Environmental Engineering Chemical Processes

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Lecture - 44
Examples related to Equilibrium of Precipitation

Hello everyone. So again welcome back to a latest lecture session. So in the last couple of sessions we have been looking at applications, right. I think we had different initial compounds that we could put in mostly with respect to aluminium hydroxide or such or Alum I believe right and then we try to calculate what the amount of solid is going to or what is the concentrational solid that is going to precipitate out from the solution.

And what the amount of the metal still present in the aqueous solution either in the form of free metal or in the form of various complexes, right. So today we are going to look at practical example here let us say. And here we are going to first try to set it up by hand, we are not going to solve it by hand at least I am not going to, right so but I am going to set up the relevant equations by hand and you know, leave it at such stage where they can be solved.

And then we are also going to look at using VMINTEQ to obviously arrive at the solution within the fraction of the time we take solving it by hand. But obviously, why do we need to set it up by hand right, because you need to understand the basics again. So you will see the difference between using VMINTEQ and setting it up by hand again with respect to understanding the basics where we set it up by hand I guess, right.

So again, let us dive into our particular example here.

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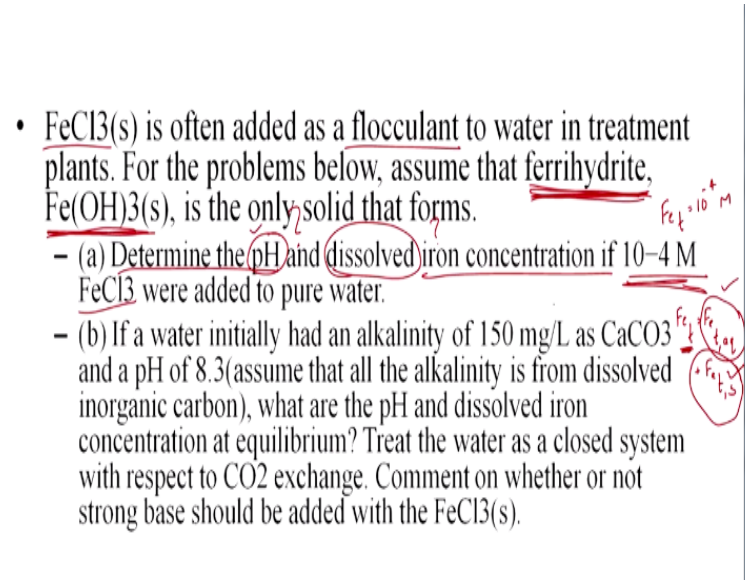

- $FeCl_3(s)$ is often added as a flocculant to water in treatment plants. For the problems below, assume that ferrihydrite, $Fe(OH)_3(s)$, is the only solid that forms.
  - (a) Determine the pH and dissolved iron concentration if 10^{-4} M $FeCl_3$ were added to pure water.
  - (b) If a water initially had an alkalinity of 150 mg/L as $CaCO_3$ 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 CO_2 exchange. Comment on whether or not strong base should be added with the $FeCl_3(s)$.

So here we have FeCl3, right is added as a flocculant you know this is a common flocculant right to water, right water in treatment plants. So here we also say that the controlling solid is ferrihydrite, right that is information you always need, and obviously again why do you need the relevant information about the controlling solid, right because the controlling solid and the relevant, what is it now, Disassociation Constant (()) (02:08) or the Solubility Product not the Disassociation Constant.

The Solubility Product depends on the kind of the controlling solid. For different controlling solid or types of solid you saw that you have different types of solubility products or solubility constants. So unless you choose the relevant solid, right or try to approximate it based on the experience that you have had, right you cannot obviously arrive at the right answer.

And in general as we discussed earlier, in general the amorphous forms, which are the most soluble form of solid, first are formed first and more or less I believe you know, ferrihydrite is a good enough example. So within the timeframes we look at in a one treatment plant with respect to coagulation and flocculation, right. Let us say formation of ferrihydrite is worthwhile approximation, right and is the only solid that forms, right.

So first we are going to look at Part 8 that says, determine the pH and also the dissolved iron concentration if initially 10 power -4 molar of FeCl3 was added, right. So here first let us try to understand the system. So let us say you had water and you are putting in let us say what is it now 10 power or you are adding FeCl3 such that the initial concentration would have been 10 power -4 molar, right. So how is the system going to change now?

