Environment Engineering: Chemical Processes
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Module No # 12
Lecture No # 56
Effect of complexation and Solid Phase on Redox

Hello everyone so again welcome back to our latest lecture session so let us say again I will have quick recap of what we discussed in the previous session so we have been looking at a particular scenario of you know two half reactions so one is FE3 + is being reduced to FE2+ and C2CL4 is being reduced to C2HCL3 right.

And then we looked at various scenario where in once scenario as in we considered no other reactions other than complex formation and which particular half reaction and then we try to understand I guess right which particular compound which reduce would reduce which compound and so on and the second case was we considered the case of redox along with relevant complex formation.

And then we saw that the situation was in the same as what we observed in case 1 right and then now for today session anyway so we are going to look at the natural conjunction and the try to understand the system right.

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$Fe^{3+} + \bar{e} \rightarrow Fe^{2+}$ $\quad$ $C_2Cl_4 + H^+ + 2\bar{e} \rightarrow C_2HCl_3 + Cl^-$

$pe^\circ = 13.03$ $\quad$ $pe^\circ = 10.84$

① $\underline{\text{No other reactions}}$ $\quad$ $pe_1 = 13.03$ $\quad$ $pe_2 = 8.84$

$$\boxed{pe_1 > pe_2}$$

$$\rightarrow \underline{C_2HCl_3} + Cl^- + 2\underline{Fe}^{3+} \rightarrow C_2Cl_4 + H^+ + 2\underline{Fe}^{2+}$$

② complex formation $\quad$ $pe_1 = 4.9$ $\quad$ $pe_2 = 8.84$

$$\boxed{pe_2 > pe_1}$$

$$\rightarrow 2\underline{Fe}^{2+} + \underline{C_2Cl_4} + H^+ \rightarrow 2Fe^{3+} + \underline{C_2HCl_3} + Cl^-$$

So let us try to look at what where we are so believe you would looking at FE3+ being reduced to FE2+ right and also with respect to C2 CL4 right + H+ + 2 electron right would go to C2H CL3 + CL- right and I believe we had PE naught values to be 13.03 and 10.84 right and so we working out two cases when one was we had no other reaction only the redox and we saw that PE value came up to be 13.03 + right.

So here F there were no other reactions present it would have been no other reaction or C2HCL3 would have reduced FE3+ to FE2+ and this is what you would have observed but we saw that when we considered the other particular case when we also have complex formation along with the redox we saw that the PE1 drop to I think 4.9 and PE 2 would still be the same right 8.84 and so now PE2 is greater than PE1 so thus the overall reaction would be 2 times FE2+ right going to 2 times FE3+ right while reducing C2CL4 right to C2HCL3 right.

So obviously in this case ferrous iron can reductively dechlorinate so we are dechlronating right that is what you see here and by reducing the oxidation state of carbon that is what you see let us reductive dechlroination of PCE here right the tetra or per I think. And why is that again because now unlike the other case when we had PE1 greater than PE2 to now have PE2 greater than PE1 right.

So you see that when we considered complex formation which is what you would observe of that the scenario change.

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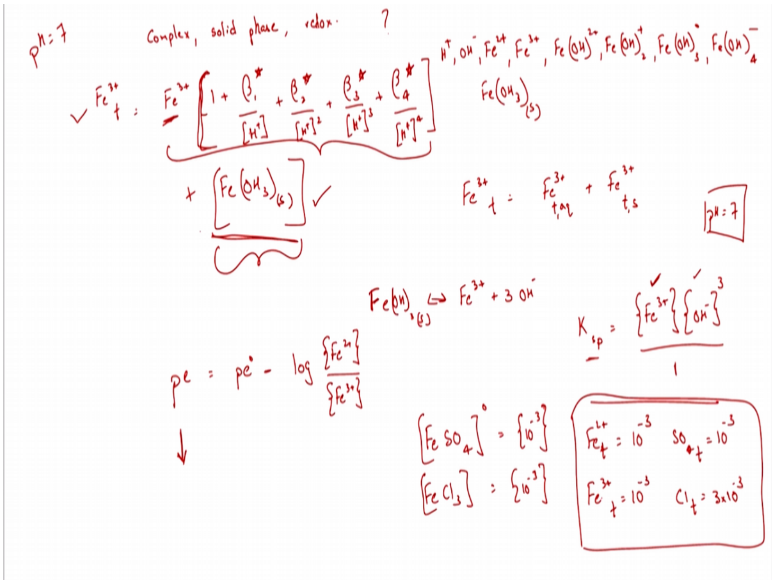

pH = 7

Complex, solid phase, redox. ?

