# Environmental Engineering Chemical Processes
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## Lecture - 35
## Anaerobic Digester: Acid Formation and Neutralization

Hello everyone. So welcome back to our latest lecture session. So we were looking at a practical example on the theoretical definition of alkalinity is not valid yes because we have I think we are looking at the case of an anaerobic digester where we have acetic acid being formed thus you know your theoretical definition is not going to be valid.

Because your acetate ion can either take the proton or either the acetic acid can donate the proton. So we try to calculate by looking at H total 1 and H total 2 and the difference. We try to calculate H total and CO3 total and we end up doing that. So now we need to look at the other aspects of the question. So let us look at what the so obviously the question here is.

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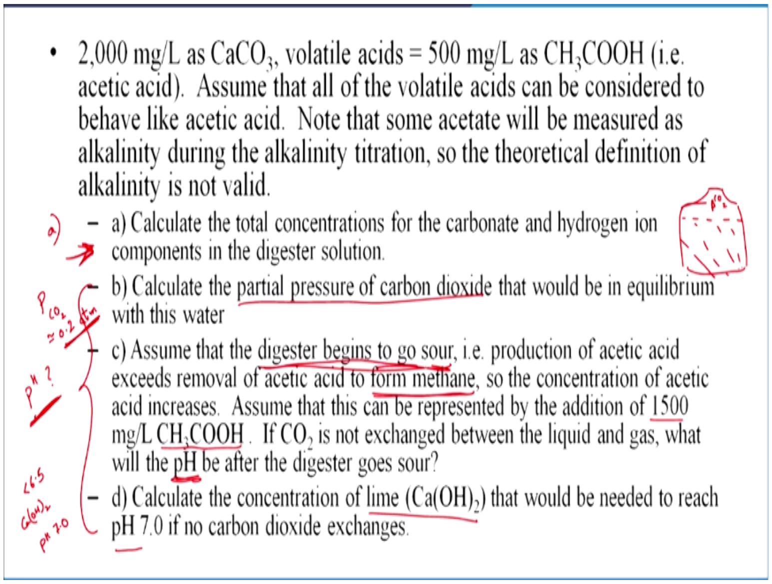

- 2,000 mg/L as $CaCO_3$, volatile acids = 500 mg/L as $CH_3COOH$ (i.e. acetic acid). Assume that all of the volatile acids can be considered to behave like acetic acid. Note that some acetate will be measured as alkalinity during the alkalinity titration, so the theoretical definition of alkalinity is not valid.
  - a) Calculate the total concentrations for the carbonate and hydrogen ion components in the digester solution.
  - b) Calculate the partial pressure of carbon dioxide that would be in equilibrium with this water
  - c) Assume that the digester begins to go sour, i.e. production of acetic acid exceeds removal of acetic acid to form methane, so the concentration of acetic acid increases. Assume that this can be represented by the addition of 1500 mg/L $CH_3COOH$. If $CO_2$ is not exchanged between the liquid and gas, what will the pH be after the digester goes sour?
  - d) Calculate the concentration of lime ($Ca(OH)_2$) that would be needed to reach pH 7.0 if no carbon dioxide exchanges.

About calculating the partial pressure of carbon dioxide that would be equilibrium with this water. So in general let us say your anaerobic digester (()) (01:17) a graph here, so you are going to have your particular solution here and you are going to have some what do we say head space here, so you are going to obviously have a partial pressure of carbon dioxide. So the question asked is what is the partial pressure of carbon dioxide that would be in equilibrium with this particular solution?

We are not adding any other component. So that is something we should look into and also let us look at the other cases and see why we need to go through that and say that assume that the digestion begins to go sour and in general let us say your acidic acid I know it is going to form methane or ended up after the Redox process you are going to have methane being formed, but the kinetics is slower let us say what is going to happen you are going to have additional or you know more formation of acetic acid so that is what happening here at I believe.

Assume that the digester begins to go sour as in production of acetic acid exceeds the removal of acetic acid to form methane so the concentration of acetic acid increases. So here the rate at which methane is being formed from acetic acid is looks like is slower than rate of production of your acetic acid so the digester is beginning to go sour. So assume that this can be represented by the addition of 1500 mg per liter of acetic acid.

So, additional amount of acetic acid present is equivalent to 1500 mg per liter of acetic acid. If CO2 is not exchanged between liquid and gas what will be pH after the digester goes sour. So assuming that it is a close system let us say what would be the pH. So again why do you need to calculate the pH now right in this particular anaerobic digester you have different phases hydrolysis acidogenesis, acetogenesis, and methanogenesis and the relevant what do we say?