So Cl- right it is relatively not react to at least with respect to the aspects we have covered thus far and it does not play any further role, you know in general let us see. It can form minor complexes but it usually is not what do we say relevant in this particular context with respect to the iron anyway the ferric iron. But obviously as you know putting in ferric iron can lead to formation of what now, both the complexes, acequos complexes that you are aware of, so Fe OH complexes are formed.

So in affect when you take out OH- from the solution and form a complex what is that going to lead to, right. So that is more or less like an acid right for adding an acid because you are taking out OH- or adding H+, so the pH you would expect it to drop, yes. So obviously that is the reason we are trying to look at what is the pH going to be, right. And obviously the other aspects is other than the relevant complexes and the acid based relevant change in pH.

We also know from our precipitation background that ferric hydroxide can precipitate out in the form of ferrihydrite, right. So once just, let us say a fraction of this 10 power -4, right this is Fe total let us see. Fe total is 10 power -4 molar, right. So we know that Fe total will be in the form of Fe total after it reaches equilibrium and the acequos phase and also in the solid phase, right. So here obviously you are also concerned with what is the dissolved iron concentration.

As in what is Fe total in the acequos phase, right. So obviously for that you need to be able to calculate your Fe total that has or you know the ferric iron that has precipitated out. Once you calculate the amount of iron that is precipitated out you can subtract that from the initial or Fe total and then get the Fe total in the acequos form, right.

So obviously, again keep in mind that when we are talking about dissolved iron concentration we are also taking into account not just the free metal but also the complexes because they are also you know, in the dissolved phase right and different forms of iron, so we consider even the complexes to be different forms of dissolved iron. So again, how do we solve for pH and also obviously the Fe total acequos.

So obviously, what is our approach here? We always have the component balance right.

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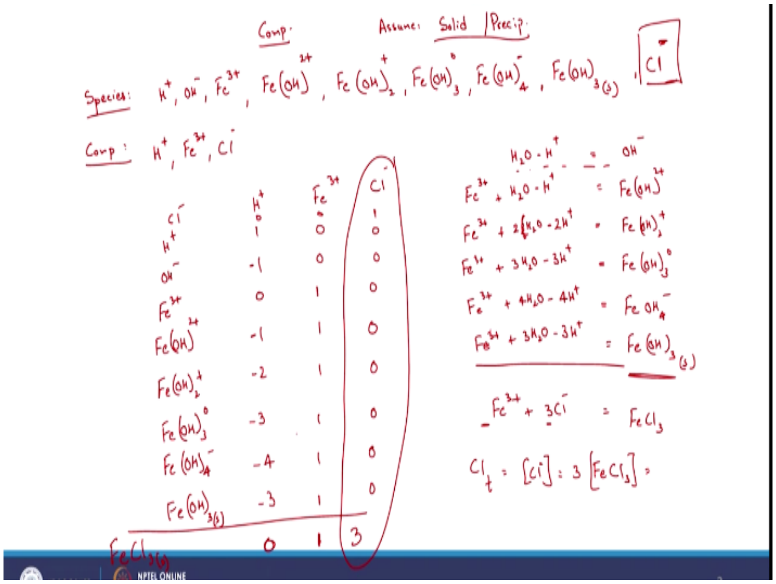

Comp.

Assume: Solid / Precip.

Species: H^+, OH^-, Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_3^0$, $Fe(OH)_4^-$, $Fe(OH)_{3(s)}$, $\boxed{Cl^-}$

Comp: H^+, Fe^{3+}, Cl^-

	H^+	Fe^{3+}	Cl^-
Cl^-	0	0	1
H^+	1	0	0
OH^-	-1	0	0
Fe^{3+}	0	1	0
$Fe(OH)^{2+}$	-1	1	0
$Fe(OH)_2^+$	-2	1	0
$Fe(OH)_3^0$	-3	1	0
$Fe(OH)_4^-$	-4	1	0
$Fe(OH)_{3(s)}$	-3	1	0
$FeCl_{3(s)}$	0	1	3

