Environmental Engineering: Chemical Processes

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Lecture – 40
Precipitation & Dissolution: Introduction & Applications

Hello everyone. So welcome back to the latest lecture session. So we have, in the lecture session, we were done discussing the aspects related to acid-base complexes, right and the relevant applications. So we are going to move on to the next logical aspect which is going to be precipitation and dissolution, right. Let us just take a moment to understand what case we are talking about.

So obviously let us say, you know, you have salt and you take a litre of water or, you know, a glass of water and you add some salt, you know. Initially, you will see that everything dissolves, right. But if you keep adding or increasing the amount of salt added to that glass of water, you know, I am sure that at certain, you know, after certain level of or addition of this salt, you are going to start seeing that there is no more, the salt does not, what you say, dissolve anymore.

Whatever you put in, starts precipitating out at the bottom of your particular container, right. So again here, what, what are we looking at? We see that the solution holds the maximum extent of that particular soluble form of those salts possible and once you reach the threshold obviously, right, you know, the salt starts precipitating out in the solid form. So here initially when we add the salt, they dissociate, right and they stay in there, let us say, relevant, as a relevant ions, right in the solution.

But once you keep adding or keep adding, keep adding the relevant salt let us say, at a certain threshold, you know, the solution you can say that cannot take the or hold these cations or anions anymore and now you are going to see your precipitation, let us say, right or no more, no further dissolution, right. So let us just try to understand what you are going to talk about here again.

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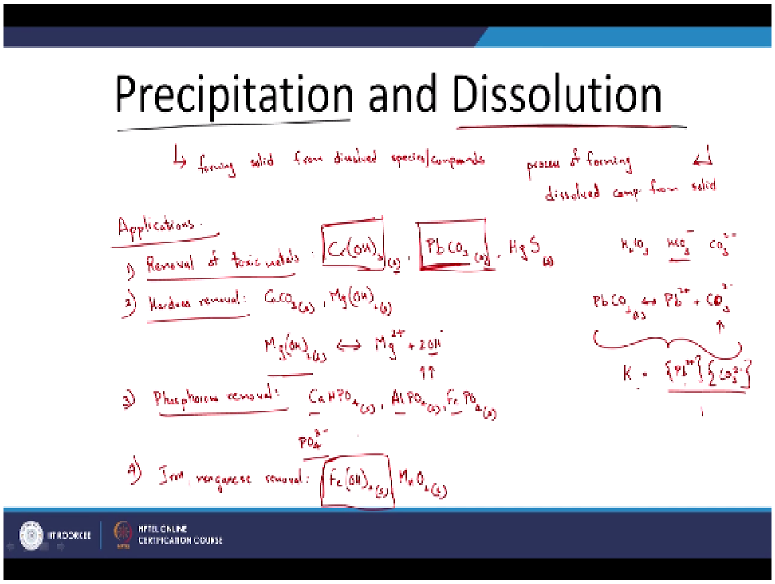

Precipitation and Dissolution

↳ forming solid from dissolved species/compounds

process of forming dissolved comp. from solid ↵

Applications.

1) Removal of toxic metals: $\boxed{Cr(OH)_3}_{(s)}$, $\boxed{PbCO_{3(s)}}$, $HgS_{(s)}$

H_2CO_3, HCO_3^-, CO_3^{2-}

$PbCO_{3(s)} \leftrightarrow Pb^{2+} + CO_3^{2-}$

$K = \{Pb^{2+}\}\{CO_3^{2-}\}$

2) Hardness removal: $CaCO_{3(s)}$, $Mg(OH)_{2(s)}$

$Mg(OH)_{2(s)} \leftrightarrow Mg^{2+} + 2OH^-$

3) Phosphorus removal: $CaHPO_{4(s)}$, $AlPO_{4(s)}$, $FePO_{4(s)}$

PO_4^{3-}

4) Iron, manganese removal: $\boxed{Fe(OH)_{3(s)}}$, $MnO_{2(s)}$

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So 2 aspects here, precipitation and dissolution, right. So again, what is precipitation about now, right? It is a process of forming a solid compound from the soluble species, right. So again understand that and we do not need to mug definitions up, right. This is just for your understanding. So we are talking about or we are trying to understand the precipitation as, you know, formation of solid from soluble species.

So the example that I gave before, you know, is not directly applicable here but it helps you understand the system, right. So again, whenever we have a process that leads to formation of solid from soluble species, we call that, you know, we refer that, we refer to that as precipitation and obviously, dissolution, right. It is the vice versa of your precipitation, right. Let us just get that down here.

And obviously what is dissolution about, you know, it is inverse of this more or less, right. So what is this going to be equal to now or equal to the process of forming dissolved species or compounds from your solid here, right. Again, and then, I guess, that pretty self-explanatory right, you know, once you look at the term dissolution, so in one case, you have solid being formed from your dissolved compounds and the other, the vice versa, more or less you dissolve compounds forming a, or in a process of forming dissolved compounds from the solid, right.

The solid, you know, forms the dissolved compounds in dissolution, yes. So again, lets us move on. Obviously, we are going to discuss this in relevant detail over the next couple of classes or sessions, pardon me, right. So first we need to understand why is it that I am concerned with it, right? So let us look at the applications here. So obviously, right, what are we trying to achieve here by understanding this particular system with respect to precipitation?

