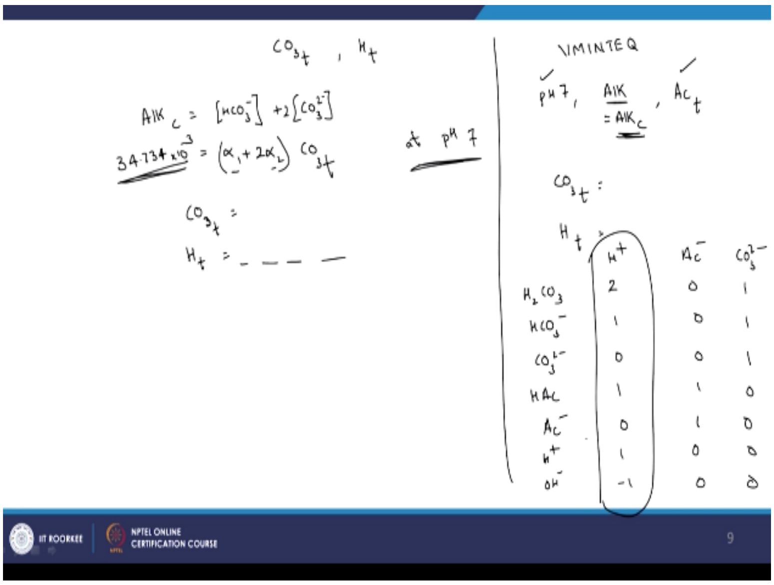

So now what are we trying to find if you remember the question we were asked to find HCo3 total and H total. So by hand how can you do this let us say. You know that alkalinity due to the carbonate species is due to HCo3 – and Co3 2- 2 times Co3 2- which is nothing but alpha

1 + 2 alpha 2 * Co3 total. So I now have the alkalinity due to the carbonate species and that is nothing but 34.734 * 10 to the power -3.

So I can look up to the values for alpha 1 and alpha 2 at pH 7 right, which was our initial case, alpha 1 and alpha 2 at pH 7. I can plug them in and I can calculate Co3 total right and then again you know the relevant speciation, I can plug in the values for H total or in the alkalinity equation let us see and then I can end up calculating the H total too. So again that is by hand. So let us see how we can do that by VMINTEQ.

So obviously in VMINTEQ what am I going to do right we are obviously going to have pH 7 right, I am going to plug in alkalinity, but alkalinity I am going to plug in as equivalent to the alkalinity due to the carbonate species only why is that VMINTEQ can only consider alkalinity as the alkalinity due to carbonate species right. So and what else can I plug in. I can also plug in the acetate total right.

And so once I plug this in I should you know get the relevant output and from the output I can calculate Co3 total and H total which we are going to look at now. So let us see where we are up to now right. So let us close the different XL sheets okay. I am going back to VMINTEQ back to input menu. So now the pH is the initial value what was that please that as we knew was at 7.

So pH is at 7 and view edit list what else so acetate is still 8.33 millimolar right, but what else do I need to plug in let us go back to our particular sheet we already have acetate total we have pH 7. We need to plug in the alkalinity as we just calculated our alkalinity that is due to the carbonate species that is 34.734 * 10 to the power -3 right. So we need to plug that in here and let us go back to here.

And how do we do so parameters specify alkalinity and their equivalence per liter. So I will choose milli equivalence per liter let us say and 34.734 right, yes and I am going to say okay and run VMINTEQ and I have the relevant what do we say aqueous species concentration at equilibrium.

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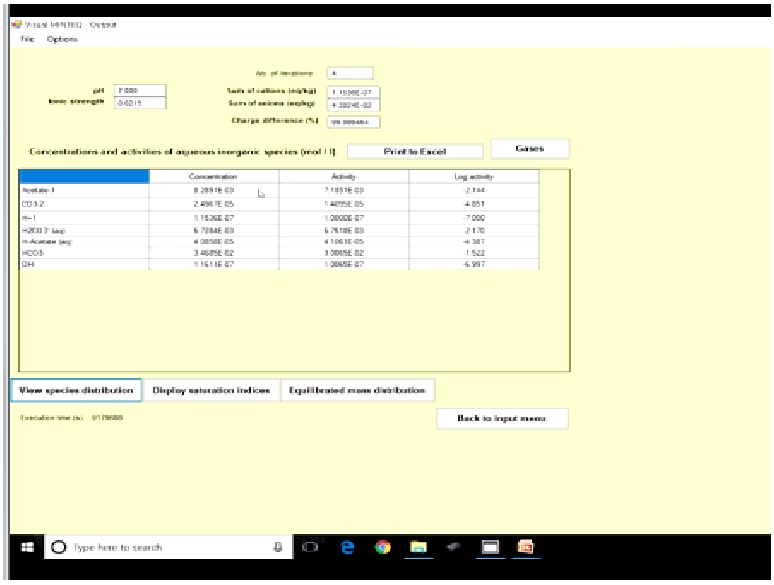

So I am going to print that to XL and I have the relevant cases here.