$H_2O - H^+ = OH^-$

$Fe^{3+} + H_2O - H^+ = Fe(OH)^{2+}$

$Fe^{3+} + 2\{H_2O - 2H^+ = Fe(OH)_2^+$

$Fe^{3+} + 3H_2O - 3H^+ = Fe(OH)_3^0$

$Fe^{3+} + 4H_2O - 4H^+ = FeOH_4^-$

$Fe^{3+} + 3H_2O - 3H^+ = Fe(OH)_{3(s)}$

$Fe^{3+} + 3Cl^- = FeCl_3$

$Cl_t = [Cl^-] : 3[FeCl_3] =$

"Professor – student conversation starts" So for this particular example I guess I am going to set it up in a relative detailed manner but I am not going to solve for the relevant values that I am going to leave to you, let us say as part of the homework or such. But with the VMINTEQ we are going to go through with the calculations, right. **"Professor – student conversation ends"**

So component balance right, so first component balance we need to identify the species, so species are the what is it now relevant compound that would be present once the system has reached equilibrium. So obviously, what do you have obviously you always have H+ and OH- and then you will obviously have the ferric iron right, free metal and then you will also have the relevant complexes.

And I think from our background ferric hydroxide complexes usually they are four types form, right that are usually predominant and that is what I am going to list. If you are not sure obviously you can look at the relevant standard books and find out how many constants there are, right and then come up with the relevant number of complexes. And also obviously you are going to have or we are going to consider that, what to say, the solid is precipitating out.

So I am going to go ahead with the assumption that solid is formed. So first assumption is obviously that I am assuming that, assume that solid is formed or precipitation occurs, right. So thus with that in mind I am going to list my species, so H+ OH- and then the free metal, right and then I am going to list all the complexes right with respect to Fe and OH and 2+ charge Fe and OH twice +1 charge Fe and OH thrice the complex the 0 charge or neutral.

Fe OH 4 and negative charge, and obviously, I am going to be left with my solid Fe OH thrice and the solid and obviously Cl- but in the case that we are considering right, you now Cl- we are assuming that it does not play any further role, so actually we can neglect Cl -2. But obviously, if you are looking at charge balance would have had to consider that but for further calculations as you see in all the species that have listed, right Cl- does not play any further role.

So I can neglect the role of Cl- in my further calculations. So obviously, what are the components here? So usually we choose H+ right and we choose the metal and obviously Cl- but I am going to neglect that later on right. So we are done with the listing of species and then the relevant components, the building blocks right. So then what next, I need to list my formation equation, as in how I am going to form the relevant specie from my components.

So here we are only going to work it out for the non-components species as in I am not going to show the relevant formation equation for H+ Fe3+ and Cl-. So we are going to have to look at the formation equations OH-, Fe OH 2+ FeOH twice +, Fe OH thrice 0 charge, Fe OH 4 negative charge and then the solid 2, right. What I am going to start neglecting Cl- from here on, right. So am I missing anything else, okay.

So how do I use or come up with these particular species from the components, so that is the formation equation, right. So here obviously H2O-H+ right, and here it is going to be =Fe 3+ and I need to have one OH- right so that is going to be equal to what now, +H2O –H+ hopefully that does resolve it, Fe3+ + H2O-H+ OH- right. So here Fe3+ plus I need to in affect have 2 OH- right so that means I am going to have 2 times of H2O.

Anyway I write this as two times H2O – 2 times H+ , right and Fe 3+ would be Fe OH thrice would be 3 times H2O- 3 times H+ and Fe 3+ + 4 times H2O – 4H+ and Fe 3+ + 3 times H2O- 3 times H+ even for the solid I guess, right. So now let me just tabular this I guess, I will just list the tabular here. And keep in mind that I am starting to neglect the role of Cl- here listed that in any of these species here.

So I am going to list only the two components here which are H+ and Fe 3+. Say again need to list all the species so again because I said I am going to do it relatively detailed manner here and going to set this up. So I am just obviously listing all the species here, right. And once you have the relevant background we could or we can skip writing the formation equation and just directly list the relevant species and the tabular right.

So anyway for now I am listing this. So how do I get to H+, I need one H+ to form one H+ and 0 Fe 3+. How do I get 2 OH- I look at this particular equation right so I need -1 H+ and no Fe 3+. Obviously, Fe 3+ 0H+ is required; 1 Fe 3+ required. How I form this complex? Again I look at the relevant equation here. So 1 of Ferric and -1 of H+.