$H^+, OH^-, Fe^{2+}, Fe^{3+}, Fe(OH)^{2+}, Fe(OH)_2^+, Fe(OH)_3^0, Fe(OH)_4^-$

$Fe(OH_3)_{(s)}$

✓ $$Fe^{3+}_t = \underbrace{Fe^{3+}\left[1 + \frac{\beta_1^*}{[H^+]} + \frac{\beta_2^*}{[H^+]^2} + \frac{\beta_3^*}{[H^+]^3} + \frac{\beta_4^*}{[H^+]^4}\right]} + \underbrace{\left[Fe(OH_3)_{(s)}\right]}$$ ✓

$$Fe^{3+}_t = Fe^{3+}_{t,aq} + Fe^{3+}_{t,s}$$

$\boxed{pH = 7}$

$$Fe(OH)_{3(s)} \leftrightarrows Fe^{3+} + 3\,OH^-$$

$$K_{sp} = \frac{\{Fe^{3+}\}\{OH^-\}^3}{1}$$

$$pe = pe^0 - \log\frac{\{Fe^{2+}\}}{\{Fe^{3+}\}}$$

↓

$[FeSO_4]^0 = \{10^{-3}\}$

$[FeCl_3] = \{10^{-3}\}$

$$\boxed{\begin{array}{ll} Fe^{2+}_t = 10^{-3} & SO_{4,t} = 10^{-3} \\ Fe^{3+}_t = 10^{-3} & Cl_t = 3\times10^{-3} \end{array}}$$

So obviously now we are going to consider to the aspect wherein we have complex formation precipitation being solid form being present right and also the redox obviously I guess let us see how the situation changes now right. So for this obviously again we need to come up with our total component balance with our respect to FE3+ right and for this again let us try to see how to work it out by hand and then by VMINTEQ to be able to understand the relevant basics and also to be able to understand the relevant software right.

So here we are going to have a new phase right so for that I am going to list relevant species so here I am going to again assume FE2+ does not form any complexes or does not precipitate which is not bad assumption right and that is why had only FE2+ here but we know F3+ will have the complexes right FEOH2+ FEOH twice + and FEOH thrice neutral charge and FE OH4 negative charge and obviously the solid phase FEOH solid right.

So obviously here we need to look at the relevant component balance with respect to FE total so if I can write that down I guess FE3+ total would not be equal to FE3+ into 1 + beta star by H+ concentration which we know in this case because we assume that the PH or we considering the case when the PH = 7 right + beta 2 star by H+ square + beta 3 star by H+ cube right + beta 4 star for divided to the H+ of 4.

And obviously we need to consider the other unknown which is your concentration to the solid that has precipitated out right. This again is you known here so again keep in mind here to again refresh our memory the FE total FE3+ total would be the sum of FE3+ in the aqueous phase + the FE3+ in the solid phase right.

So this obviously is the aqueous and this obviously is the solid phase right so here though unlike the previous case with respect to the complex formation only where by knowing the PH to be 7 we could have solved for FE 3 + concentration the free metal we cannot do that because we have these second unknown which is these are concentration of the solid or the amount of solid what has precipitated out from the solution the unit volume of the solution right.

So again keep in mind again to refresh your memories in general we look at activities of solids they are relatively 1 in their 1 in that case when the solid is pure mud right but here to be able to solve the system we are coming up with these value or you know these variable this concentration of solid which is equal to the equal to the amount of solid that has precipitated out from the solution per unit volume of solutions.

So that is this particular variable right and we need to able to solve that how do we solve that by hand now. So here I have two variables only one equation so do I get that done so obviously we need to look at the relevant what do we say precipitation and resolution based equation FEO thrice the solid you need to know will be equilibrium with FE3+ + 3 OH- right.

So from these again I will have my solvability product to be equal to FE3+ activity times activity of OH- to the power of 3 by activity of the solid which will be equal to 1 right. So from this particular background with respect to our precipitation and dissolution we have the relevant solvability products are solvability constant and with these we now have or second equation.

So this is our second equation we still have a FE3+ we know what the volume of OH- is because the PH assuming to be 7 right so the only unknown is FE 3+ right and here we have FE3+ and what is it here please FEOH thrice the solid right. So from here i can calculate the what do we say I have an additional unknown right so from here I can plug this particular value here right or substitute or the relevant value of A3+ and calculate FEO+ thrice of solid and get the relevant aqueous phase concentrating of FE3+ or obviously the FE3+ metal free metal concentration.

