Environmental Engineering: Chemical Processes
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Lecture - 45
Other examples of Equilibrium of Precipitation

Hello everyone, so welcome back. I believe we have been discussing a relevant practical problem right and I think here the case was we are adding FeCl3 as the flocculant right and in the initial case or part A we looked at simple scenario as in what is the pH and what is the total amount that precipitates out or the total amount of iron that is present in the solution in the dissolved phase right.

So with that we are done but part B you know slightly increase the complexity in that it tries to mirror some of the aspects of water quality that would actually be present in nature. So what is that obviously?

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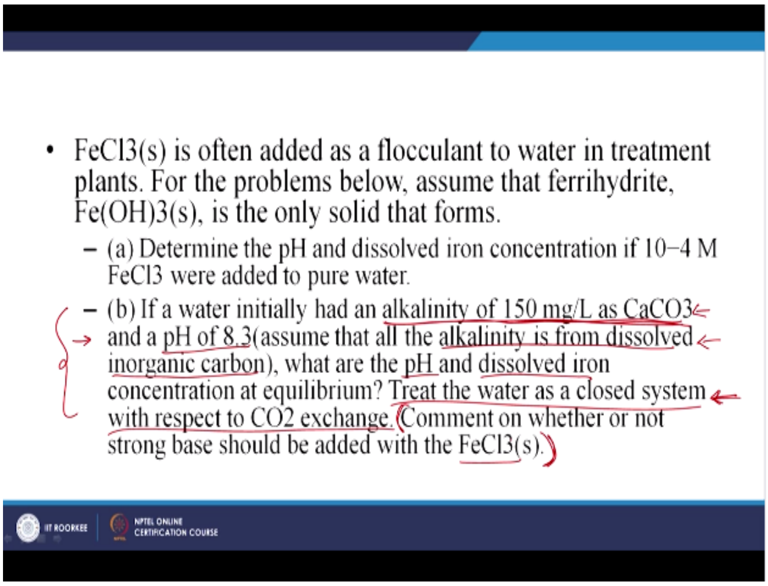

- FeCl3(s) is often added as a flocculant to water in treatment plants. For the problems below, assume that ferrihydrite, Fe(OH)3(s), is the only solid that forms.
  - (a) Determine the pH and dissolved iron concentration if 10−4 M FeCl3 were added to pure water.
  - (b) If a water initially had an alkalinity of 150 mg/L as CaCO3 and a pH of 8.3(assume that all the alkalinity is from dissolved inorganic carbon), what are the pH and dissolved iron concentration at equilibrium? Treat the water as a closed system with respect to CO2 exchange. (Comment on whether or not strong base should be added with the FeCl3(s).)

So here now we have a new aspect as in we have alkalinity too present and which is what you would usually expect right. Alkalinity is ever present in your water or waste water. So this is something you should usually consider and let us see now let say how that is going to affect our particular calculations right. So obviously again I think this is same aspect but with an additional aspect of alkalinity is present and initial pH is 8.3 right.

And so here also alkalinity is only due to dissolved inorganic carbon as in there are no other predominant conjugate acid base species other than H2CO3, HCO3- and CO3 2- that is what it means right, otherwise as you remember in alkalinity when we looked at I think phosphate or such particular example when we add other relevant conjugate acids and bases at high concentrations, we had to look at or we have to consider the effect of these bases on the alkalinity too right.

Again what is alkalinity, it is nothing but acid neutralizing capacity. So we need to look at all the bases. Again I am just trying to refresh your memory here and so obviously we have an alkalinity of particular value and we have pH of given value or certain value and so again what is the pH and dissolved iron concentration at equilibrium, so same case as earlier but with a few other variables.

So treat this as a closed system, so they are saying okay do not increase the complexity, just treat this as a closed system and then more or less based on the relevant aspects that we are going to look at here we need to be able to comment on whether or not a strong base should be added along with FeCl3 in this particular scenario okay. So let us try to understand the system here I guess.

So obviously pH was or is now 8.3 and there is also alkalinity. So let say I am putting in ferric iron in the form of FeCl3 from part A if you remember that the pH drop from I mean from the neutral solution to 3.5 right but in the earlier case the initial pH was 7 right that is what we would presume right water and also that it had no alkalinity but in this case obviously the pH is relatively higher 8.3 and more importantly alkalinity is present as in the particular solution can neutralize any acid that is added to the solution.

So you would obviously not expect such a great drop in the pH right that is something that we should be able to understand you know before we start our calculations yes and then let us see what we end up with and go through with that and then try to analyze the system with respect to the effectiveness of the flocculant right FeCl3. So again first I am going to solve this by hand but not in as detailed manner as I guess we did it in the previous session right.

But we are going to set up the relevant equations first by hand and then obviously solve it by VMINTEQ right. So I am going to go through with setting of the relevant equations in hand.

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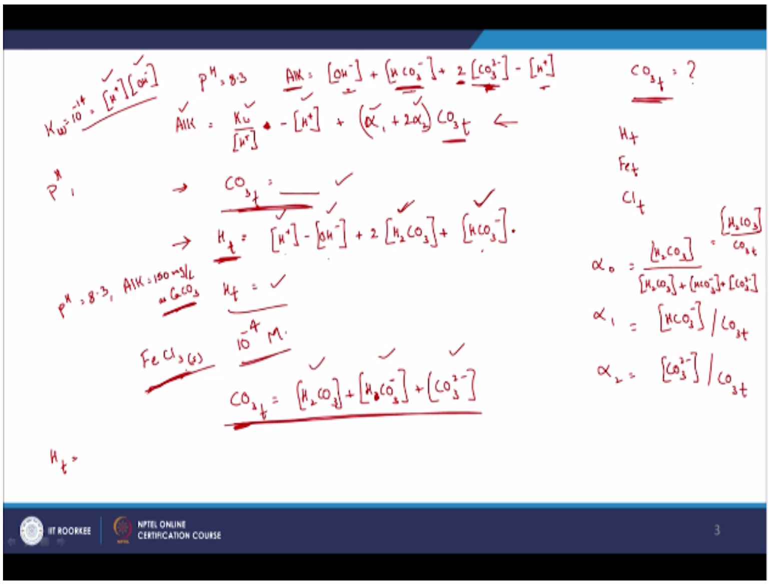

$K_w = 10^{-14} = [H^+][OH^-]$

$pH = 8.3$

$Alk = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$

$CO_{3t} = ?$

$Alk = \frac{K_w}{[H^+]} - [H^+] + (\alpha_1 + 2\alpha_2)CO_{3t} \leftarrow$

$pH,$

H_t

Fe_t

Cl_t

$\rightarrow CO_{3t} = \_\_\_$

$\rightarrow H_t = [H^+] - [OH^-] + 2[H_2CO_3] + [HCO_3^-].$

$\alpha_0 = \frac{[H_2CO_3]}{[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]} = \frac{[H_2CO_3]}{CO_{3t}}$

$pH = 8.3$, $Alk = 150$ mg/L as $CaCO_3$

$H_t = $ ✓

10^{-4} M.

$FeCl_{3(s)}$

$\alpha_1 = [HCO_3^-]/CO_{3t}$

$\alpha_2 = [CO_3^{2-}]/CO_{3t}$

$CO_{3t} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

$H_t =$

So here though the key is that I already have pH and I have alkalinity right and what is the alkalinity now? You know that alkalinity is the acid neutralizing capacity but here obviously again the key was that only the carbonate species are the relevant species so we are only going to consider them so what are all the bases present here? They are OH- right +HCO3- right+2 times CO3 2- because it can neutralize 2 moles of H+ right and obviously –H+ right.