First we look at some of the applications with respect to precipitation and then move on to dissolution, right. So again, precipitation, think of before we go further in this particular aspect, think of what we discussed in the previous sessions, right, complex formation. So let us say when I put in, let us say a metal and in the presence of a ligand which is an electron-rich compound, you saw that a complex is formed, right.

So to understand how precipitation occurs, let us say? Think of this particular complex, let us say, with one central atom or the metal and the relevant number of ligands as a nucleus, let us say. Think of that as a nucleus or let us say a monomer, let us say. So over the time, let us say, as you keep increasing the concentration of the metal and the ligand, let us say, the concentration of the complexes or complex keeps increasing.

And you have, let us say, formation of what can you say, a kind of a 3D structure with, let us say, if I call this initial complex a nucleus, right, the other complexes are going to be formed, let us say, around it, let us say, right. And, let us say, more or less going to be an arrangement in a 3D structure. So as this keeps going further, right, as this particular 3D, what shall I say that, call that, let us say, 3D matrix keeps developing further.

So the innermost complexes are now no more exposed to the bulk solution, right. So now what it is that we are trying to say is that when they are no more exposed to or in the bulk solution, what is that mean? They are no more in the dissolved or aqueous phase. They are now in a solid phase, right. So you can try to link the complexation, right, to your precipitation to, right. Initially think of that we have nucleus where in that considers, where we are calling a nucleus to be one particular complex with one central atom or the metal.

And, you know, the relevant number of ligands, as we keep increasing the number of, what do we say, or the concentration of complexes. So think of this, this is a complex, you have them developing all around that, the various other complexes surrounding the nucleus if you want to call that, right and as this particular, you know, structure gets bigger or let us say progresses further, the, those complexes within the matrix, let us say, are going to be no more in the bulk solution which was the aqueous phase earlier, right.

So now, let us say, you are going to have or look at the initial stages of your particular precipitation, yes. Again, so again, that is your particular understanding or how we are going to link that to the aqueous complexes, right. So here, let us say, we are talking about obviously applications here of precipitation. So why I linked that to aqueous complexes? Whenever we looked at aqueous complexes, we always looked at metals, right.

So let us say here in this case, if I have, let us say, a metal that is toxic and I want to remove that from the solution. Obviously what is it I can try to promote, I can try to promote its precipitation, right. So let us say I have chromium, let us say, in its oxidation 8+3, let us say, right and why would I want to promote +3 rather than +6 form of chromium because +3 is more insoluble, right or less soluble.

So it will precipitate out. So I can promote formation of chromium and we could precipitate out as CrOH3, right. So again one certain application is obviously removal of toxic metals, right and examples are we just talked about CrOH3 or I am going to use this particular subscript, right to indicate that it is solid, right or lead 2, let us say, PbCO3, if I want to remove lead, right and also, let us say, if I want to remove mercury, right.

And if people can remember that we looked at an example where we looked at complexes of mercury and sulphide, right. So now obviously here we see that mercury and sulphide, right are the complex, it is a natural progression to the precipitation of mercury here, right. So again keep that in mind that precipitation is one of the most widely used methods, obviously for precipitating out or removing the toxic metals from your particular solution.

So obviously what you need to add? You need to add the relevant concentrations of your ligand, right. So the ligand if it is OH-, obviously what does that mean? It means changing or varying the pH, right. So that is obviously remarkably relevant in this particular case but in general here OH3 precipitates out at most pH but, let us say, for example, it is PbCO3, let us say, right and what is the role of pH here.

So now we need to dig back into our acid-base relevant knowledge here, right. So as you know, right, CO3 2- can also exist as, as CO3- and H2CO3, right. So obviously for Pb2+ and CO3 2-, right. In general, we write this as the dissolution reaction, right. For this particular reaction from right to left to proceed, you need to have relevant high concentrations of CO3 2-, right. So obviously, when will CO3 2- exist in solution at relatively high concentrations?

Only when the pH is relatively high, right. Otherwise, if it is at neutral pH or in that particular range, as you know HCO3- is going to be predominant and thus you are not going to have a relatively high concentrations of the relevant compound which is CO3 2-. So again, as we keep progressing further, we need to understand that each and every aspect that we have discussed earlier work in conjunction as an acid-base aqueous complex and precipitation.

As in, let us say, if somebody ask you what is the concentration of lead, let us say? You cannot just look at this particular equation now and, let us say, I can have the equilibrium constant for this particular equation and that is going to be equal to activity of lead, right and activity of CO3 2- and activity of solid which is equal to 1 because activity of solid, pure solid is 1, right. Again, you know, I cannot just directly calculate it from here.

Why is that? Because you know that it can again form complexes, right. So it is going to be linked to those particular aspects too, right, Pb2+ can form complexes too, yes. Again, so keep in mind that, you know, they are in equilibrium or, you know, it is a fine balance between all the 3 aspects that we have discussed thus far. So again we are just trying to look at those particular aspects and how acid-base relevant chemical process or a relevant here PbCO3 and so on.

So let us move on what else can we look at, let us see. So another aspect that people obviously look at or, you know, I am sure everyone came across is removal of hardness, right. So your ground water at least in or around here in Roorkee is remarkably hard as in what do you mean by hard? You have this bivalent cations, right, Ca2+ and Mg2+. So how do I remove them, alright. So here we have hardness removed.