So obviously we need to go ahead and look at those relevant aspects in such a manner yes so again this is how I would obviously work it out by add so once I do that obviously I am now going to have PE = PE naught – 1 / N which is electron transfer right log activity of FE 2+ / activity of FE3+ so in effect what would this lead to now right what would have lead to we are assuming that FE2+ as or forms no complexes or does not precipitate out right which is decent assumption and we know that F3+ will form a lot of complexes which we looked at in the previous session and we also know that it can precipitate out right.

So the FE3+ concentration is going to be now much lower so in effect what is it mean it means that value of PE is going to fall further right so let us see how to understand the system in VMINTEQ I guess right. SO let us switch over there so with respect to VMINTEQ I am going to assume I have FESO4 naught at 10 power -3 concentration right and also FE CL3 at 10 power -3 concentration right meaning FE2+ total would have been equal to 10 power – 3 and SO4 total right would be equal to 10 power -3.

And again similarly here FE3+ total would be equal to 10 power -3 and CL- total would be equal to 3 into 10 power -3 right. So now I am going to plug this values in and try to calculate what it is that I am going to expect in the what do we say scenario or out there in the nature when I also assume that the relevant solid phase is present.

So I am going to go over here to VMINTEQ and plus the relevant components in so let me first plug in the metal FE2 + and 3+ 2 + and so it is 1 milli I am going to plug this in add that to the list and FE3+ again same concentration I am going to add that into the list and SO42- is the same concentration right where is that SO2- it is right here and that again add to the list CL- though at 3 mili molal so let us where that is and CL- is that 3 milli molal.

So I am going to have that added to the list and I know that the PH we are fixing it at 7 right let us view or edit the list once 2 +, 3+ SO42- and CL – total that is fine here and obviously here the aspect is that if we try to solve for the system it would not consider the precipitation right so obviously need to specify that precipitation is possible also I need to specify which particular solid is the most possible or predominant is controlling solid.

Again what is this concept of controlling solid so if I can again refresh the memory right so we know that different solid phases or you know possible right but at a particular given time you will have one particular solid that would that we consider as controlling solid and why is that because let us say in our particular equation that we looked at here K solvable to product here right for that difference solids we would obviously have different solvability products and that would lead to different FE3+ concentration in equilibrium at that particular scenario right for that controlling solids.

So if you do not identify the controlling solid well enough right you can end up the erroneously calculating your or end with erroneous calculations with respect to your free metal here right. So here we are going to let us say assume it is the MOFS form the most solvable form so solid phases if I possible solvable phases right so limit to those solid is possible based on the compound that define.

So I am going to go with MRFS form here FE ferry hydride let us say and I am going to add that to the with respect to FEOH would not assume any what we say solid to be formed in general and going to lag that being so I am going to go back to the main menu so now I specified that the particular form of FEOH thrice can precipitate out right ferry hydride and now we also obviously need ask the system to be able to calculate the PE and EH specify PE and EH.

So we know that we need to compute PE and here it (()) (15:00) to supply I guess so earlier the value and we just considered the act to that complexes that 4.9 now it going to fall further let us say I am going to say be equal to 1 let us say the PE guess I am going to give is going to be equal to 1 so save and back to main menu so right now we have given all the components all the components yes and this is the dummy with respect to electrons I guess because it is a redox couple here okay that is something we have not done yet I guess specify redox couples.

So FE2+ and FE3+ something obviously we should have done right and back to main menu right okay so now everything seems in order we specify the relevant components A to with calculate for the complexes and we specify for the relevant solid phase for FE3 + let us say assuming that amount is solve for solvable form right and then we also specified for the redox couple.

And now we are going to ask the VMINTEQ to run for the system right or before we do so let us try to understand the system back to stuff its species let us say so I say for now I will delete the species we are going to come back to that again and without the redox couple we try to understand the system here okay I guess let me restart that because I removed VMINTEQ or the relevant aspect their seems to have a minor error let us review that I am going to fix the PH at 7.

So I am going to go with FE2+ as 10 power -3 again right at the it is FE3+ 2 at the same time concentration and SO42- the same concentration CL- at 3milli molal at 3 milli molal because we are having FE3 right add to the list right PH7 milli molal we were at list and seems fine for now species solid phases species solid possible solid phases right limit to that list I am assuming the ferry hydride can be formed and we are going to add that to the list and back to main menu run MINTEQ.