This is obviously the theoretical definition of alkalinity too if you can refresh your memories I guess right. So we have this particular piece of information. So obviously here what does the presence of alkalinity entailed I guess you know what do we need to understand from that. Obviously that means you have sources of inorganic carbonate right. So that means you need to come up with way to find out what is the CO3 total yes.

So in the earlier example if you remember we only considered H total, Fe total and Cl total right which we obviously need to consider right now too but obviously an additional aspect that you need to consider is CO3 total. Obviously that is going to have some acid neutralizing capacity, so how do I find that? First we are going to solve this by hand obviously right. So alkalinity again I know this particular value that was given I think I can change the units to moles I guess right, molar units or equivalent units if required right.

And I think what is it now 50 grams per equivalent right for CaCO3 and I can divide and get it in equivalence per liter you know anyway so alkalinity is a known value and how can I express this equation as let us see. So OH- I can calculate because pH is given as 8.3 and I know that Kw is 10 power -14 that is=concentration of H+*concentration of OH-. So pH is given or H+ is given, so I can calculate OH-.

So alkalinity=let say what now Kw/H+ +HCO3- and 2CO3 2- which I am going to plug in now but first I am going to plug in H+, so these two are known values alkalinity too is a known value. Again we need to again use some of our what do we say you know dig into our knowledge base with respect to our acid base chemical process. So how can you express these species HCO3 and CO3 2- in terms of the variable that you want to calculate in and what is the variable you want to calculate obviously?

It is CO3 total, so if you can dig in you would remember that we had ionization fractions right and that is nothing but let us say in this alpha 0 case H2CO3 concentration/H2CO3+HCO3-+CO3 2- right and that is nothing but being equal to H2CO3/CO3 total yes and alpha 1 similarly would now be HCO3-/CO3 total and alpha 2 would be CO3 2-/CO3 total right.

So obviously I am going to plug them in here, so it is going to be=1 of alpha 1 I guess it is alpha 1+2 times of alpha 2*CO3 total right. So nothing but HCO3- and CO3 2- alpha 1+2 alpha 2*CO3 total, so alpha 1 and alpha 2 again are constants at a particular pH right and for the particular compound which in this case is H2CO3, HCO3- and CO3 2- so you can calculate pardon me alpha 1 and alpha 2 right.

And I can then end up with I just have one equation and one unknown, so I can now calculate CO3 total right. So with that I can calculate CO3 total, so until now obviously what have we done? We have just analyzed the system but obviously there is one other aspect as in you also need to calculate H total that is present initially right and what is H total present as initially now? Instead of writing the relevant what do we say formation equations and then the Tableau in such obviously I am going to skip them here for now.

And then try to write them down here right, so I know it is going to be=H+ -OH- and what are some of the other species obviously H2CO3, HCO3- and CO3 2- so for H2CO3 there is going to be 2H right contribution so it is going to be H2CO3+1 times HCO3- and obviously there is no contribution of H and CO3 2- right. So thus I am not going to list CO3 2- concentration here when I am calculating the total component concentration of H+ right.

Again what is this mean? Obviously by this time, we should know that that H will be in the form of either H^+, OH^-, H_2CO_3 or HCO_3^- so even though the individual concentrations of these species might change, the total H will always be constant right that is what we understand here. Again so at this stage we have CO_3 total and from here again because I have CO_3 total I can calculate H_2CO_3 and HCO_3^- concentration right.

I also have H^+ and OH^- concentration, so I now have the concentration of H total right so initially now I have CO_3 total and H total right. So this is at the condition where the pH was equal to 8.3 and the alkalinity was I think 150 milligram per liter as $CaCO_3$ right. Obviously the units are as $CaCO_3$, it would be obviously better to have the units in the terms of equivalence per liter before you plug them in right and obviously the concentration units here in this particular formula would be the molar units.

Why is that? Obviously because you are taking into account the equivalent fact too right. The number of equivalence for CO_3^{2-} so OH^-, HCO_3^-, CO_3^{2-} and H^+ would be in terms of molar units but the alkalinity obviously would be in terms of equivalent per liter right. Again with that and the relevant background in our chemical process we can calculate CO_3 total and using that we can calculate H_2CO_3 and HCO_3^- and end up with H total.

So to this we are now adding $FeCl_3$ the salt right and we are adding it at 10 power -4 molar right. So now we need to understand how is the system going to change right. So obviously now CO_3 total think of this now, we have CO_3 total somewhere listed here, did we list that here okay we did not so let us list that here what is CO_3 total equal to you know we did find it out earlier. What is it going to be present as?

It is going to be present as H_2CO_3 HCO_3^- and CO_3^{2-} right. This is from our background in our acid-base chemistry right. Again I am skipping writing down all the species and the relevant formation equations and the relevant Tableau but by this time you should be able to understand that CO_3 total is only present in these 3 conjugate acid-base forms or the species are H_2CO_3, HCO_3^- and CO_3^{2-} right.

So that is the case but by adding $FeCl_3$ do you see that you know are you adding any source of you know this CO_3 total is that being changed at not. No, CO_3 total is still going to stay the same right but what is going to change though, obviously H total will change as in the value is going to be constant why is that? I think to better explain I had better write down the species.

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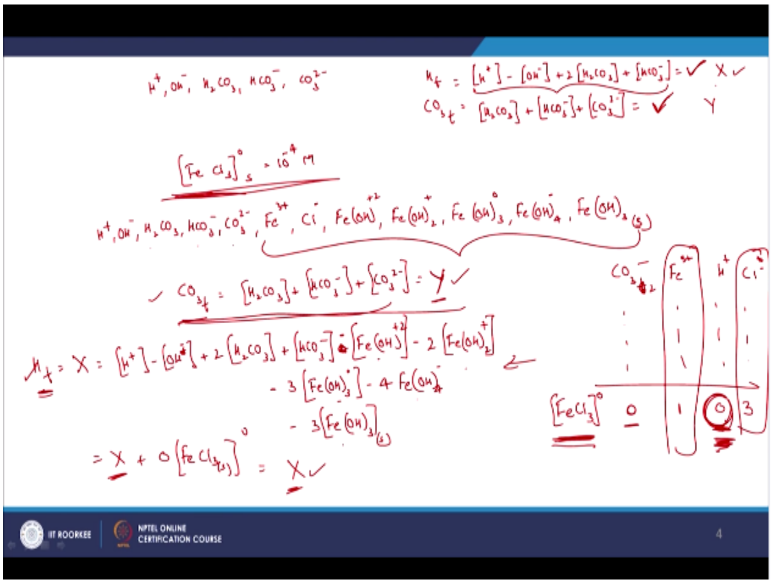

$H^+, OH^-, H_2CO_3, HCO_3^-, CO_3^{2-}$

$H_t = \underbrace{[H^+] - [OH^-] + 2[H_2CO_3] + [HCO_3^-]} = \checkmark \quad X \checkmark$

$CO_{3_t} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = \checkmark \quad Y$

$[FeCl_3]^0_s = 10^{-4}\,M$

$H^+, OH^-, H_2CO_3, HCO_3^-, CO_3^{2-}, \underbrace{Fe^{3+}, Cl^-, Fe(OH)^{+2}, Fe(OH)_2^+, Fe(OH)_3^0, Fe(OH)_4^-, Fe(OH)_{3(s)}}$

$\checkmark \; CO_{3_t} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = Y \checkmark$

$H_t = X = [H^+] - [OH^-] + 2[H_2CO_3] + [HCO_3^-] - [Fe(OH)^{+2}] - 2[Fe(OH)_2^+] - 3[Fe(OH)_3^0] - 4\,Fe(OH)_4^- - 3[Fe(OH)_3]_{(s)} \leftarrow$

$= X + 0[FeCl_{3(s)}]^0 = X \checkmark$

	CO_3^-	Fe^{3+}	H^+	Cl^-
$[FeCl_3]^0$	0	1	0	3

So earlier we had only H+, OH-, H2CO3, HCO3- and CO3 2- right and from this I have CO3 total and H total right and I wrote them down in the previous anyway let me write them down here, so it is going to be=H+-OH-+2 times H2CO3+1 times HCO3- right and CO3 total would obviously just be=H2CO3+HCO3-+CO3 2- this was the initial condition but after adding FeCl3 the solid right at 10 power -4 molar concentration.