And so similarly, 1-2; 1-3; 1-4 and here 2 is going to be equal to 1 and -3, again that is from this equation for the solid 2. And obviously, I need to add the Recipe species right. And what is the Recipe species here? Whatever it is that I am tagging initially not plugging in any part you know adding to the solution initially so that was the Fe Cl3 from the question, right we are adding Fe Cl3 right.

And I guess I should have written that here, how can I form Fe Cl3 here. So I need let us say what is it form Fe 3+ + 3CL- right, so if I would had listed Cl- this would had been 0,0,0,0,0,0,0 but I could have listed Cl- which I have not listed here as one of the species, well let me go ahead and do that Cl- 0,0 and 1 and so here what is the balance Fe Cl3—any role of H+ here? No. So that is going to be 0 here.

And Fe 3+ is 1 from here I guess, right. And how much Cl- is that? It is 3, right. So with that I have the component balance equation as we saw earlier, because I do not consider any Cl- related species here, right quadrant related species here, right. I am setting that up as just Cl- would be equal to 3 times the Fe Cl3 concentration; that is obvious right. Anyway, how do I solve for this let us see, just for purposes of Cl total = what now?

Cl- concentration of Cl- right that is what you have from the total component balance here. And obviously what is that equal to the Recipe specie that =3 times of Fe C13 concentration, right. So then I can calculate that so I am done with my one of the variables here. But obviously, I have the other two component balance equations so I guess for lack of space I am going to list them in the next particular slide here, right.

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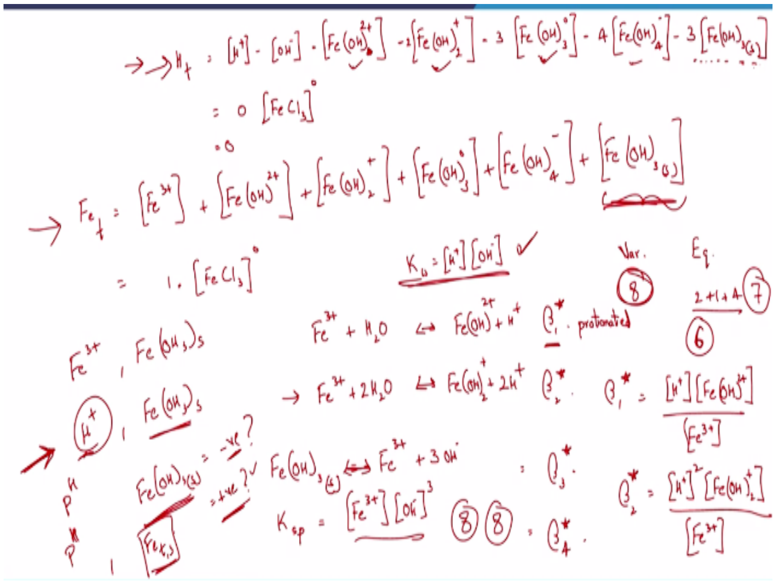

$\to\to H_t = [H^+] - [OH^-] - [Fe(OH)^{2+}] - 2[Fe(OH)_2^{+}] - 3[Fe(OH)_3^{0}] - 4[Fe(OH)_4^{-}] - 3[Fe(OH)_{3(s)}]$

$= 0\,[FeCl_3]^0$

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

$= 1 \cdot [FeCl_3]^0$

$K_w = [H^+][OH^-]$ ✓

Var. ⑧

Eq. $2+1+4 \rightarrow$ ⑦ ⑥

Fe^{3+}, $Fe(OH_3)_s$

H^+, $Fe(OH)_{3(s)}$

p^H, $Fe(OH)_{3(s)} = -ve?$ $= +ve?$ ✓

p^M, $Fe_{T,3}$

$Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+} + H^+$ β_1^* . protonated

$\to Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2^{+} + 2H^+$ β_2^*.

$\beta_1^* = \frac{[H^+][Fe(OH)^{2+}]}{[Fe^{3+}]}$

$Fe(OH)_{3(s)} \leftrightarrow Fe^{3+} + 3OH^-$: β_3^*.

$K_{sp} = [Fe^{3+}][OH^-]^3$ ⑧ ⑧ , β_4^*.