And now we have the relevant values so before we go further let us look at the species distribution we see that 89% of the total FE2+ is present as FE2+ the free metal and with respect to FE3+ you see that the free metal is nowhere in the picture yes and let us say go back to main menu and let us look at the FE3+ concentration now it is 3.15 into 10 power -18 let us plug that in here or try to understand that.

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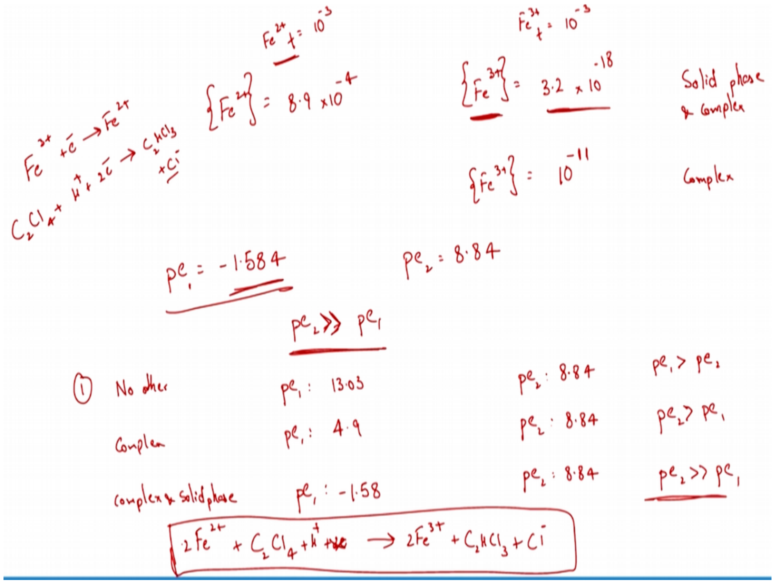

So now we have FE2+ to be 8.9 into 10 power -4 and FE3+ to be something around 3.2 into 10 power – 18 right this is of the free metal obviously 10 power -18 but how much did we plug in the total was FE 3 + total was 10 power -3 and here FE2+ we plugged in was 10 power -32. So you see that more or less this free metal concentration is more or less similar to what we plugged in with respect to FE2+.

But with respect to FE3+ when we consider the solid phase right when we consider the solid phase and complexes we see that it is much lower and to I think we consider only complex phase it was something around the activity of FE3+ or something 10 power -11 right so now you see when we consider the solid phase and the complexes the concentration of the free metal FE3+ is much lower right.

So obviously what would you expect if I plug in these values are FE2+ or F3+ in my PE equation would expect that the PE value would fall further right so this is the most realistic scenario let us see that with respect to our VMINTEQ here let us try to calculate that so I am going to say specify the redox couple right and that is going to be FE3+ 2+ so it says fixed I need to specify that so back to main menu parameters specify CH and EH and going to ask it to calculate so I am going to have the give a guess for my particular case of PE right.

So because of it going to be lower I am going to go with 1 right save and back to main menu and run MINTEQ and now you see that the PE value is remarkably low -1.584 right so now you see that PE value right for PE1 is 1.584 right and the PE2 value for C2H CL3 to C2CL C2CL3 is still going to be equal to 8.84 right and now you see that PE2 value is far greater than PE1 right again what is this mean now in this particular case this is the very strong tendency for your ferrous iron to be to want to reduce C2CL4 right.

So let us try to summarize what we have been up to thus for I guess right so again we now see that PE1 is much lesser than PE2 right but what was the case when we only consider that there were only redox reactions and no other reactions right we saw that PE1 I believe was that is 13.3 and PE2 was 8.84 right and when we consider the complexes I believe the PE1 was 4.9 PE2 states the same right and here itself we observe that here PE1 was greater than PE2 right and here PE2 is greater than PE1 right.

And when we consider the case of the complexes and the solid phase right and redox obviously we saw that the PE1 value is much lower and I think we end up with the value of -1.8 okay –

1.58 right and PE2 still going to be equal to 8.84 so PE2 is much greater than PE1 or PE1 is much greater than PE2 so again what is this mean that ferrous iron would very much strongly want to reduce let us say your particular chlorinated solvent which is C2CL4 right.

So here I guess you see the roll that relevant aspects or the relevant chemical process play here right so redox you want to know which species are present or the relevant redox couples but to be able to understand the relevant concentration of the redox couples right in the solution what do you need to know you need to know let us say what are the relevant aspect other chemical process that can influence these particular compounds right.

So from your particular background with respect to four major chemical four major chemical process we have considered we saw that let us say FE2+ and FE3+ they can form complexes we worked out the relevant scenario and then we saw that from our background we now that again solid phase can be formed and then the relevant what do we say PE values where calculated.