What are the new species now? I know that it would still be H+, OH-, H2CO3, HCO3- all the species present earlier certainly and also the free metal right and also let the salt Cl- and what else now all the other complexes Fe OH+2 charge Fe OH twice+1 charge Fe OH thrice neutral charge, Fe OH 4 negative 1 charge and also the solid right. So these are the additional species that I am going to have in my solution.

Because I am putting in or adding FeCl3 to my particular solution which initially had only the carbonate species and H+ and OH- right. So this is what I have, so I need to be able to incorporate these aspects into my solution. So obviously now if I look at it again and write CO3 total, CO3 total would still be equal to is there any CO3 on this particular species, nope right so I am only going to go with the same case as earlier it is still going to be equal to H2CO3+HCO3-+CO3 2- right.

And keep in mind that we already calculated what this value is in the previous section right. We already calculated what CO3 total was and from that we already calculated what H total initially was. So we already have the initial value of H total let say x right and let say CO3 total was equal to y we already calculated that and here by adding FeCl3 right if you keep in mind now the Tableau is CO3 total Fe total or CO3 2- Fe 3+ and H+ and Cl- and I list all the species and formation from the formation equation bla bla I am not going to list that.

And if I write down the (()) (15:05) species here; is CO3 2- affected here, no right; Fe 3+, yes; is H+ affected here, no; is Cl- affected here, yes by 3 times right. So what I am trying to show is by addition of FeCl3 you are not changing the CO3 total nor are you changing the H total right but within H total so CO3 total is still what is it here Y right, it is still equal to Y but H total now is no more just equal to this particular set of variables though right.

But because as you see FeCl3 does not entail any increase or effect on H+, it is still going to be equal to X but the number of variables or species are going to change and what are they? H+ -OH- pardon me +2 times H2CO3+HCO3- right and +the relevant species here and what are they going to be=Fe OH+2 but obviously it cannot be +, from our part A if you remember that it is going to be – because it is OH here right and -2 times Fe OH twice+1 charge right-3 times Fe OH 3 neutral charge-4 times Fe OH 4 negative charge.

And again -3 times the solid that has precipitated out right and again what is this still equal to now? It is still going to be=X+0 times of FeCl3 this solid right and why is that? As you see from your particular balance equation, addition of FeCl3 causes no further change in H total. So H total is still going to be=X that you calculated earlier but obviously you are now going to have additional what do we say species right and they are 1, 2, 3, 4, complexes and 1 solid phase right.

So again keep in mind that you are adding FeCl3 that does not change let say earlier H total was let say 10 power -4 you know just for an example let say. By adding FeCl3 as you see from the total component balance here you know there is no source of H+ in FeCl3 right. So the H total is still 10 power -4 but this is now distributed over a few more species as in a few more complexes and the solid too right.

Earlier H+ was only present as H+, OH-, H2CO3 and HCO3- but now H+ is also present in the form of all the Fe OH complexes and the solid and that is what we have just identified here right. So what do I have here, I still have CO3 total right, I have H total which is still equal to X and these are values that I calculated, they are not unknown values keep that in mind right. So I have CO3 total and H total and I now can calculate Fe total too right and Cl total too yes.

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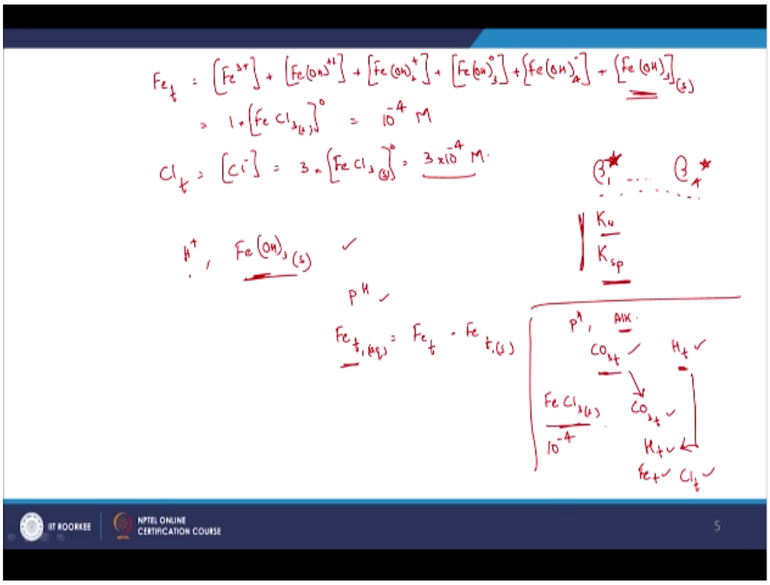

$Fe_t = [Fe^{3+}] + [Fe(OH)^{+2}] + [Fe(OH)_2^{+}] + [Fe(OH)_3^{0}] + [Fe(OH)_4^{-}] + [Fe(OH)_3]_{(s)}$

$= 1 \times [FeCl_{3(s)}]^0 = 10^{-4}\ M$

$Cl_t = [Cl^-] = 3 \times [FeCl_{3(s)}]^0 = 3 \times 10^{-4}\ M.$

$\beta_1^* \ldots \beta_4^*$

K_w

K_{sp}

H^+, $Fe(OH)_{3(s)}$ ✓

pH ✓

$Fe_{t,(aq)} = Fe_t - Fe_{t,(s)}$

pH, Alk.

CO_{3t} ✓ H_t ✓

$FeCl_{3(s)}$

10^{-4}

CO_{3t} ✓

H_t ✓

Fe_t ✓ Cl_t ✓

And Fe total I guess I calculated that from last time so I am not going to go through the relevant what do we say write up but I am just going to list the equation here, Fe 3+ + what else Fe OH+2 charge+Fe OH twice+1 charge Fe OH thrice neutral charge+Fe OH 4 negative charge right and the solid right.

Again the assumption here that I am going with is obviously that the solid is formed and which we know will probably be formed from our particular what do we say background from part A too right. So this is it and what is this equal to that is equal to 1 times FeCl3 0 so 1 times FeCl3 0 as in what we are putting in initially that as you know is=10 power -4 molar right. So same case I can write Cl total, it is just equal to Cl- concentration that is equal to 3 times FeCl3 that I am putting in initially.

And why is that because it is 3 times here FeCl3 right that is equal to 3*10 power -4 molar right. So now again it is same case as earlier, I need to now list beta 1 star so on up to beta 4 star right and obviously Kw and also K solubility product for this particular solid ferrihydrite right. So again it is similar to what I had earlier. I have the relevant number of variables and I need to come up with the relevant number of equations.

So for that I am going to look at the various equilibrium coefficients or solubility products and then as we did so in part A we can then go ahead and calculate the relevant number of unknowns that you want right and what can I do from here let say, so I can minimize the particular equation such that what is it now that I am going to end up with, just two equations in H+ and Fe OH thrice solid.

And what am I going to use to minimize them? I am going to use beta 1 star to beta 4 star and the two equilibrium coefficient related Kw water dissociation and solubility product for this particular solid and come up with 2 equations and 2 unknowns and solve for them and once I solve for them obviously you know I can calculate pH and once I have this solid obviously Fe total in the aqueous phase will be nothing but Fe total-Fe total in the solid phase which is what we just calculated right.