$\beta_2^* = \frac{[H^+]^2[Fe(OH)_2^{+}]}{[Fe^{3+}]}$

So first let me try to list H total and then Fe total, right H total, so it should be H+ - OH- right – the complexes, right Fe OH twice and I believe +1 charge obviously – Fe 2 times now right -2 times; Fe OH, I guess minor issue here 2+ right Fe OH twice and + here -3 times Fe OH thrice 0 charge, right -4 times Fe OH 4- right and I believe the last one was the solid 3 times Fe OH thrice. This is the solid.

“Professor – student conversation starts” Now keep in mind that this was the aspect that we talked about earlier, right. So in the earlier classes remember; how do we set it up with respect to the solid now right. **“Professor – student conversation ends”**

So in general when we talk about the concentration of this particular complex or such we are talking about the number of moles of that particular complex in dissolved in particular volume of water. But here with respect to solid we do have it as variable but keep in mind that you know you need to get your basics right it is not dissolved in water it has precipitated out or it is in different phase, right.

But for our lead to calculate the relevant the amount of solid that has precipitated out we are having a variable here and the units here obviously are going to be moles of solid that has precipitated out from the solution for the volume from which it has precipitated out, right. Anyway that is the basic what do we say understanding that you need to have. And Fe total, so how do we get this particular equation now?

Obviously, right from this particular set of component balances, right and that is what we here. And what is that equal to and – anyway I will plug that in later, I am not really I am going to just show that here right now. And obviously from my Recipe species too what do I have H total to be equal to now? H total =0, right. H total—which is =0 times Fe Cl3 naught right. So that is =H total = 0.

And now Fe total is going to be = Fe 3+ concentration. Again how I am writing this or how we are writing this. I am just balancing this particular set of slide. So Fe total is in the form of what now, Fe 3+, Fe OH 2+, Fe OH twice with the +1 charge and so on. So this is nothing but the component balance here, right. So Fe 3+ + what else please Fe OH 2+ charge + Fe OH twice + 1 charge + Fe OH thrice no charge + Fe OH 4 negative charge and also the solid, right.

And obviously again, what is this equal to, and again I am going to go back here. I see that it is 1 times the Recipe specie concentration, right, so that is =1 times Fe Cl3 naught, right. So here let us list the number of variables we have. So there 1, 2 and 4 complexes, right so that would be 6

+1 7, 7+ another free metal concentration, so we have 8 variables, right. But I have only, how many equations do I have so far? I have 2. So have 8 variables and have 2 equations.

And I still need to come up with 6 more equations, right. So how do I come up with that now, right? So obviously have one equation Kw=H+ * OH- right so that is one particular equation, yes. So what are some of the other equations here obviously? I still need to come up with 5 more equations. So you know that for each of these four complexes I can I have the relevant beta 1*, beta 2*, beta 3* and beta 4* right.

And how do we come up with this or what is the relevant equations for these beta 1*, beta 2* and so on? Remember, we had with respect to complexes we defined four types of coefficients, right and different book have different kinds of these coefficients listed. But in general for the component balance it would be worthwhile to look at beta 1* and so on, why is that? Because beta 1*, if I remember right it is a direction addition of the protonated ligand.

So let us see one particular relevant equation here let us see, how am I going to form let us say my complex here I am going to consider for beta 1 obviously should be Fe OH 2+, so it is going to be inequilibrium with I start with the metal right. So beta 1* direction addition does not make too much sense here because it is only one particular ligand here but here beta 1* refers to the protonated ligand, right, protonated ligand. So ligand is OH3- the protonated form would be H2O, right.

So to balance it out obviously I need to have H+ here right. So again for the relevant beta 2* what would the equation be Fe 3+ + so it is needs to go to Fe OH 2+ 1 charge right. So here the aspect of direction addition comes into picture so it is going to be 2H2O right, direct addition to Fe 3+ rather than coming through or coming utilizing Fe OH twice and so on, right Fe OH 2+. Again Fe 3+ + direct addition of the protonated ligand would leave me with 2 H+, right.

So again I am not going to list them for the other equations but let us just right down what is beta 1* going to be equal to, that is going to be equal to the concentration of H+, right * concentration of Fe OH 2+ right/Fe 3+, yes. And for beta 2* what is it going to be here? It is going to be equal to H+ square, right it is from this equation obviously times Fe OH twice, positive charge/Fe 3+. Again in same manner you can list it for beta 3* and beta 4* you get the picture.