There are different methods but almost all of them, or what is the principle here, it is precipitation and precipitation in the form of CaCO3 solid and MgOH2 solid, right. So again as you see calcium carbonate, it can precipitate out. So again what is the requirement here? Obviously you need to keep the pH high. Why is that? Because if you do not keep the pH high enough, CO3 2- would exist as HCO3- I guess, right.

So CaCO3 again and the relevant acid-base process and again MgOH2 again depends upon pH as you can see. The higher the pH, the greater the concentration of OH-, thus the greater the tendency to form the solid, right. So think of this again what we just mentioned here. So, let us say, MgOH2 solid is going to be in equilibrium in your solution with a certain concentration of Mg2+ and certain concentration of OH-, right.

So as you keep increasing, let us say, this particular system, is at equilibrium right now, right. If it is at equilibrium, right and I keep increasing this particular variable or the concentration of OH-, what happens now? So it is no more at equilibrium, right. So the equilibrium has shifted now and so again the system wants to, what we say, reach equilibrium, yes. So what is going to happen again?

The reaction from right to left, right, it is again based on the Le Chatelier's principle, yes, that Mg2+ would again, what do we say, react here with, what is it now, 2 moles of OH- and then precipitates out in the form of MgOH2, right. So again that is the key here. Obviously if you want to promote precipitation, you want to increase the concentration of the relevant ligand whoever which in this case is OH-, right.

So what else now? We looked at removal of toxic metals, what we used. Hardness removal, what we used. So I guess people also look at it for phosphorus removal. So phosphorus is a nutrient that you want to, you know, remove from your particular waste water, let us say, before discharging that in the surface waters. Why is that, let us see. Excessive, you know, availability of this particular nutrient along with nitrogen, let us say, can lead to an algal bloom, right, you know.

And that can lead to eutrophication, right and the relevant effects and I am not going to go into that obviously. So there are biological processes that can assist in removal of your particular phosphorus but obviously we can again, we have chemical processes too whereby you can precipitate out phosphorus, right and some of the forms in which we can precipitate them out are CaHPO4 solid, AlPO4 solid and FePO4 solid.

So here more or less what is the PO4, PO4 3- right? So it is more or less a ligand, right. Here you want to remove the ligand, right. Unlike removing the metal earlier, here you want to remove the ligands. So what do you need to add now? You need to add an electron poor compound or electron deficient compound, right. So what is it that we are adding. We are either adding calcium, aluminium, or ferric, right.

So that is what we are doing in this particular case again. So again this is obviously linked to your aqueous complex based chemical process and again the next further or next logical step which would be your precipitation. So next aspect we are going to move on is, we also need to, let us say, people look at iron and manganese removal, right. In this case, we can remove ferric in the form of FeOH3, right and manganese as MnO2, let us say, right.

And this applications of or the applications of FeOH3 precipitating out are, you know, remarkable. So think of where is it that we come across, you know, applying this particular principle of precipitation of ferric hydroxide now, right. So people might remember that, you know, you would come across ferric, at least in your water treatment or sometimes in which water as being used for coagulation, right or a coagulant, right.

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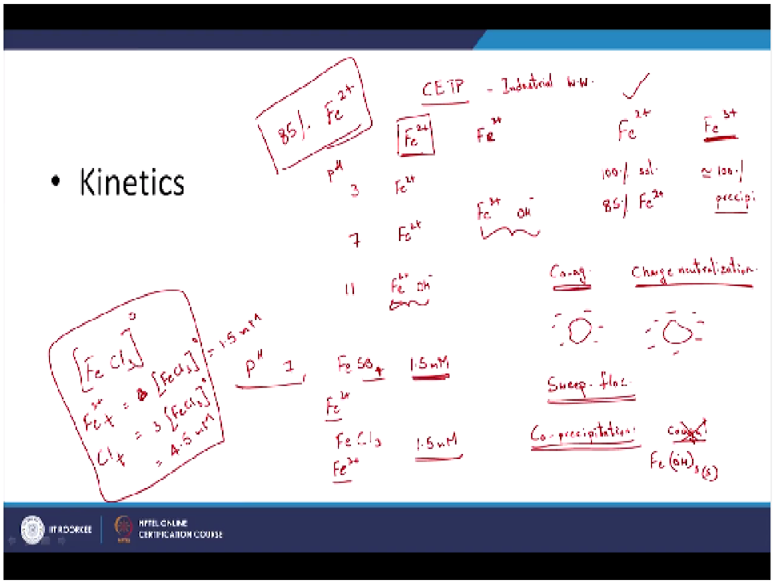

- Kinetics

So again here if you remember I guess one of our initial, what do we say, examples we looked at was where we had to CETP, right. If people remember that as one of the first classes, I believe, was second class of this particular course. We talked about CETP personnel and he was adding a source of Fe2+, right. Fe2+ as is a coagulant and his reasoning being that it is in general cheaper and he did not believe that there is great deal of difference in the mechanism with respect to either Fe, addition of Fe2+ and its action as a coagulant or Fe3+ and the relevant action as the coagulant, right.

But here, let us say, in general in that particular case keep in mind that these are industrial waste waters, industrial waste waters, right. So and Fe3+, let us say, right. So we are just going to discuss this particular case, right and where, let us say, the removal of Fe3+ in the form of or precipitation of Fe3+ in the form of FeOH3, right, is going to play a relevant or important role here, right.