And obviously that is what the question asked for right, again keep in mind what is it that we have been up to, first we analyze the initial conditions and calculated, so let us just summarize what we have been up to so initial pH was given and alkalinity was given right. So from this we end up calculating CO3 total initial and H total initial right. So we have these 2 values.

And then because of plugging in FeCl3 solid we see that there is no further change in CO3 total or H total, so they are still going to be the same values that we had earlier right but now we are also going to have Fe total and Cl total right which we have from FeCl3 as 10 power -4 addition and then we solve for the relevant variables and get the total iron concentration which has precipitated out and also the pH.

And then calculate the relevant variables from that, so again this is for your purpose of understanding. Obviously you know by hand even though you use excel let say it is going to take you is relatively more time consuming right. So now we are going to solve this by VMINTEQ. So let us see how we go about that right. So let us move on to VMINTEQ.

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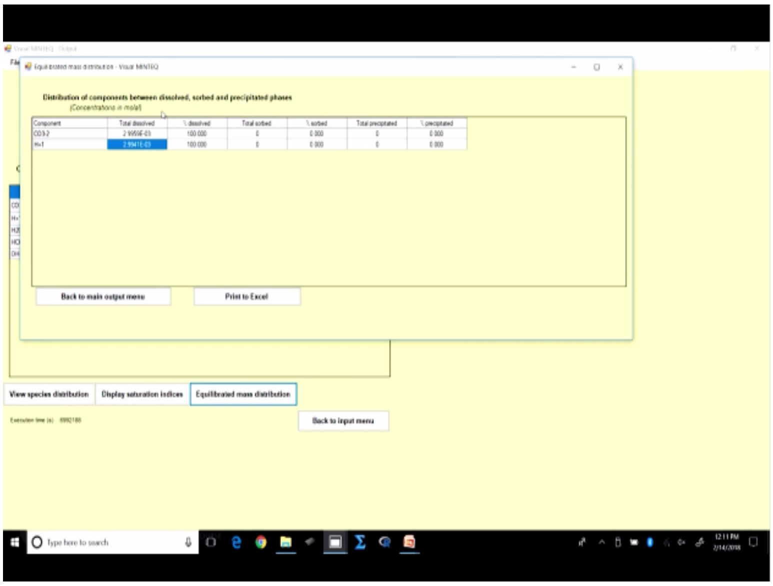

Distribution of components between dissolved, sorbed and precipitated phases
(Concentrations in molal)

Component	Total dissolved	% dissolved	Total sorbed	% sorbed	Total precipitated	% precipitated
CO3-2	2.9959E-03	100.000	0	0.000	0	0.000
H+1	2.9941E-03	100.000	0	0.000	0	0.000

So first I need to plug in the pH and that was at 8.3 right and then I need to specify for alkalinity parameters and alkalinity and where is that here, it was milligram per liter as CaCO3 and it was 150 if I am not wrong 150 right and so I am going to say okay and just run MINTEQ right and if I look at equilibrated mass distribution I can get the relevant H total and CO3 total right.

Let me write this down so that I need them later so it is 2.99 bla bla*10 power -3 let me write that down somewhere.

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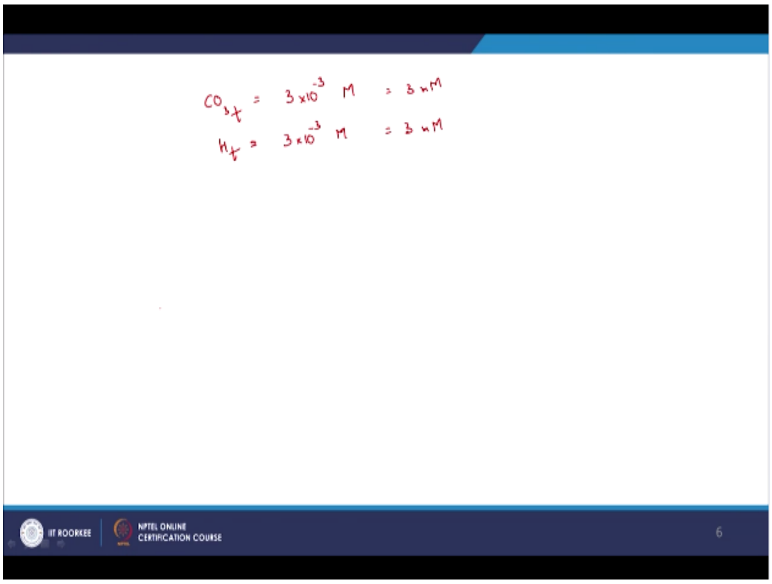

$CO_{3_T} = 3\times10^{-3}\ M = 3\ mM$

$H_T = 3\times10^{-3}\ M = 3\ mM$

So CO3 total comes out to be what now 2.99*10 power -3 I will list that as 3*10 power -3 molar concentration right or 3 millimolar right and what was H total=so 2.99*10 power -3 which I will approximate by again 3*10 power -3 molar that is=3 millimolar right. So obviously if I wanted to I could have just not just also looked at the sum of CO3 2-, H2CO3 and HCO3- as I did earlier.

But obviously you can also look at equilibrated mass distribution and go through with that or you know just for sake of understanding let us see if that is going to be the case or not here I am going to try to calculate CO3 total here.

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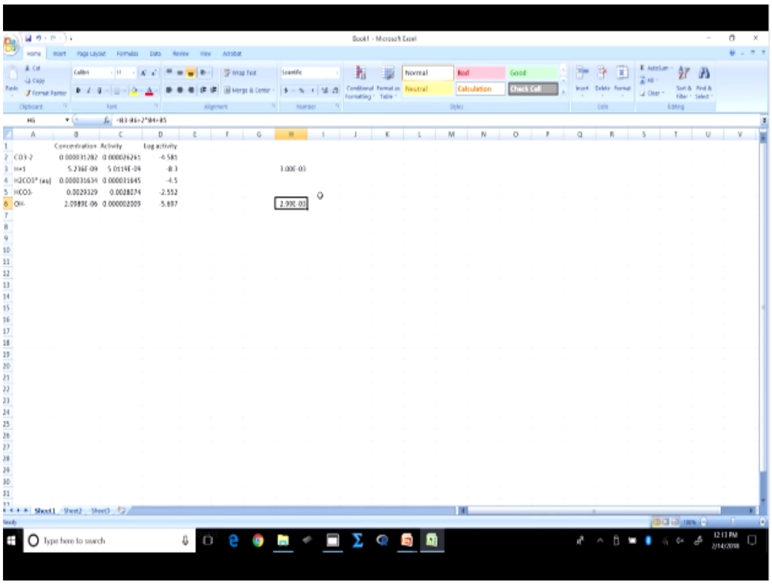

H6 =B3-B6+2*B4+B5

	A	B	C	D	E	F	G	H
1		Concentration	Activity	Log activity				
2	CO3-2	0.000031282	0.000026261	-4.581				
3	H+1	5.236E-09	5.0119E-09	-8.3				3.00E-03
4	H2CO3* (aq)	0.000031634	0.000031645	-4.5				
5	HCO3-	0.0029329	0.0028074	-2.552				
6	OH-	2.0989E-06	0.000002009	-5.697				2.99E-03

So I will print this to excel and let me try to calculate CO3 total so that is going to be equal to CO3 2- concentration+H2CO3+HCO3- and enter. So that is again equal to as you see 2.99*10 power -6 right or 3*10 power -3 which is what we had from that equilibrated mass distribution. In the same manner, let us try to calculate H total. So H total will be=H+-OH-+2 times H2CO3+HCO3- and enter.