So now we have how many more additional equations? We have one earlier, so 2+1 from Kw, water dissociation constant and beta 1, 2, 3 and 4, so I have 4 more equations here, right. So 2+1; 3+4 I think I have only 7, right but I still need to have one more equation to be able to solve for this particular set of problems, right. And what is that equation now, right. And keep in mind here obviously we have a particular aspect related to precipitation, right.

So obviously, you know the solubility product Fe OH thrice, this solid will be = or will be inequilibrium with pardon me, right Fe 3+ 3 OH- right. So you know that this K solubility product for Ferrihydirte you can get the constant, right it is going to be equal to nothing but Fe 3+ times OH-1 cube. By the activity of the solid which for a pure solid you know it is going to be equal to 1. So now you have the additional or the final equation.

So you now have 8 equations and 8 variables, right. But obviously what are we going to do? You are going to transform all the variables such that right these 2 equations such that we are going to only have let us say either of Fe 3+ and the solid Fe OH thrice the solid right or just H+ and Fe OH thrice solid as the two variables right.

You are just going to plug-in the relevant what do we say the equations in these two particular equations such that you are only going to narrow down the number of variables to two variables right that is just substitution that I am not going to go through here obviously. So but because our particular question ask you to solve for pH right, so obviously it make sense that or have the relevant variables to be H+ and Fe OH thrice solid, right.

So and then I can solve for it and if the particular solution for Fe OH thrice, the solid turns out to be negative, what is that mean? That means obviously the solid has does not precipitated out and you need to not consider the solid and then redo the calculations, right. But obviously, if it turns out to be positive what does that mean, I have arrived at my two solution, right and obviously then I do not need to go further anywhere right.

So let us say I am assuming that it should turn out to be positive in this case. So you will now get the Fe total in the solid, right and by solving for H+ I can also calculate the pH. So I calculate the pH and Fe total solid and what is the question asked for, so it says calculate the pH which we are able to do and it ask for the dissolved iron concentration. And how can I get that?

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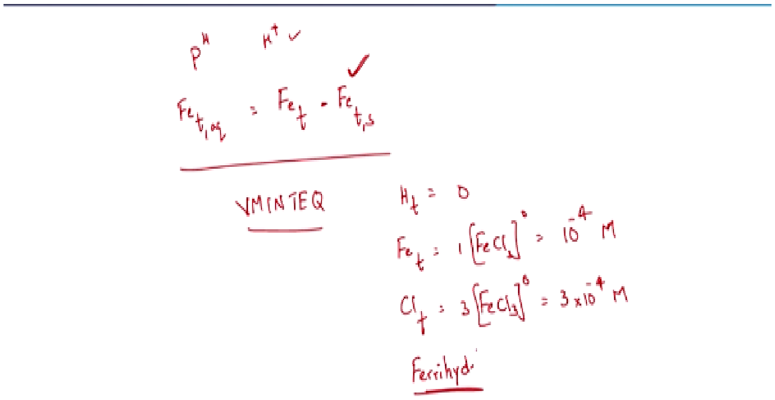

pH H^+ ✓

$Fe_{t,aq} = Fe_t - Fe_{t,s}$ ✓

VMINTEQ

$H_t = 0$

$Fe_t = 1[FeCl_3]^0 = 10^{-4}$ M

$Cl_t = 3[FeCl_3]^0 = 3\times10^{-4}$ M

Ferrihyd.

So we solve for pH from H+, right. And dissolved iron nothing but Fe total in the acequos phase that is =Fe total – the iron that has precipitated out and this is something you just calculate, right. So with that at least by hand right this is the procedure to go about solving for your particular this particular scenario, right. Again keep in mind that we started with the assumption that the solid is going to precipitate out, right.

And if that variable turned out to be a negative value then you would have had to remove that particular variable meaning you would consider that obviously that no precipitation has occurred and go through with the relevant calculations right. So now obviously you know this is by hand and you can use solver to solve for those two equations, solver is a function excel that you can use where in you can set or ask excel let us say to change set of cells such that another cell will be either equal to minimum, maximum or in this case equal to 0.

Anyway that is for you, you can look it up in excel I guess, right. But now let us how set it up by VMINTEQ, right. So what are the aspects that we need to look for? I need to give the total component concentrations so I know that if you remember that H total is =0 and Fe total that = I believe 1 times Fe Cl3 naught that was = what is the concentration that we plugged in please, 10 power -4 molar, 10 power -4 molar, right.