Microorganisms that are required for acetogenesis and methanogenesis you know they are acting only in a very narrow pH range as and I think 6.5 to 8 or 7.5. Do not take my word for it, but any way near the neutral pH now. So when we have excessive formation of acetic acid you know that is taking place what would you observe? You would have observed that the pH false down. So the pH falls down what is going to happen?

You whole what do you say process is going to trash because obviously the methanogenesis is not going to go through. You are not going to have formation of methane which is what you are trying to produce. A gas that has high calorific value which can be used for commercial purpose let us see. So that is one of the reasons why you would want to maintain a particular pH. So obviously you can either monitor the pH regularly or obviously you can look at or calculate using VMINTEQ or by hand and predict.

What is going to be pH and be ready with the relevant remedial actions? So again let us look at part D2. So obviously now calculate the concentration of lime which is a source of OH - ions that would be needed to reach the pH 7 if no carbon dioxide exchanges. So in this case we are just trying to calculate the partial pressure of CO2 that would be need in equilibrium with the case as calculate in part A and in part C we are trying to predict what would be the pH or drop in pH if you have digester going sour yes.

And then because obviously you cannot let the pH fall below let us say 6.5 what we are trying to do we are trying to add lime a source of OH - the base so that you bring up the pH again to what pH now pH 7 and so now that we understand what it is that the questions are about or what is it that we are trying to achieve let us go through and see how do we go about the situation. So here obviously calculate the partial pressure of carbon dioxide that would be in equilibrium with this water so that can be achieved just by plugging in the values from the last time.

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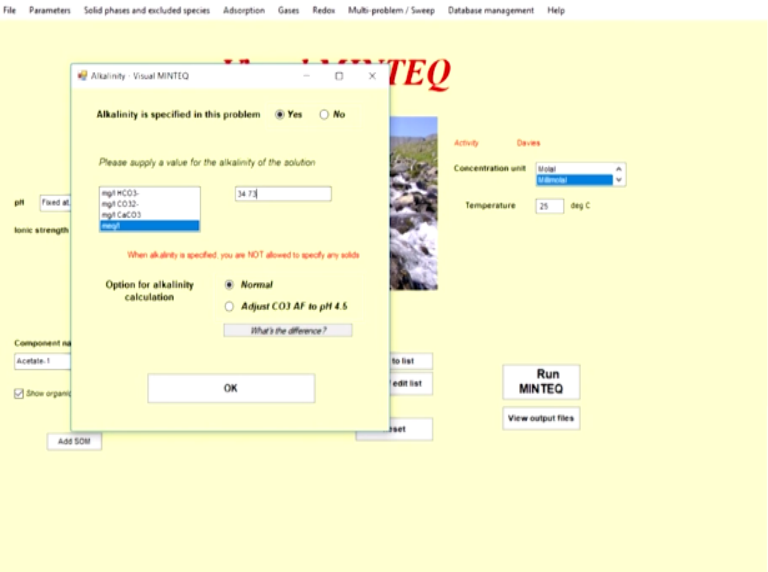

Alkalinity is specified in this problem ● Yes ○ No

Please supply a value for the alkalinity of the solution

meq/l: 34.73

When alkalinity is specified, you are NOT allowed to specify any solids

Option for alkalinity calculation ● Normal ○ Adjust CO3 AF to pH 4.5

pH: Fixed at

Ionic strength

Activity: Davies

Concentration unit: Millimolal

Temperature: 25 deg C

Component na: Acetate-1

☑ Show organic

So I believe I should have showed them. I have not reviewed them from my particular case, but let me see if I remember how to do so. So earlier I believe we looked at pH was fixed at 7 and what else we need to have state concentration. We had a state at 8.33 if I am not wrong. 8.33 and the units are millimolar add that to the list and what else is required. We had pH 7 and I believe we also had to add alkalinity and alkalinity was what is it now?

And I think we had the milliequivalents per liter I think it was 34.7 or 34.734 I believe. 34.734 in milliequivalents per liter so I am going to add that and so we ran the VMINTEQ and we calculated from this particular table CO3 total and H total which we obviously do not need to do that because we already have that, but it is just asking what is the question asking for. What would be the partial pressure of carbon dioxide that would be in equilibrium with this particular system?

So as if it is not as you are now opening of the system or such if it were open what partial pressure of carbon dioxide would maintain this particular pH and this particular CO3 total. So we know VMINTEQ has already what is the solution for that. It says you know if you just click on gases it will give you an idea about the partial pressure that would be you know in equilibrium with this particular solution and that we have means 0.02 atmosphere so I guess.