So and you see that each case you see that FE3+ concentration value keeps decreasing with each case and thus obviously the PE values too keeps decreasing so you see that FE without complexes right you see that C2HCL3 would have what do we say reduce FE3+ right but now you know let us say considering what you would expect out their in the nature right with respect to the solid and the complexes and again keep in mind that the solid phase that we assume was the most solvable form of the ferric iron that we looked at right.

Obviously the scenario will change if I looked at the or consider the more insolvable forms let us say let us look at that later but try to understand the system. So when I consider this consider this case of what I would actually expect out their I see that FE3+ concentration is remarkably less meaning that PE1 value is FE3+ going to FE2+ or FE3+ being reduce to FE2+ is much lower meaning in that case FE2+ would act as a strong reducing agent right the PE value is negative their right.

Or PE – PE naught is relatively low right strong reducing what do we say FE2+ would want to obviously reduce the relevant compound and oxidize to B oxidized to FE3+. So let us write down what it is that that would have expected so relevant half reactions where FE3+ + electrons goes to FE2+ right and we also had C2CL4 + H+ I think it as hydrolyses right 2 electrons goes to

C2HCL3 + CL- because PE is far greater than PE1 what is that men FE2+ is going to be oxidized to FE2+.

So what is that mean again FE2+ is going to reduce C2CL4 right so FE2+ to balance out the electrons I guess 2 FE2+ right 2FE3+ and what does it try to do wants to reductively be chlorinate right. So this is what you would observe I guess right and the system strongly favors this particular to go from or proceed from left to right and this is what obviously we have been able to look at.

So I guess the last aspect we are going to consider before I wrap up today session is for with respect to solid phase I believe we consider ferry hydride right the more solvable form of your particular case which is for FE3+ right so but let us say if I consider the either insolvable forms or more insoluble forms how would it you know after the system as in let us say initially you now that the most soluble form of the solid will be precipitate out first and then as you (()) (25:59) and hyphening you know that you are going have the more insoluble forms form later on.

So how would the system change let us say with respect to PE or redox values if the system where allowed to proceed further let us say so in that case i will say let us say solid phases specify solid phases and instead ferry hydrate let us say I have the aged form right and list of possible back to main menu right and run MINTEQ and now you see obviously the PE value as fallen for the why is that instead of just very hydride I lead the system know that both the ferry hydride age form right.

Let us say the crystalize form probably and also the you know the ferry hydride probably the MRFS form probably again right or what do we say possible solids so obviously the more insoluble solid would be the one that system takes to be at equilibrium now if you give enough time when the more insoluble form which is the ferry hydride age form right is present obviously what is that mean the FE3+ concentration is now going to be much lower may be let us say look at that okay.

So it is now the 10 power -19 1 hard draft molecule lesser than what it was earlier when we consider just very high. So obviously what it that translate into that the PE value is much lower than 1.5 or something that we observed earlier. So what would happen if I looked at more insoluble form let us see let me delete these two back to main menu space five possible solid phases and I think magnitude is one of the more insoluble form I am going to have magnitude list of possible species okay that is magnitude as that main menu and I run VMINTEQ let us say right.

So obviously you now see the PE value is much lower -8.048 so that means again obviously because FE3+is much lower or the free metal concentration right FE3+ is much lower which is 10+ -25 and again why is that again the solid phase concentration pardon me the solid phase is remarkably soluble here compare to the other solid phase that we have considered earlier which was which were I guess ferry hydride and ferry hydride form right.

And thus more insoluble forms means lesser concentration of FE3+ meaning obviously again is PE value is going to drop further as in the system is going to want to strongly favor the reaction of FE2+ reductive dechlorinating C2CL4 right. So I guess with the last couple or I guess the three sessions we the system should be clear respect to why we had to look at all the relevant aspect as in the chemical process and how there is a inter place between each of these process right.

So again I guess we are now going to move on to a few more aspects in our particular redox process later on right with respect to the electro chemical cell or such and also set up the equation by hand for being able to calculate PE for example here we are asking VMINTEQ to be able to estimate the equilibrium PE right how would you or how can you calculate by hand you would not go into that in great detail later we only look at that have a generic core you.

Because again you know these for PE it is native log activity of electrons that is a hypothetical what do we say compound right that would exist at equilibrium. So there are some issues their but we are going to have the generic about how to be able to solve and then we look at trying to understand the electro chemical cell and so on so I guess with that I will end today session and thank you.