And again that is what you see here that it is=2.99*10 power -3 which is what we have from our particular excel in the equilibrated mass distribution right. Again these are values we are now going to note down I guess. So back to main output menu, back to input menu and now what do I need to do? I have H total and CO3 total and now what else do I need to do, I need to plug in the aspects for Fe total and Cl total and also mention that the ferrihydrite is a possible solid right.

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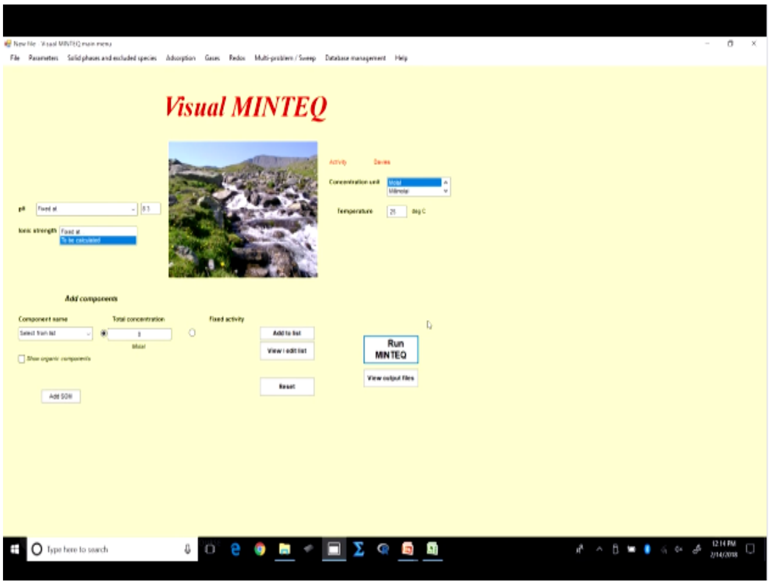

pH: Fixed at

Ionic strength: To be calculated

Concentration unit: Molal

Temperature: 25 deg C

So let us do that, so before I do so I need to say that alkalinity is not going to be listed because I am already considering CO3 total as a particular species, just to be on safer side I am going to reopen or restart VMINTEQ okay and pH should now be calculated from mass balance right. So what else now I need to plug in H total and where is H total here, H total and as you remember I think that was 3 millimolal right that was 3 millimolal.

I am going to use the millimolal units and the key here and that is 3 millimolal right. So I am going to add that to the list and same case with CO3 total and that is again 3 millimolal I believe, add that to the list right and now I need to plug in the values for Fe total and Cl total and if you remember it is equal to based on FeCl3 that you are plugging in initially that was 10 power -4.

So I am going to plug in Fe 3+ initially and where is Fe 3+ here please, Fe 3+ so I think we are going to go with millimolal units right and it is now going to be=0.1 millimolal right because it was 10 power -4 if I am not wrong and now I am going to add Cl, Cl was 3*10 power -4 right, so it is 0.3 millimolal so I am going to add that to the list. I am going to just confirm the components here.

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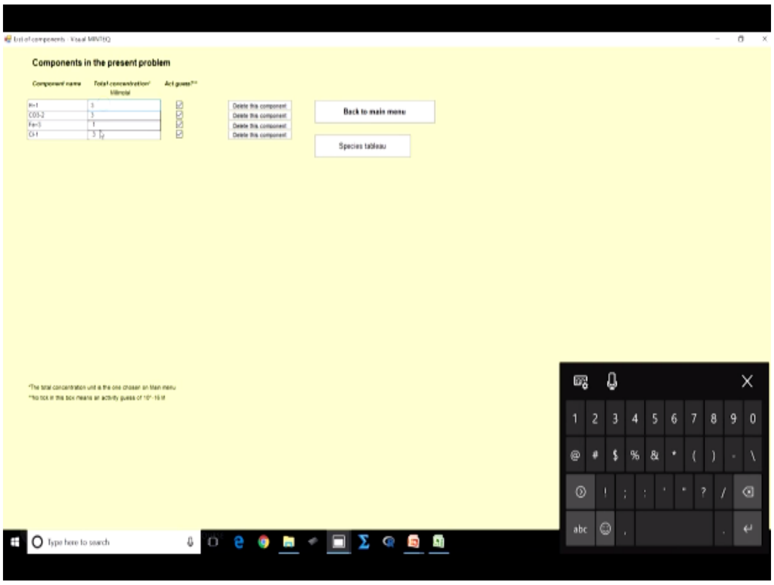

Components in the present problem

Component name	Total concentration* Millimolal	Act guess?**
H+1	3	☑
CO3-2	3	☑
Fe+3	1	☑
Cl-1	3	☑

*The total concentration unit is the one chosen on Main menu
**No tick in this box means an activity guess of 10^-16 M

H+ was 3 millimolal, CO3 was 3 millimolal and I am putting in FeCl3 at 10 power -4 right or 0.1 millimolal that is why Fe 3+ is 0.1 millimolal and Cl- is 3 times that that is going to be=0.3 millimolal.

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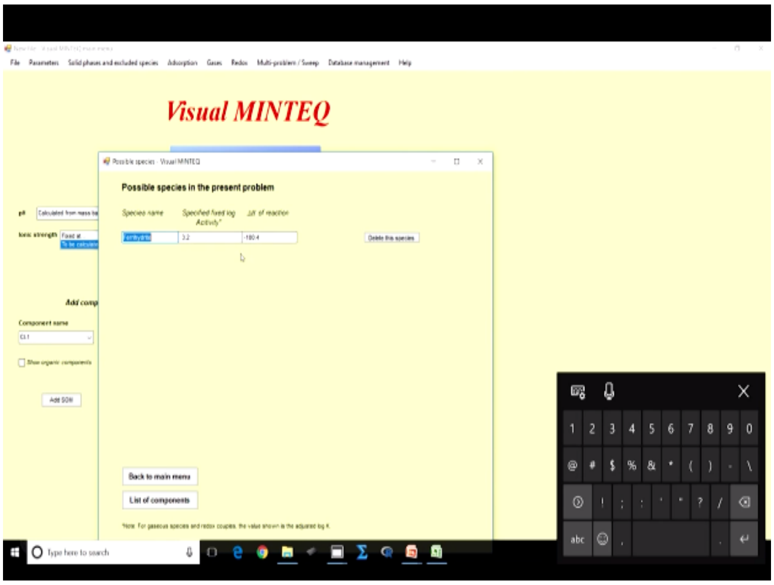

Possible species in the present problem

Species name	Specified fixed log Activity*	ΔH of reaction
Ferrihydrite	3.2	-100.4

So back to main menu and obviously I need to specify that precipitation is feasible and that a particular or the solid that it can precipitate out is as ferrihydrite and I am adding that to the list right and go back to list of possible species to see that it is included, yes it is included, back to main menu and now I can run my MINTEQ.