So but 1 key aspect that you remember I guess this is a theoretical I mean practical question but some of the values might have been off because the carbon dioxide in anaerobic digester the partial pressure would be you know much greater than 0.2 atmospheres. But anyway that is something for you from practical point of view but the gas that would be present here in equilibrium with the solution would be what is now 0.02 pardon me 0.2 atmospheres.

Anyway let us be done with that and now move back to our particular case. So I am going to restart VMINTEQ so that I do not have issues further because now I am not going to plug in alkalinity again. So let us look at the question here. So what is the first aspect? This aspect we have done partial pressure of CO2 I think we calculated that particular value to be approximately equal to what now 0.2 atmospheres by just looking at the short cut tab we may take as first and now we move on to estimating the pH if the digester begins to go sour.

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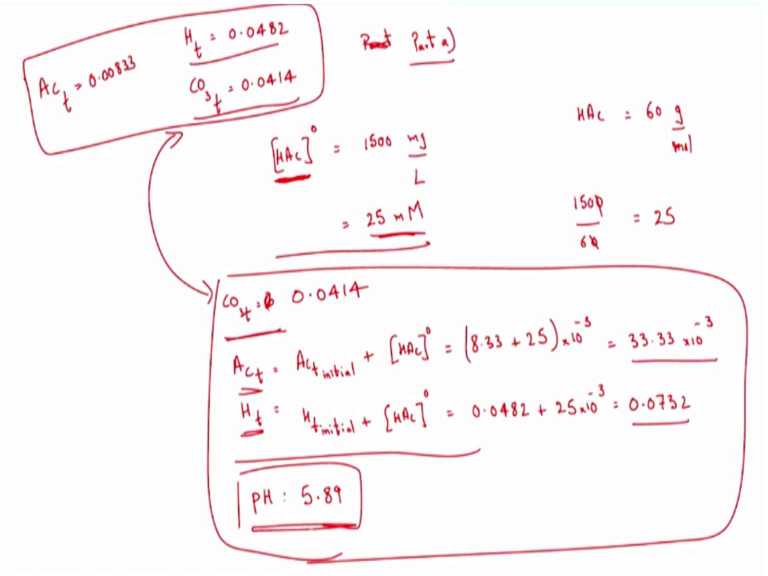

$Ac_t = 0.00833$ $H_t = 0.0482$ $CO_{3t} = 0.0414$

Part a)

$[HAc]^0 = 1500 \frac{mg}{L}$

$= \underline{25\ mM}$

$HAc = 60 \frac{g}{mol}$

$\frac{1500}{60} = 25$

$\underline{CO_{3t} = 0.0414}$

$Ac_t = Ac_{t\,initial} + [HAc]^0 = (8.33 + 25) \times 10^{-3} = \underline{33.33 \times 10^{-3}}$

$H_t = H_{t\,initial} + [HAc]^0 = 0.0482 + 25 \times 10^{-3} = \underline{0.0732}$

$\boxed{pH : 5.89}$

So let us look at what we have here and these are the values of H total and CO3 total from part A and this is what we I believe we calculated from part A and now let us say what is the new aspect that we have now. We have additional acetic acid HAC not and that the concentration of 1500 milligram per liter. So I want to convert this into millimolar units I think earlier we calculate the molecular weight of acetic acid as 60 g per mole.

So dividing by 60 what is that going to be 1500/60 and so I think it should be around 25 = 25 millimolar. So what does this mean now? So in effect the digester has gone sour to the extent that 25 millimolar of acetic acid or millimolar, pardon me, milimoles of acetic acid has been formed. So now we need to take this into our account and be able to go further. So how do we go further now? So what factors are going to change now?

If CO3 total going to change? No, because we have any components or you know of CO3 total here now CO3 total is going to change, but what is going to change obviously you are acetate total and H total are going to change I should have also written down the acetate total here, but I think we note that is 8.33 * 10 power - 3 so I am going to write that down here. So by adding HAC at 15 or 25 millimolar per liter how are these particular total components will change?

So that is going to be = acetate total initial + this new edition of acetic acid and that is going to be = what is now 8.33 + 25 * 10 power - 3 and that is going to = 33.33 * 10 power - 3 and H total is again going to = H total initial + HAC not and that is going to = what do we have initially it is 0.0482 + 25 * 10 power - 3 so let us use excel to may be plug the cell and I think we already have this value. This is our particular case of H total so + 0.025 and enter so we now have 0.0732 let us say and where do we have that that is = 0.0732.