So keep in mind that we have Fe2+, right and we have looked at it, looked at the complexes formed at different pH if you remember in one of our couple of sessions ago, 3, 7 and 11 and we saw that Fe2+ stays as Fe2+ at pH 3 and pH 7 and only at relatively high pH that it starts forming Fe and OH complexes, right. We looked at at that particular aspect, yes. But we saw that for Fe3+, more or less at almost all the pHs, it forms Fe3+ and OH- complexes, right.

That is something that we, you know, understood when we, you know, plugged in the relevant values in VMINTEQ in a couple of sessions ago, right. So here again we are going to try to use the same principle here. Let us say, I am going to first demonstrate formation of, what is it now, a precipitate when we add either Fe2+ or Fe3+ and I believe the case, I am going to look at is a pH at, let us say, 7, okay.

And one case is when I add FeSO4 which is source of Fe2+ at, let us say, 1.5 millimolar which is what people generally use in the common effluent treatment plant, right and also the other one I am going to add, let us say, a source of ferric, let us say, in this case I am just going to take the example of FeCO3 source of ferric Fe3+, same concentration of 1.5 millimolar, right. But unlike the previous sessions when we did not consider precipitation as feasible, right.

Here I am going to consider, you know, precipitation as a feasible process. So now let us understand or try to see how the system changes or varies here. So let us say again we are going to look at pH 7. Initially, we are going to plug in Fe2+ at 1.5 millimolar, obviously SO4 2-2 will be at 1.5 millimolar. So in the second case, I am going to plug in at pH 7, FeCl3, with Fe3+ at 1.5 millimolar, so the Cl total will be 3 times 1.5, so 4.5 millimolar, I guess, right.

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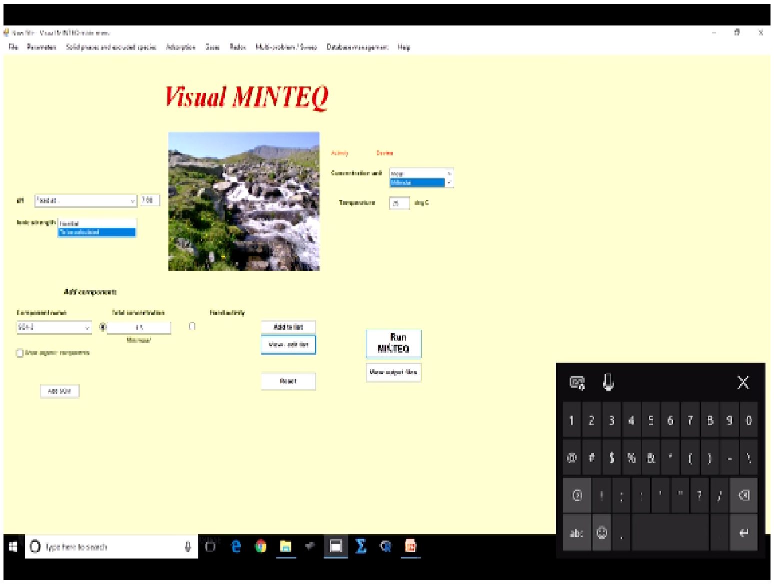

So let us plug in those values and let us look at where we are going to be? So we usually maintain the pH at 7, let us see, right. And I am going to plug in F32+ initially, Fe2+, right and I am going to use units of millimolar, right and the concentration, let us say, I, we just mentioned that, it is going to be equal to 1.5, right and that is 1.5, right and I am going to add that to the list and now.

And so for 2- at the same concentration because I am putting in Fe2+ in the form of FeSO4 and where is that? Okay. Is that the only case or do we have anything else S2-, SO4. S as SO4 S-2 oxidation state, so on, S2 and this is SEO4 2-, not SO4 -2, so I am going to skip that. Okay, here I have SO4 2- and I am going to add that to my list.

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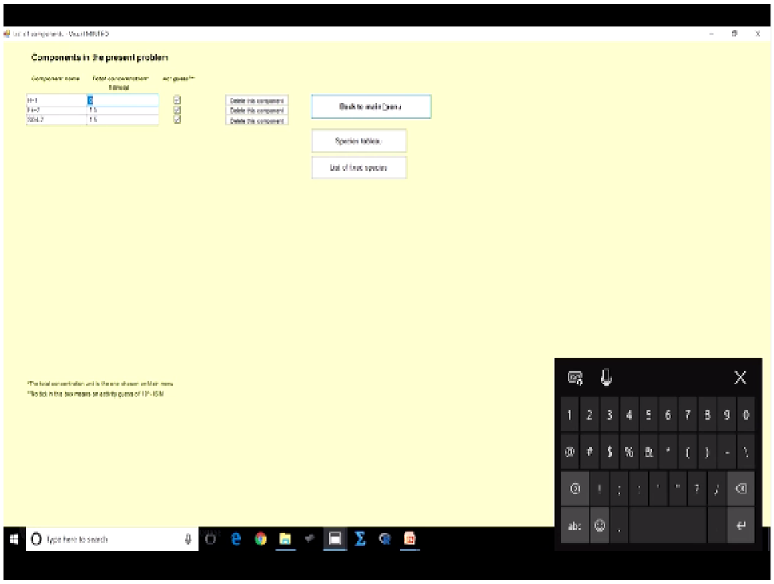

I need to view edit my list, right, okay. And I am going to go back to the main menu and here though I am going to plug in, you know, put in few aspects that might not be remarkably apparent here but what I am going to, try to do now with limit the case, I am going to specify that precipitation is feasible, right. How do I do that?