And also Cl total is =3 times Fe Cl3 naught right, and that is =3*10 power -4 molar right and obviously you also need to specify the solid and we know that ferrihydrite is something that you need to consider. So we are going to just plug-in these total components into the VMINTEQ and specify ferrihydrite as the possible solid I guess, right.

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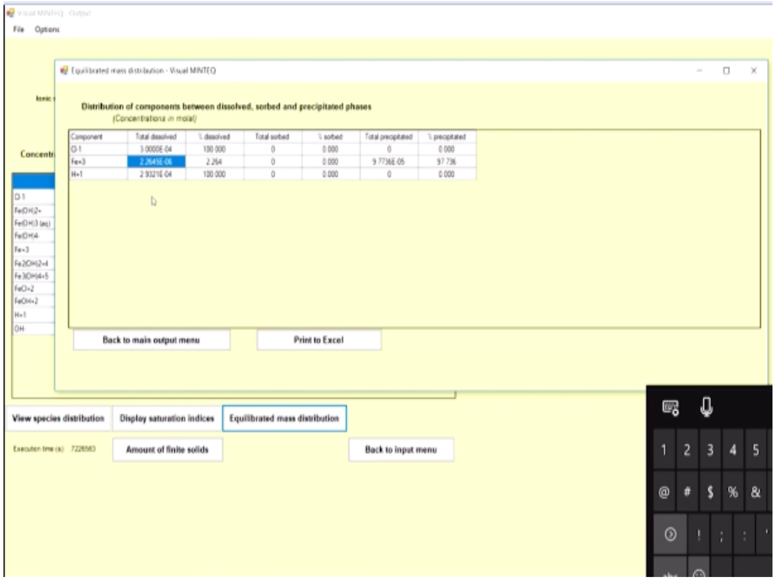

Distribution of components between dissolved, sorbed and precipitated phases
(Concentrations in molal)

Component	Total dissolved	% dissolved	Total sorbed	% sorbed	Total precipitated	% precipitated
Cl-1	3.0000E-04	100.000	0	0.000	0	0.000
Fe+3	2.2645E-06	2.264	0	0.000	9.7736E-05	97.736
H+1	2.9321E-04	100.000	0	0.000	0	0.000

So let us move onto VMINTEQ. So Fe total, first let look it up and that is out here; I am going to use millimolar units to be, to make it easier for me to plug them in, I guess so 0.1+10 power -4 molar, right. So 0.1 add that to the list and Cl total what was that equal to, and Cl total was =0.3 millimolar 0.3 add that to the list and I need to specify the possible solid phases, so obviously that is going to be equal to ferrihydrite right so I am going to add that.

And you can see that it is listed in the Possible species present in the problem. Back to main menu and I am going to run my MINTEQ. So obviously because we put in ferric, right ferric can or not can you know that it would form the complex or can precipitate out more or less it is going to remove the OH- from the solution right. So thus obviously that is going to bring down the pH and that is what you see here, the pH is now 3.537, right.

And then also look at amount of finite solids and ferrihydrite is formed at almost 10 power -4 9.7*10 power -5 means more or less 10 power -4 as in almost all the ferric iron that you added as precipitated out, right. So let us look at Equilibrated mass distribution. So here for Fe 3+ the percentage dissolved is only 2.2% of the total that you plugged in initially but the percentage that has precipitated out is 97.7% or 97.8% of the total iron that you plugged in right.

So 90—almost 98% of the ferric source of ferric that you plugged in Fe 3+ precipitated out, right and only 2% is present as or in the dissolved phase in the various complexes. Again, within this 2% let us see which particular, what we say acequos complex predominates. So I think we can look at that here and I think it is Fe OH, right with +2 charge if I reading that right. Yes, Fe OH with the +2 charge is relatively predominant, right.

So again this what we expected and that is what we saw here too. So obviously the dissolved, so the question asked for if you remember pH, so pH is 3.537 and ask for the dissolved iron concentration, so that is going to be = 2.2*10 power -6 or 2.3*10 power -6 molar units, right. Okay, so I guess with that I will be done with part A. So in the next particular session we are going to solve for part B I guess, right.

And with that I guess I be dado and thank you.