So now we have our new conditions what are they? We have CO3 total that is still same at earlier because addition of HAC will not affect CO3 you are not putting any source of CO3 so that is going to = 0.0414. So I have CO3 total, I have acetate total and I have H total. So plug in this in what can I calculate I can calculate now the pH. So again if you know try to look at it holistically, you are adding in, you are producing acetic acid which is equivalent to adding more acetic acid to your initial solution.

So thus we included the affects of this addition of 25 millimolar, acetic acid on our total components. You have case 1 and case 2 and you have more acetic acid so that is what we considered and calculated the total components of what is it CO3, H total and acetate total when we added acetic acid obviously CO3 total is not going to change obviously because you are adding HAC, H total and AC total are going to increase and that is what we calculate it.

So we now need to calculate the pH. So once you add this amount of acetic acid to the initial solution what is the pH going to be. So that is what we are going to plug in and look at here I guess. So let us go back to VMINTEQ and hopefully we can come back to these numbers when we want to and I think we need to calculate the pH so we are not going to look at that. I need to show the organic compounds because I am going to have acetate total.

And now I am going to have acetate total and what is that particular value please that = 33.33 millimolar and where is this particular case and then what next I also have CO3 total and where is that and let us look at that particular value where is that value please CO3 total is 41.4 let us say. Millimolar and let us plug that in here and now I need to plug in H total I believe and where is that H total was = 73.2 * 10 power - 3 millimolar I am going to add that list just check to make sure look right let us run it.

And see if we have materials I guess so run VMINTEQ and obviously now I means seems okay and what do you see now obviously if you added acetic acid at 25 millimolar to a particular solution so we now see that the new pH has fallen down to 5.88 so let us just plug this in here and so now so what is the new pH it is now 5.89 so that is something that we need to keep in mind. So again once now the digester went sour as in you are the rate at which acetic acid was being produced was greater than the rate at which the acetic acid was being.

What is it reducing it to methane? So what is happening here? you have accumulation of acetic acid so thus you are ending up decreasing the pH and we wanted to calculate the pH so now that is 5.89 which is considerably < pH of 6.5 which is I guess in general the lower threshold for affective production of this methane or you know for the methanogenesis so that is particular case so now see that the pH is less than what do you want.

So obviously you need to maintain the pH so thus part D asks us what would be the amount of lime required to bring the pH back to your particular value of pH 7. So that is what we are going to calculate. So let us look at that and let us just look at the question 1 last time. So calculate the concentration of lime that would be needed to reach the pH 7 if no carbon dioxide exchanges I mean considering that it is a clear system more or less.

So we need to go back to pH 7 from what is it now 5.9 pH. So let us see how to go about that and I believe we need to again write down some of our initial values but we can come back to this slide if required I guess. I believe we will need to look at some of these values or these values too so that is just highlight them here. So how do I calculate this now?

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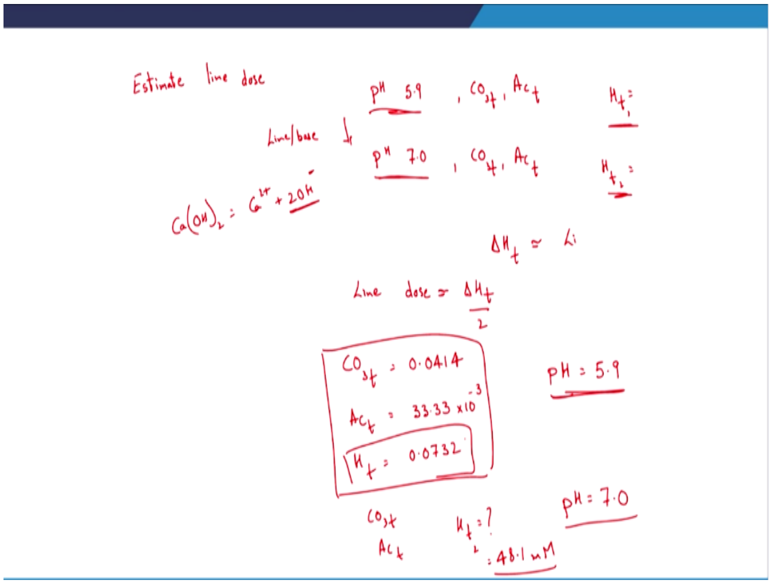

Estimate lime dose

pH 5.9, $CO_{3t}$, $Ac_t$ $H_{t_1}$ =

Lime/base ↓

pH 7.0, $CO_{3t}$, $Ac_t$ $H_{t_2}$ =

$Ca(OH)_2 = Ca^{2+} + 2OH^-$

$\Delta H_t \approx$ Li

$\text{Lime dose} = \frac{\Delta H_t}{2}$

$CO_{3t} = 0.0414$

$Ac_t = 33.33 \times 10^{-3}$

$H_t = 0.0732$

pH = 5.9

$CO_{3t}$

$Ac_t$

$H_t = ?$

$= 48.1\ mM$

pH = 7.0

I can estimate lime dose now. How can I estimate lime dose now? This is similar to your alkalinity of carbonated and non carbonated and how would you estimate that. You estimate that by adding the amount of acid required to bring down pH from 7 to 4.5. So here you are going to you know have a trial and error approach. So we are going to you know we know the cases for the total components for pH of 5.9.