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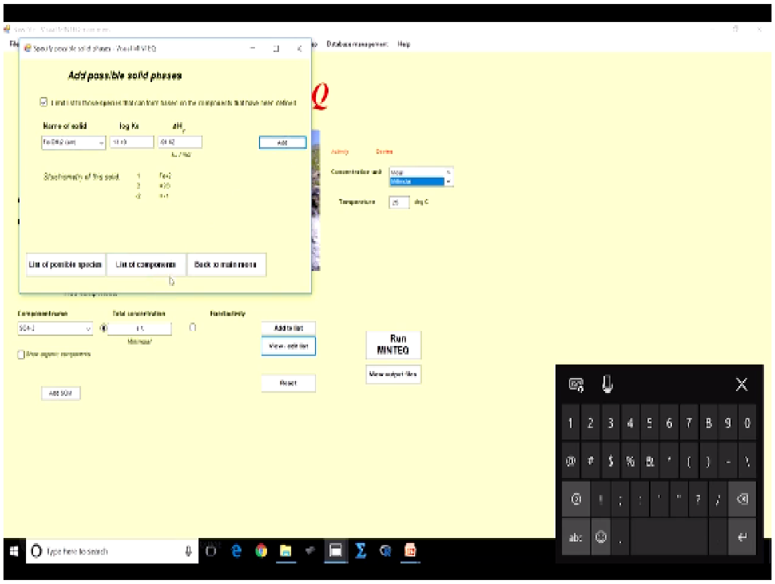

As in I need to specify possible solid phases. So here VMINTEQ will give an option to add possible solid phases. So I can add multiple solids, right but obviously it is going to be time consuming and I do not know, let us say, if at this stage I do not know what Fe2+ can precipitate out or in what forms it will precipitate out. Obviously VMINTEQ can help you by limiting, you know, I take this up here, take this particular option here or consider this option to those species that can be formed based on the components that have been defined, right.

So because I, I did not find Fe2+. So here this is, it is FeOH2 amorphous and crystalline and (()) (21:42) I guess, right, if I pronounce that right. So in general initially you will have amorphous form, form first. We will discuss that later. So I am just going to say thus the amorphous form of Fe2+ can precipitate out and I will add that and I will go back to the main menu. And now I am going to run MINTEQ.

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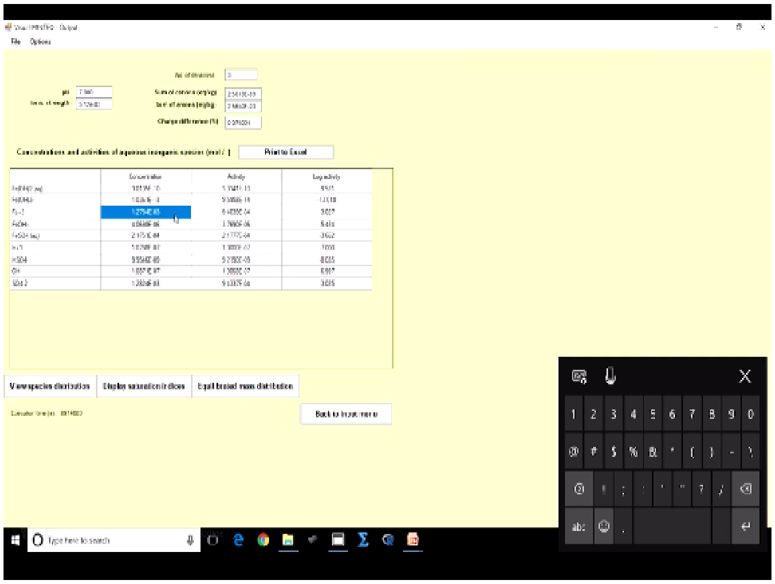

Okay, obviously again we look at different, what we say species here, which is what we expect. Again the major aspect is that Fe2+ is mostly present as Fe2+. It is 1.3*10 power -3. If you remember, we put in, I think, 1.5*10 power -3 and keep in mind that Fe2+ stays as Fe2+ for what it is like 80% may be or 90%, god knows, right. 1.3/1.5*100. So anyway that is fine, I guess. So most of it, keep in mind, stays as Fe2+.

And we have relatively little formation of, what we say, the relevant complexes here, right, either in the form of FeOH, FeSO4, OH2 and so on, right. Keep in mind that the complex formation or the concentration of the complexes is almost negligible. But here I am not looking at complexes, I am trying to look at amount of salt that is going to be formed, let us see. So how can I look at that, species distribution?