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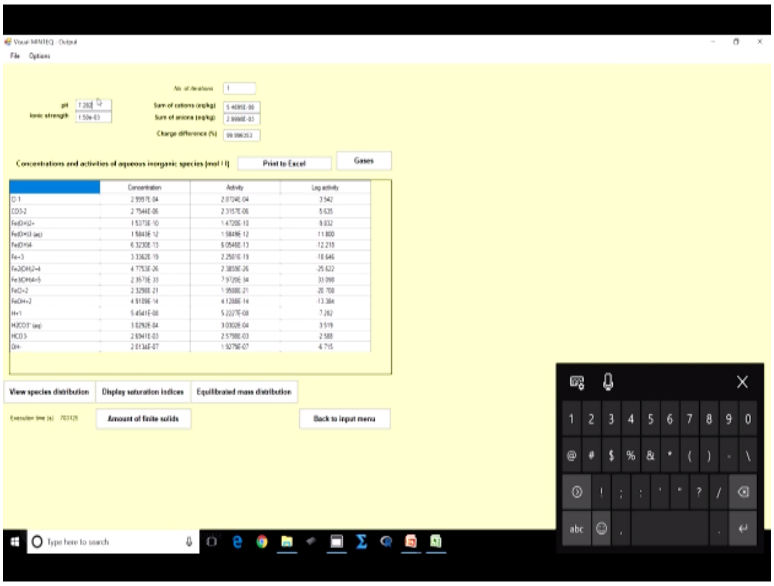

And what I see here obviously that the pH now has not fallen down to 3.5 or so. The pH is now at 7.28 or 7.3 right. So why is that now, that is probably because of alkalinity and why is that alkalinity means acid neutralizing capacity or alkalinity consist of the bases in the form of HCO3- and CO3 2-. Obviously, CO3 2- does not play huge role at 7.3 or 8.3 pH values right but HCO3- should be have been at considerable concentration so let us just look at that let say.

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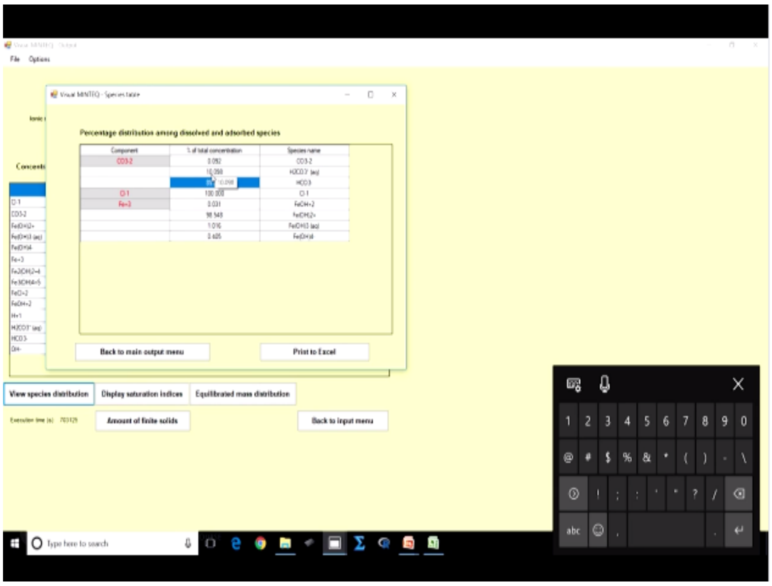

Percentage distribution among dissolved and adsorbed species

Component	% of total concentration	Species name
CO3-2	0.092	CO3-2
	10.098	H2CO3* (aq)
	[illegible]	HCO3-
Cl-1	100.000	Cl-1
Fe+3	0.031	FeOH+2
	98.548	Fe(OH)2+
	1.016	Fe(OH)3 (aq)
	0.405	Fe(OH)4-

Use species distribution so as you see considerable amount of CO3 2- is present as HCO3- and HCO3- obviously would have taken in or you know taken in or neutralize any H+ that would have been formed due to the addition of Fe right. What happens when you add Fe 3+, Fe OH complexes are formed thereby releasing H+ right. So this H+ though can be neutralized by the HCO3- that is going to be predominant at this particular pH.

And so thus unlike in part A, in part A if you remember that our pH fell from not fell from let say fell to 3.5 but here from an initial pH of 8.3, it fell down to only 7.3 right and why is that because we had alkalinity which has some acid neutralizing capacity in the solution.

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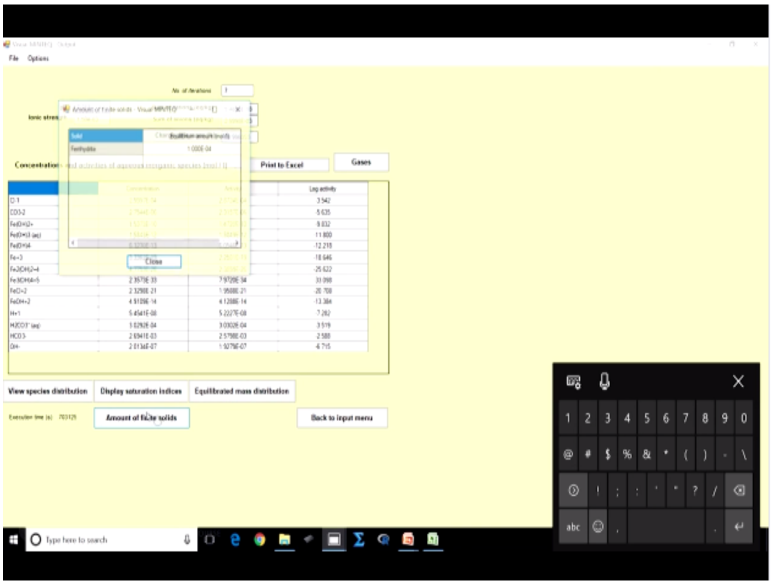

Solid	Equilibrium amount (mol/l)
Ferrihydrite	1.000E-04

So again let us go back to our particular case and look at equilibrated mass distribution or okay before that amount of finite solids present. So ferrihydrite is present at 10 power -4 molar. What is that mean? So keep in mind that FeCl3 and Fe total in that case was 10 power -4 molar or 0.1 millimolar right. So here from the amount of finite solids, we see that ferrihydrite concentration itself=10 power -4 right.

What is that mean that all the solid has precipitated out more or less right. So let us look at that.

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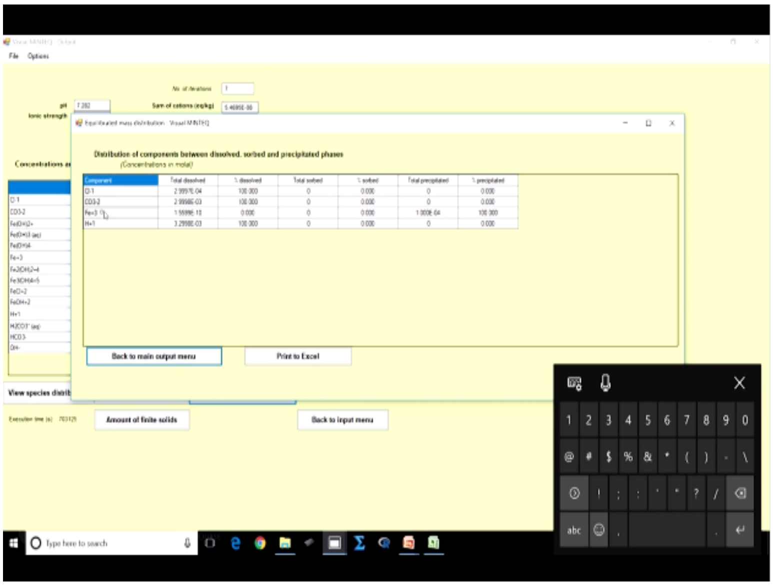

No. of iterations 1

pH 7.282

Distribution of components between dissolved, sorbed and precipitated phases
(Concentrations in molal)

Component	Total dissolved	% dissolved	Total sorbed	% sorbed	Total precipitated	% precipitated
Cl-1	2.9997E-04	100.000	0	0.000	0	0.000
CO3-2	2.9998E-03	100.000	0	0.000	0	0.000
Fe+3	1.5999E-10	0.000	0	0.000	1.000E-04	100.000
H+1	3.2998E-03	100.000	0	0.000	0	0.000

Equilibrated mass distribution so Fe 3+, so if I look at that it means almost not almost 100% or almost all I guess it can never be truly 100% right. So because it is equilibrated you will always have some free metal or some complexes present in the solution. So almost all the particular Fe 3+ has precipitated out that is what you see here and little to none is present in the dissolved form right.