So we are now just going to plug in the same total component at pH of 7 which is the pH that we want to go to and we are going to calculate the difference in H total and from that we can calculate the equivalent amount of the lime required. That is from trial. So again what is that we are trying to do? So let us say we have pH of I think 5.9 and we have the relevant CO3 total and acetate total at this particular case and you can calculate H total and let us say if I am going to go to pH of 7.0 and maintain the same CO3 total and acetate total.

I am going to calculate new H total and what is this or how can this particular pH increase to 7 only when lime or a base is added. So by calculating the difference here delta H total I can estimate the amount of lime that is required. So it is equivalent obviously because CaOH were twice CaOH whole twice that is = Ca 2 + + 2 times OH -. So it needs to be balanced by a normalized by a factor of 2.

So this particular lime dose is obviously done because it is 2H - per mole of lime so it is going to = delta H total/2 so that is going to = the approximate concentration of lime dose. Why do I say approximate because we have not yet covered the relevant aqueous complexes I guess but you know Ca2 + will have can form complexes but here you know we have more or less constraint that Ca2 + is non-reactive?

So we have then first estimate the amount of lime dose required plug that in and then see if that particular value reaches to pH 7 if not we will have some trial and error procedure. So again what are we trying to do? So first plug in you know trying to find H total 1 and H total 2 at different values of 5.9 and 7.0 and go through from that. So let us go through from here please and I need to go to VMINTEQ here. VMINTEQ back to input menu.

Did I specify any alkalinity? I specified alkalinity to be on safer side. I am going to restart VMINTEQ. Now we are going to VMINTEQ and let us look at R particular values here what are our CO3 total and acetate total please. They are CO3 total is where is our case. CO3 total is new to CO3 total is still 0.0414 so I am going to write that down here CO3 total = 0.0414 and acetate total is = 33.33 * 10 power - 3 acetate total = 33.33 * 10 power - 3 and thus is the pH of what was the pH we approximate that 5.9.

So because I am going with an approximation and I guess I calculate H total or I can also just use the pH H total from the previous case what was the previous case H total it was 0.0732. So H total was 0.0732. This was the initial case. So I am not going to run that so what is the case I am looking for. How much base is required to bring up the pH to 7.0. So now I am going to plug in CO3 total same case is about acetate total, same case is above and fix the pH at 7 and then calculate what is the H total?

So let us go back to VMINTEQ now and plug in CO3 total 0.0414 and acetate total. So let us go back to VMINTEQ. So pH is now fixed at a particular value and what is that 7 and I need to plug in acetate total and CO3 total and first I am going to plug in acetate total I think we mention that it was 41.4 millimolar and let us look at that 41.4 and I just made a mistake here. 41.4 And it is millimolar and I am going to add to the list and what about CO3 2 - was it 33.33 millimolar or something else. Where is CO3 2 - it is right here. What is the CO3 total was. I think I messed up the values acetate total was 33.33 * 10 power - 3 and CO3 total was 0.0414 is that right.

So I need to I guess plug that in CO3 total was 0.0414 and what did I plug in. I plugged in the reverse I think I need to just change that here. So CO3 total is 0.04 acetate total is 33.33 so I am going to plug that till here and then CO3 total and that I think is 44.4 millimolar and let us just check that to 41.4 millimolar. We are on the right track. So I am going to add that to the list. 41.4 CO3 2 - acetate total is 33.33 back to main menu. pH 7 is fixed and so I am going to run the VMINTEQ and now I need to calculate H total obviously.