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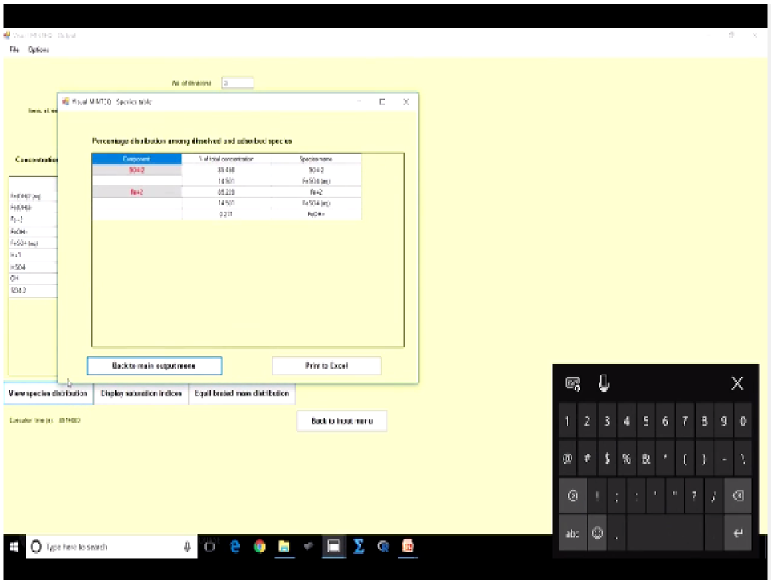

Will that really help me? Not really, it just says 85% stays as Fe2+, right. So that is it. I cannot say anything related to precipitation here.

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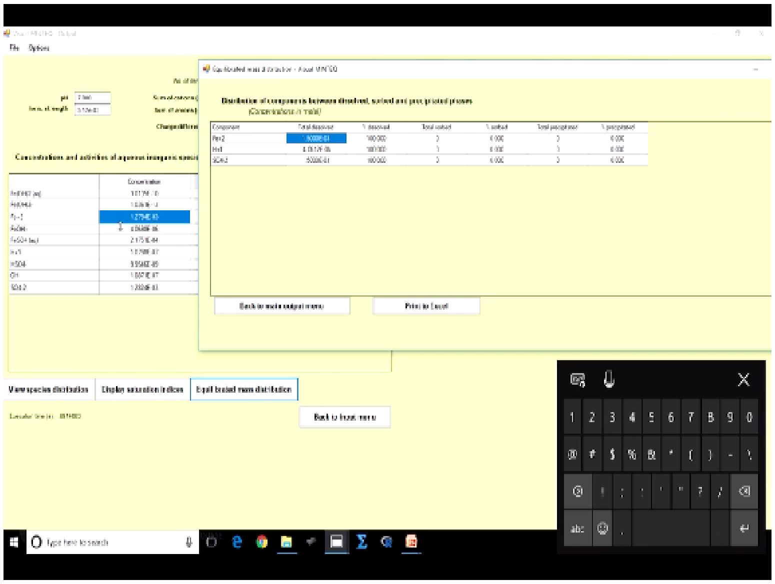

So I am going to look at, let us say, equilibrated mass distribution here. So here it gives me an idea about what is the percentage dissolved and what is the percentage that is precipitated out, right. So as you can see here almost, not almost, the 100% of Fe2+ is in the soluble form as in, it is either as Fe2+ which is soluble or the other complexes which are still soluble, right. So keep in mind that at 1.5 millimolar concentration of Fe2+, there is no precipitate form even when we specified that, I think a form of FeOH2, the amorphous form is a possible solid, right. So now let us try it out with the Fe3+, let us see.

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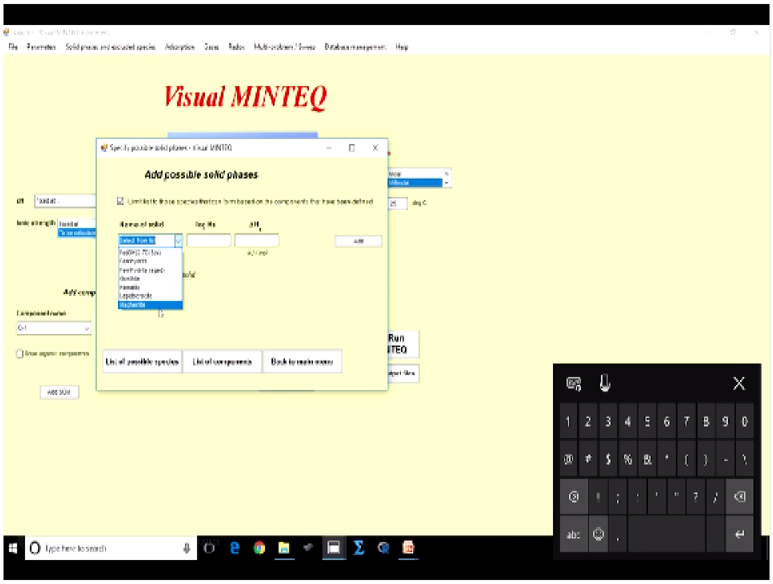

So that main output menu, input menu, I am going to, let us say, delete these components, right and I will still fix the pH at 7. So now I need to put in Fe3+, let us see where we have Fe3+. Okay, we have Fe3+ here and 1.5 millimolar, right. So what is it that we were trying to do here? So if I have FeCl3, right, FeCl3 and that is my initial recipe concentration, how do I plug it in into VMINTEQ. So I need to plug in Fe total and Cl total, right.

So obviously that is going to be equal to Fe3+ total and Cl total I guess. Three times or, you know, just FeCl3 0 but obviously what is Cl total here? It is 3 times FeCl3 0 and that is equal 3*1.5 which is 4.5 millimolar, this is nothing but based on your formation equations and then writing up your tableau and so on, right. So Fe total, what is the source? It is the, source is the FeCl3.