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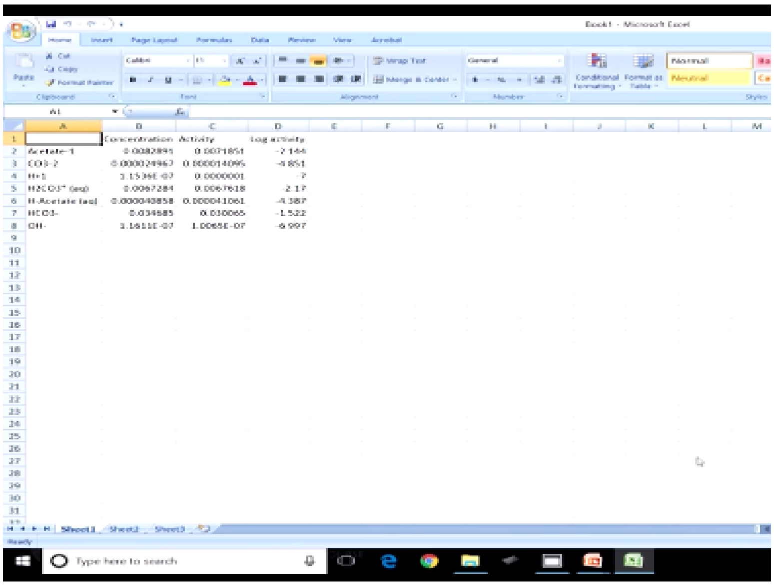

So first let me try to calculate what it is now Co3 total. So that is going to be equal to Co3 2- + HCo3- pardon me, I think I made an error here. I need to go back right now + HCo3- + H2Co3 and enter and so I now have my value for Co3 total right and next I need to calculate H total. So here I need to be relatively careful so I am going to first work it out in VMINTEQ here H total what are the species here.

We know that they are H2Co3, HCo3-, Co3 2- HAc, Ac- H+ and OH- right. So this H+ what is the contribution 2 here and obviously Ac- and Co3 2- which I am not going to plug in here right. So anyway for the sake of ease why not do that to 2, 0 and 1. Here it is 1 0 1 0 0 and 1 how many H+ for HAc 1, how many Ac- for HAc 1 and 0 and again this is 0 1 0 and here it is 1 and -1 0 0.

So how do I calculate H+, it is nothing but this or H total pardon me is nothing but his component balance so 2 times H2Co3 + 1 times HCo3- + HAc + H+ - OH-. So let us plug this in to our XL sheet. So let us see where we are here. So that is going to be equal to 2 times H2Co3 right + 1 times HCo3- right and what else do we have + HAc and where is HAc + HAc right + H+ - OH- and where is OH- here and we now have our Co3 total and H total. So let us just write this down so that we can solve the next parts of the question.

And we have Co3 total = 0.0414 and let me write that down here.

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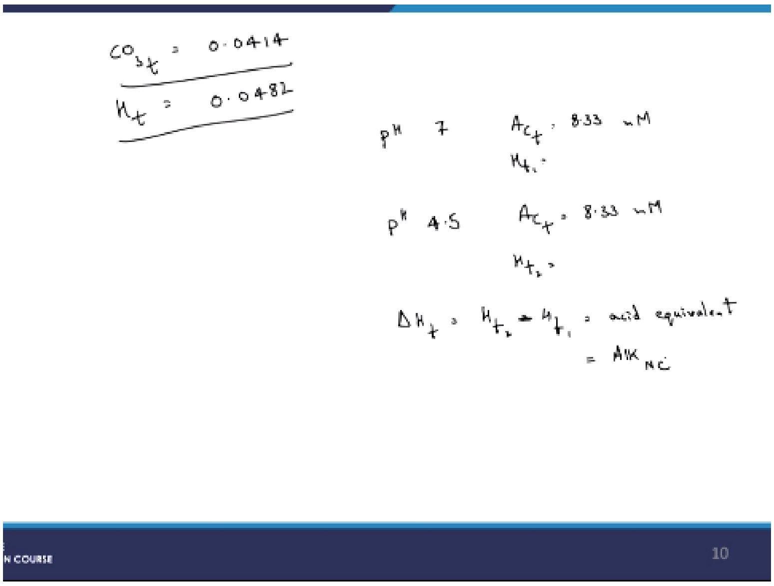

Co3 total = 0.0414 and what is H total = 0.0482 let us say, right, again so let us just review our approach and end today's session and continue the parts B, C and D in the next session but let us just review what we are up to. So again we because theoretical alkalinity you know is not the same as measured alkalinity in this case why is that you have acetate. The anaerobic digester you have acetate formation.

So thus you cannot use that particular 2000 mg/L in the relevant equations and plug that in and go through. So how do I simplify this as we divided total alkalinity into carbonate species alkalinity and alkalinity due to the non-carbonate species and first we had to calculate alkalinity due to the non-carbonate species. How did we do that by you know using VMINTEQ you know to take a short cut right how did we do so.

So we said pH 7 in acetate total we calculated the H total required and again pH 4.5 which is our endpoint for alkalinity and acetate total in VMINTEQ we calculate another H total so the difference between these 2 H totals what does that give us it gives us the amount of acid added to bring down the pH from 7 to 4.5 given that the total acetate concentration is what is it now 8.33 * 10 to the power -3 millimolar right so that is what we had. We had pH 7 and acetate total = 8.33 millimolar.

So if I want to calculate alkalinity due to the non-carbonate species how do I do so. I need to titrate so I looked at this particular case I calculated H total 1, calculate H total 2 and what is the difference here that is nothing but the amount of acid that you are adding to the system right. Acid equivalent right and what is that equal to obviously alkalinity due to the non-carbonate species.

So once we calculate this non-carbonated species alkalinity due to the non-carbonate species we can then calculate alkalinity due to the carbonate species and then we just used VMINTEQ or you know how to use, how to solve the situation or scenario by hand too right. Where alkalinity due to the carbonate species = alpha 1 + 2 times alpha 2 * Co3 total. So you can either use hand or you know simplify and save time by looking at VMINTEQ. So with that I will end today's session and we will look at the other 3 or 4 parts of the question in the next class and thank you.