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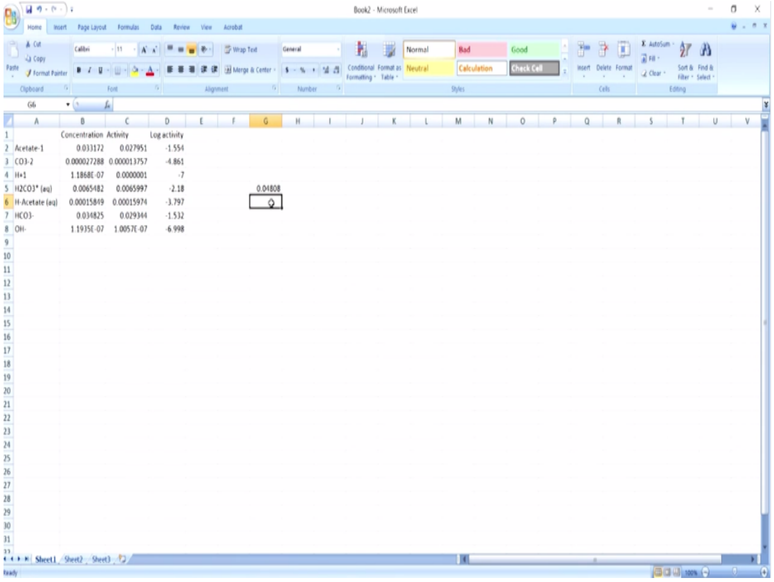

|  | Concentration | Activity | Log activity |  |
|---|---|---|---|---|
| Acetate-1 | 0.033172 | 0.027951 | -1.554 |  |
| CO3-2 | 0.000027288 | 0.000013757 | -4.861 |  |
| H+1 | 1.1868E-07 | 0.0000001 | -7 |  |
| H2CO3* (aq) | 0.0065482 | 0.0065997 | -2.18 | 0.04808 |
| H-Acetate (aq) | 0.00015849 | 0.00015974 | -3.797 |  |
| HCO3- | 0.034825 | 0.029344 | -1.532 |  |
| OH- | 1.1935E-07 | 1.0057E-07 | -6.998 |  |

So I am going to print to Excel and here we have the relevant output I believe. So H total would be = what are the components that are need to look at H + + 2 times H2CO3 + HEAC + HCO3 - - OH - and enter. So I get a value of 0.048 or 48.1 millimolar let us say. So let me plug till here so now H total was = H total 2 was = 48.1 millimolar and what was the H total earlier it was 73.2 millimolar. So let me just write that down here.

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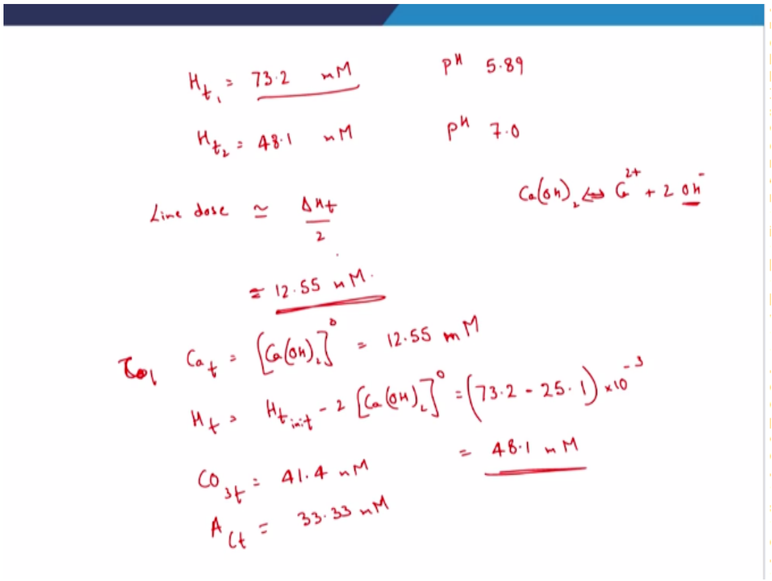

$H_{t_1} = 73.2$ mM   pH 5.89

$H_{t_2} = 48.1$ mM   pH 7.0

Lime dose $\simeq \frac{\Delta H_t}{2}$   $Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^-$

$= 12.55$ mM.

Tol $Ca_t = [Ca(OH)_2]^0 = 12.55$ mM

$H_t = H_{t_{init}} - 2[Ca(OH)_2]^0 = (73.2 - 25.1)\times 10^{-3}$

$= 48.1$ mM

$CO_{3t} = 41.4$ mM

$A_{Ct} = 33.33$ mM

So H total 1 was = 73.2 millimolar and H total 2 was = 48.1 millimolar and this was obviously at pH of 5.89 and this is obviously at a pH of 7. So what causes this particular increase in pH 7 or the decrease in H total only when we add base so the base that we are considering that we are adding here is lime. So as we looked at earlier we know Ca OH twice = Ca 2 + and 2 times OH -. So the lime dose approximate lime dose would be = delta H total/2 so 73.2 - 48.1 let me plug that in = 73.2 - 48.1.