So I need to plug in Fe total 3+ as 1.5 millimolar and Cl total as 4.5 millimolar, right. So let us plug in this, millimolar concentration is set, right, add to the list and then Cl, Cl and I need to plug that in as 4.5, right and 4.5, okay. Add that to the list and again I am going to specify relevant possible solid phases, right here again because I limited it those species that can be formed, I can get, what do we say, screened forms of Fe3+ that can precipitate out. So in general here as you see Fe3+ can precipitate out in different kinds of forms. So we are going to discuss the relevant stages later with respect to precipitation and how they are relevant.

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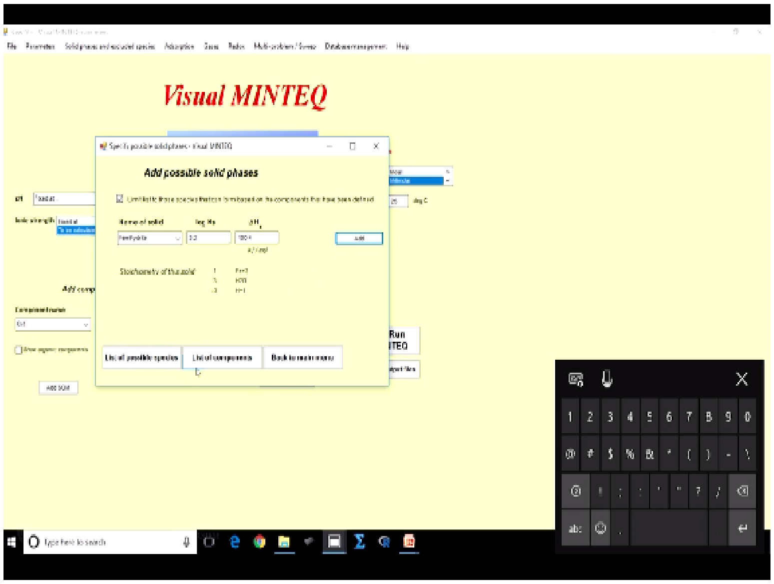

But here for now, let us say let us look at ferrihydrite which is usually the first form that is formed, right. Is it okay?

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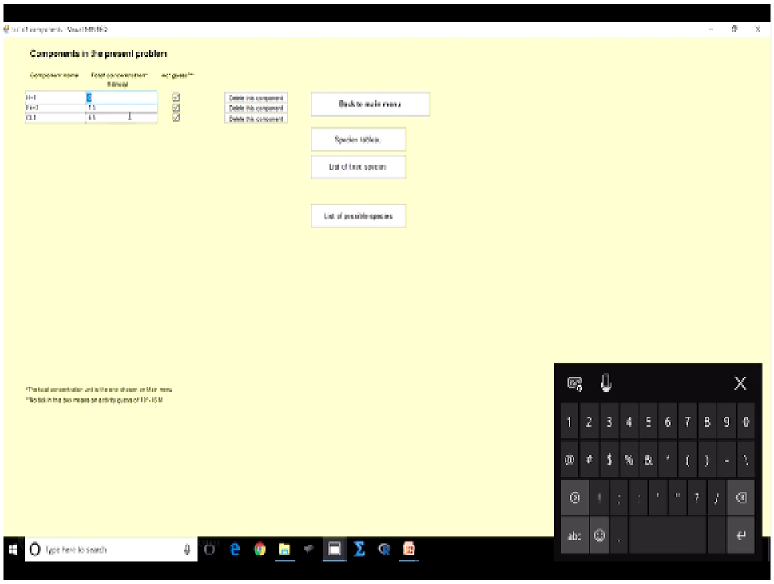

And back to main menu and pH 7, view and edit list and everything seems fine. And I am going to run MINTEQ.

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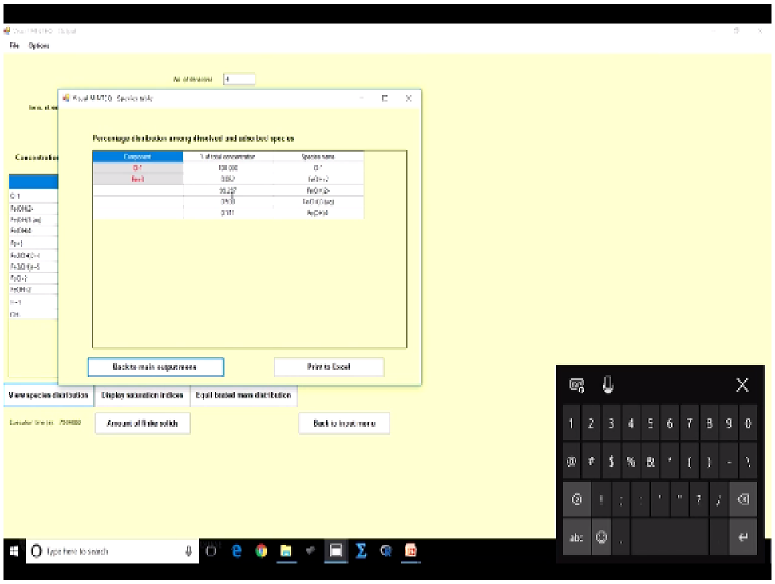

So again now, let us look at what we say view species distribution. So most of it is as the complex, most of what now? Fe3 that is in the dissolved form, whatever ferric iron is in the dissolved form is mostly present as a complex, right. So but does that give you the true picture? Not really. Why is that? If you look at the equilibrated mass distribution, you see that Fe3+, right, 100% Fe3+ or almost 100%, I guess, right, is precipitated out. Make sense hopefully.