And that is what you would obviously expect here right and back to main menu and different kinds of species but they are all going to be at relatively very low concentration right. Why is that because iron almost 99.99% or 100% has precipitated out as ferrihydrite even at pH 7.2 right.

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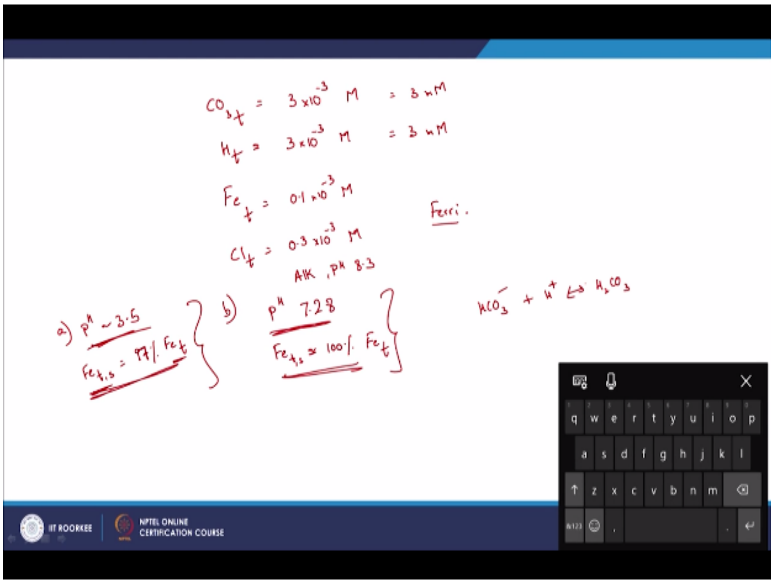

$CO_{3,t} = 3\times10^{-3}$ M $= 3$ mM

$H_t = 3\times10^{-3}$ M $= 3$ mM

$Fe_t = 0.1\times10^{-3}$ M

Ferri.

$Cl_t = 0.3\times10^{-3}$ M

Alk, pH 8.3

$HCO_3^- + H^+ \leftrightarrows H_2CO_3$

a) pH ~3.5
$Fe_{t,s} = 97\%\ Fe_t$

b) pH 7.28
$Fe_{t,s} \approx 100\%\ Fe_t$

So let us go back to our particular case, so I think here what else did we plug in, we plugged in Fe total was=0.1*10 power -3 molar and Cl total as 0.3*10 power -3 molar and we mention that ferrihydrite was a possible solid and with that we calculated the pH to be 7.28 right, this was for part B when we had alkalinity and initial pH was 8.3 but for part A when we had no alkalinity, the pH dropped out to be I think around 3.5 right.

So keep that in mind and I believe the Fe total solid was equal to I think 97% of the Fe total if you remember from our previous part A right, Fe total solid was 97% I believe of Fe total and in this case though the Fe total the solid that has precipitated out is almost=100% of the Fe total right. Again where is that from obviously we saw that from here that 100% of it has precipitated out, out of the Fe total 100% has precipitated out.

So that is what I am trying to you know illustrate here I guess right. So compare that particular case so not a great deal difference in the amount of precipitation 97% or 100% but the key is that the pH does not fall down to very low value but it is at the relatively neutral pH range right and why is that again that is because alkalinity and HCO3- can neutralize any H+ present or you know that is produced due to the addition of your particular source of Fe 3+ or the complexes right.

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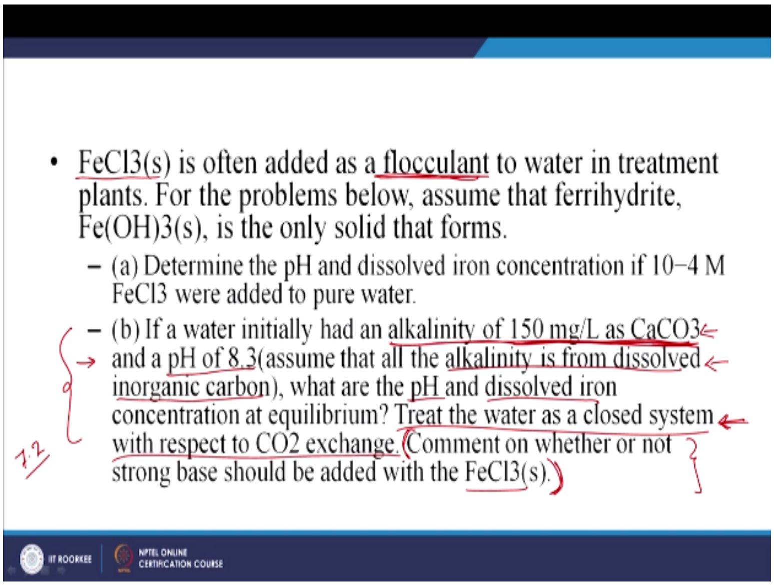

- FeCl3(s) is often added as a flocculant to water in treatment plants. For the problems below, assume that ferrihydrite, Fe(OH)3(s), is the only solid that forms.
  - (a) Determine the pH and dissolved iron concentration if 10−4 M FeCl3 were added to pure water.
  - (b) If a water initially had an alkalinity of 150 mg/L as CaCO3 and a pH of 8.3(assume that all the alkalinity is from dissolved inorganic carbon), what are the pH and dissolved iron concentration at equilibrium? Treat the water as a closed system with respect to CO2 exchange. (Comment on whether or not strong base should be added with the FeCl3(s).)

So that is what we have here so again one aspect that we need to now understand or look at is where we adding FeCl3 in the first case so because it can act as a flocculant right in the coagulation-flocculation process and here obviously we need to understand the system and also the key here is that for this particular case when the pH end up to be 7.2 right comment on whether or not strong base should be added along with FeCl3 right.

Usually let say if there was no alkalinity and the pH fell down to a very low or acidic value then you would have thought of adding maybe some OH- let say right but even in that case you need to see if that is going to be beneficial, why is that so here the key is to understand obviously what we talked about earlier.

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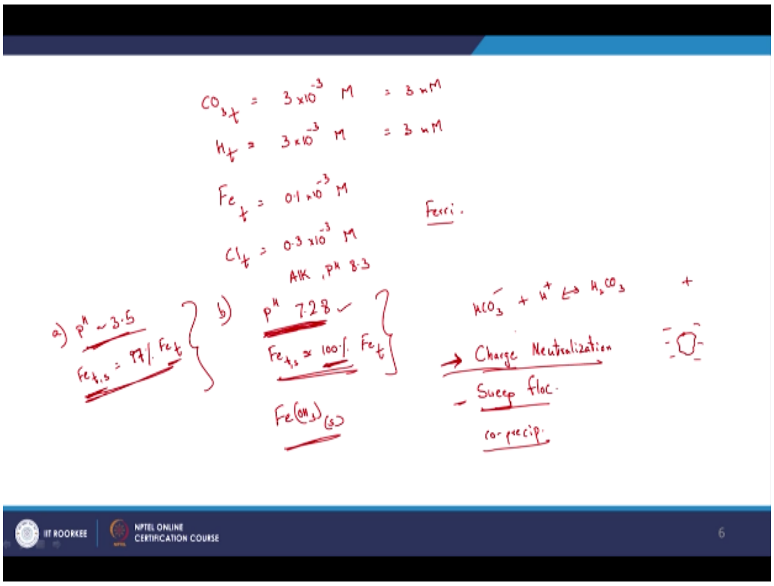

$CO_{3,T} = 3\times10^{-3}$ M = 3 mM

$H_T = 3\times10^{-3}$ M = 3 mM

$Fe_T = 0.1\times10^{-3}$ M

Ferri.