So obviously it needs to be half of this value is = 25.1 = this/2 so I get a value of 12.55 millimolar. So I am going to switch back here so lime dose is approximately = 12.55 millimolar. So this is what we have so but first again this is the case when we assume that Ca2 + is relatively nonreactive which is generally valid, but in the pH is still going to slightly off when you consider this exact dose so we need to confirm whether or not when we plug in this value of 12.55 millimolar lime dose we will achieve our particular case.

So we need to just run the confirmatory run. So let us run that here. So the Ca total calcium total is the new component right. Ca total = Ca OH whole twice not and that is obviously = 12.55 millimolar and what else we need to also calculate H total = H total initial - 2 * Ca OH whole twice. This is the amount of base we are adding. 2 times because 2 OH -. H total initial - this and that is something let us calculate that.

What was H total initial that was 73.2 - 2 * 12.55 I think was 25.1 this * 10 power - 3 molar so let us just plug this in 73.2 - 25.1 that is = 73.2 - 25.1 and so 48.1 so that is = 48.1 I guess it is more or less same of what we arrived at earlier, but let us just plug this in and in VMINTEQ and see if we are going to get the relevant values or not. So obviously we need to plug in H total, Ca total, and what else CO3 total and acetate total and what are these values CO3 total.

So CO3 total was 41.4 millimolar, 41.4 molar and acetate total was 33.33 millimolar. 33.33 millimolar so let us plug this in to VMINTEQ back to input menu. So I think CO3 total and acetate total should still be present here. Acetate right so we do not need to change that. We need to add Ca total and where is that equal to and the value of Ca total was supposed to be = 12.55 millimolar.

So this has to be 12.5 and units are millimolar I am going to add that to the list and obviously I need to plug in H and how much was the H total now what is the H total here and I need to look it up here H total = 46.1 millimolar 48.1 millimolar and I need to change that value here 48.1 millimolar, units are also millimolar, so obviously the pH needs to be calculated. It is not fixed at a particular value.

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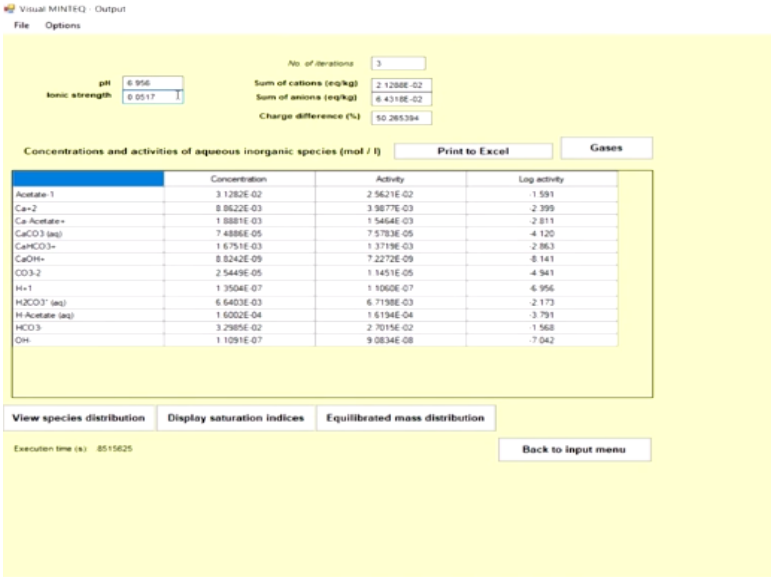

No. of iterations: 3

pH: 6.956

Ionic strength: 0.0517

Sum of cations (eq/kg): 2.1288E-02

Sum of anions (eq/kg): 6.4318E-02

Charge difference (%): 50.265394

Concentrations and activities of aqueous inorganic species (mol / l)

| | Concentration | Activity | Log activity |
|---|---|---|---|
| Acetate-1 | 3.1282E-02 | 2.5621E-02 | -1.591 |
| Ca+2 | 8.8622E-03 | 3.9877E-03 | -2.399 |
| Ca-Acetate+ | 1.8881E-03 | 1.5464E-03 | -2.811 |
| CaCO3 (aq) | 7.4886E-05 | 7.5783E-05 | -4.120 |
| CaHCO3+ | 1.6751E-03 | 1.3719E-03 | -2.863 |
| CaOH+ | 8.8242E-09 | 7.2272E-09 | -8.141 |
| CO3-2 | 2.5449E-05 | 1.1451E-05 | -4.941 |
| H+1 | 1.3504E-07 | 1.1060E-07 | -6.956 |
| H2CO3* (aq) | 6.6403E-03 | 6.7198E-03 | -2.173 |
| H-Acetate (aq) | 1.6002E-04 | 1.6194E-04 | -3.791 |
| HCO3- | 3.2985E-02 | 2.7015E-02 | -1.568 |
| OH- | 1.1091E-07 | 9.0834E-08 | -7.042 |

Execution time (s): .8515625

So let us just review and edit the list. H total 48.1. Acetate total 33.33 and the other values back to the input main menu and I am going to run MINTEQ. I see that the pH is 6.95 not exactly 7?

So I need to obviously increase the concentration of what now. I need to increase the concentration of lime slightly to be able to arrive at my particular pH of what is this now 7 so why is this?

If you look at that the reason for this particular case is that you know Ca acetate ca CO3 and Ca CO3. You have some particular complexes being formed. In the earlier case when we looked at this particular example of you know adding lime and calculating H total difference we assume that the Ca total or Ca 2 + was relatively nonreactive, but that is not the case here. You have aqueous complexes going to be formed and this is going to be our next session.

So until now we have discussed acids and bases. So here as you see the Ca2 + is not relatively nonreactive. It has or it binds with the other ligands which are acetate ion, HCO3 - and CO3 2-. So these are called aqueous complexes when you have a metal and a ligand which is an electron rich species. Metal is an electron deficient species and then you have a more soluble complex that is formed that is going to be called the aqueous complex which you are going to discuss further in the next set of classes.

So, with this particular so how I will go further? I just need to increase the lime dose to be able to arrive at my pH that is a trial and error case so that I can do that, but we are not going to do so. So in the next set of classes we are going to obviously start looking at the next major aspect which is acids and bases. So at this stage you know it is just worthwhile to look at what we have been up to so far. So until now what have you been up to?

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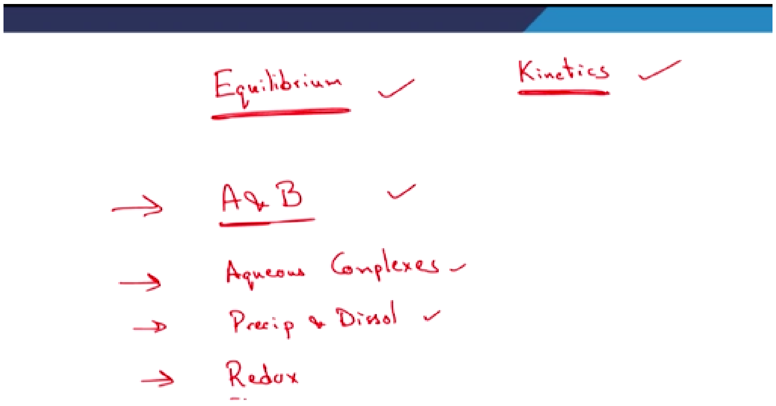

Equilibrium ✓
Kinetics ✓

→ A&B ✓
→ Aqueous Complexes ✓
→ Precip & Dissol ✓
→ Redox

We looked at the basics equilibrium how far can a system go or travel and kinetics. This gives us an idea about how fast can this system go. How far can the system travel how fast can the system go let us see. So after this particular aspect we moved on to the major aspect of acids and bases which we discussed for 1 third of the class until now or more than half of it which is the major aspect in our environmental engineering.

And now we are going to move on to aqueous complexes which would be of great practical application in most cases where you have any metals present or you know when you have natural organic matter present. So metals will be present in let us say in coagulation and flocculation when you are choosing the type of coagulant use let us say or when you have contamination due to a particular metal and soil or ground water.

Again you have complexes being formed and that in either another aspect that you need to look at why is that when you have complex being formed in general the metal or the total metal concentration tends to increase why is that because aqueous complexes are generally more soluble and that will in general lead to a total concentration of your particular metal increasing. Anyway we will go through this in the next set of classes.

So aqueous complexes and then we are going to look at precipitation and dissolution and the last aspect we are going to consider is Redox. So we have done with this, this and this. So we are going to briefly talk about these 2 aspects aqueous complexes and precipitation and dissolution and you want the next major topic which is Redox process something that is backbone of environmental engineering I guess.

So again what is the common factor between how can I differentiate between these 3 aspects and Redox reactions obviously the acid bases, aqueous complexes and precipitation and dissolution the oxidation number or oxidation state of your particular atom or your particular compound does not change. It is only the coordination number that changes, but in the Redox process you have a change in oxidation state of your particular compound or the atom part.

With that I will end today's session and we will move on to aqueous complexes from the next set of classes and thank you.