$Cl_T = 0.3\times10^{-3}$ M

Alk, pH 8.3

a) pH ~ 3.5

$Fe_{T,s} = 97\%\ Fe_T$

b) pH 7.28 ✓

$Fe_{T,s} \approx 100\%\ Fe_T$

$Fe(OH)_{3(s)}$

$HCO_3^- + H^+ \leftrightarrow H_2CO_3$

→ Charge Neutralization

- Sweep floc.

co-precip.

So how is this particular mechanism going to work, we know that there are two aspects or three, there is going to be charged neutralization right, as in the colloids are negatively charged right. So any positive charge that you add you know that is going to neutralize these colloids I mean the net charge on the colloids or suspended particles allowing them to overcome their forces of repulsion I guess.

And the second aspect is sweep flocculation as in now you have this Fe OH thrice solid that precipitates out that is what you saw here right. So these particles right are either go into what we say aggregate on the existing suspended particles and create a bigger particle allowing it to settle down or you know they themselves act as let say adsorbents or sides for the other particles to be entrapped on them let say right.

So sweep floc mechanism I guess right so either sweep floc or charge neutralization and I believe we also came across the term co-precipitation in the last couple of classes right. So here the question is if the pH is already 7.2, should you add more of a strong base. I would say not, why is that because let say if you keep adding OH- right you know sweep floc you know would not be affected because anyway even at 7.2 pH we had 100% precipitation of the particular iron right.

So sweep floc here should not be any further change even if we increase the pH right but what happens if you keep increasing the pH from 7.2 let say right. So if any you know right now you have little to know charge neutralization right because all the Fe 3+ right has precipitated out.

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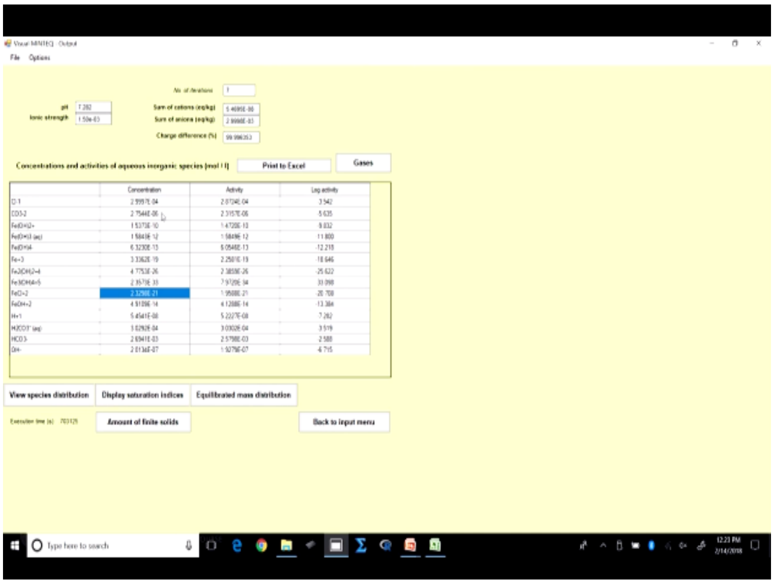

No. of iterations: 1

pH: 7.282

Ionic strength: 1.50e-03

Sum of cations (eq/kg): 5.4695E-08

Sum of anions (eq/kg): 2.9998E-03

Charge difference (%): 99.996353

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

	Concentration	Activity	Log activity
Cl-1	2.9997E-04	2.8724E-04	-3.542
CO3-2	2.7544E-06	2.3157E-06	-5.635
Fe(OH)2+	1.5373E-10	1.4720E-10	-9.832
Fe(OH)3 (aq)	1.5843E-12	1.5849E-12	-11.800
Fe(OH)4-	6.3230E-13	6.0546E-13	-12.218
Fe+3	3.3362E-19	2.2601E-19	-18.646
Fe2(OH)2+4	4.7753E-26	2.3850E-26	-25.622
Fe3(OH)4+5	2.3573E-33	7.9720E-34	-33.098
FeCl+2	2.3298E-21	1.9588E-21	-20.708
FeOH+2	4.9109E-14	4.1288E-14	-13.384
H+1	5.4541E-08	5.2227E-08	-7.282
H2CO3* (aq)	3.0292E-04	3.0302E-04	-3.519
HCO3-	2.6941E-03	2.5798E-03	-2.588
OH-	2.0134E-07	1.9279E-07	-6.715

Execution time (s): 7.03125

So any complexes that are present let say you know we can look at that here. So the complexes are present all the positively charged complexes right, they are present even right now at very low or remarkably low concentrations right yes but as you keep increasing the OH- concentration what would happen now, even these low concentrations they would now you know the net positive charge would keep decreasing right.

So Fe OH twice would now go to let say Fe OH thrice, so the positive charge will be neutral or Fe OH thrice can go to Fe OH 4 negative charge and so on as in you would increase the negative charge or decrease the net positive charge right.

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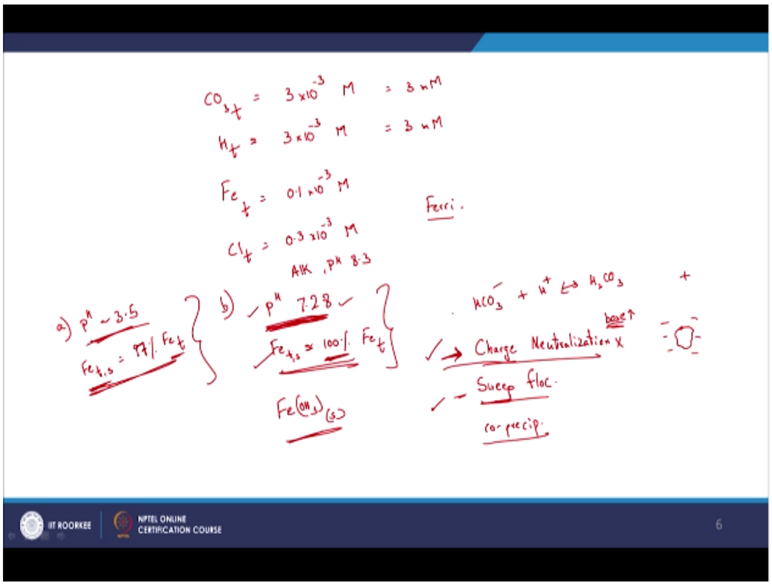

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b) pH 7.28 ✓

$Fe_{t,s} \approx 100\%\ Fe_t$

$Fe(OH)_{3(s)}$

$HCO_3^- + H^+ \leftrightarrow H_2CO_3$

✓ → Charge Neutralization x base↑

✓ – Sweep floc.

co-precip.

So charge neutralization if any right if any out there the purpose would be defeated if you add the base right. So again sweep floc is not going to be affected when you add the base but the pH will further increase you know and defeating the purpose of charge neutralization if any that is occurring in the system. So obviously for this particular scenario you would not add the base but obviously maybe if the pH was very low right you can consider that particular addition of the base right.

So again with that I guess I am done for today's session and I believe we are going to look at a few other aspects as in until now we only looked at precipitation of one solid but in general though it will never not never let say you can have more than one particular solid you know precipitating out right as in CaCO3 two can precipitate and COH twice 2 can precipitate let say. So we need to see which particular process will be the controlling process I guess right.

So we are going to look at competing precipitation or competitive precipitation in the next session and I guess with that we should be done with our precipitation and dissolution aspects and then move on to the redox process right. So with that I guess I will end today's session and thank you.