So only a very little form or, you know, little amount is in the dissolved form. What is that now? That is 2.9*10 power -10 and keep in mind that we have put in Fe initially at 1.5*10 power -3. So almost 7 orders of magnitude difference or 10 power 7 times lesser is in form of what to say a dissolved form and that is why almost all of it, right which this particular VMINTEQ considering as 100% has precipitated out and in which form has it precipitated out?

In the form of that ferrihydrite that we just discussed. So again, let us come back to what it is that we are discussing right? So let us move on to our particular system here. Is it okay. So let us see why is this relevant now? So keep in mind that earlier the, what do we say, the CETP personnel was putting in or plugging in Fe2+, right and we see that with Fe2+, right, most of it would stay as Fe2+, right, 85% and almost, not almost, 100% is soluble.

Let me write it down here. Fe2+ and Fe3+, 100% is soluble and 85% of that particular soluble species are present as Fe2+, right. But with Fe3+, we see that almost all of it, 100% has precipitated out, right at pH, what is it now? 7 which is more or less within the ballpark of the pH that the people at the CETP try to main, right. So let us look at why this is relevant now. So in general, how does coagulation occur now, coagulation, right?

There are different mechanisms. The first mechanism is charge neutralization, let us say, right. Again, that is self-explanatory I guess, charge neutralization as in your suspended particles or collides people presume that they have an entry charge, right. That is a good enough presumption actually, right. And even in industrial waste waters, people presume that. Again I am saying people presume that but it can vary.

There are sometimes cases when you have the collides with in at positive charge rather than negative charge. Anyway charge neutralization as in you add the counter charge, so if the collides are negatively charged, right. Let us say, this is my suspended particle with negatively charged and, right, 2 negatively charged collides, you know, repulsion here, right. So that is why I add the coagulant which can neutralize this particular negative charge, right, allowing the particles to form collides, let us say, right.

And that is one particular simplistic way of explaining charge neutralization. So which one, which one would work better in that case if charge neutralization was the principle involved here? Fe^{2+}, right. But for industrial waste waters, that is not always the case. What happens is, you know, in coagulation, you have other mechanisms as in sweep coagulation, right. A sweep floc, let us say.

As in the precipitating form from addition of your particular initial coagulant which is Fe^{3+}, let us say, forms a kind of a mesh, right. $FeOH_3$, let us say, forms a kind a mesh and as it settles down, you know, it can capture or encapsulate the relevant suspended particles too. That is one particular case. But more importantly though we have co-precipitation. So people mistakenly call this coagulation but this is not coagulation, right.

This is a principle involved. It is co-precipitation. Why are we calling it co-precipitation? As and when we add Fe^{3+}, you see that it can precipitate out in the form of $FeOH_3$ almost all of it, right.

So these particular sites of, you know, solid Fe3+ act as sites for adsorption, right or for the other suspended particles to be formed or agglomerate on this particular solid. It makes sense hopefully.

So they add either act they as in FeOH3, the solid, you know, that is formed when you add Fe3+ source of Fe3+ to your solution at pH 7 which we just saw is 100% precipitating out, right. It will act as an adsorbent, let us say, right for the other relevant particles, right. So that is why we call that co-precipitation, let us say. It makes sense hopefully, but people mistakenly call that coagulation.

Keep in mind that there are different principles involved here. But can Fe2+ play the role of, what we say, for sweep flocculation, right or co-precipitation now? No. Why is that? It cannot form precipitate. We see that 100% of it is in the soluble phase. That is why if the CETP personnel had, what do we say, put in the source of Fe3+ rather than Fe2+, he could have had sweep flocculation and also co-precipitation and turns out for industrial waste waters that he was receiving, it was not charge neutralization that was relatively important.

But co-precipitation was the relevant mechanism that was leading to the removal of the relevant particles here or decreasing his particular turbidity, let us say. So but what was he doing there in that case? He could differentiate between Fe2+ and Fe3+ and the relevant mechanisms involved. So obviously he did not have, let us say, the relevant background with respect to the complexation or the precipitation.

So he just plugged in Fe2+ but that ended up adding to the turbidity because for his industrial waste waters, charge neutralization looks like was not an important, what do we say, mechanism for coagulation and the relevant flocculation. Yes, it was a sweep floc, formation of the sweep floc and more importantly co-precipitation. So obviously for that particular aspect, what do you need to have?

We need to have a source of precipitate and how can you get that? From your Fe3+ addition which can form your FeOH3 solid, right. So again, I guess, I am just trying to link why, I guess, right, you need to learn the aspects that we are learning to what you would see out there in the field, right. Same way, I think, we are running out of time. So with that I will end today's session and we look at a few more applications in the next, what do we say, session.

And then we are also going to move on to look at kinetics and equilibrium, right. So kinetics plays an important role here because solid formation, may be, you might have observed in nature is not as fast as you would presume for acid-base or complexes now. So in this particular case of precipitation and dissolution, we are also going to consider the aspects related to kinetics and obviously related to equilibrium too, right.

And another aspect we need to consider is that, if you remember, for $Fe3+$, you saw that there were different types of salts formed, right. So precipitation occurs in stages. An initially one type of solid is formed, then the other type of solid and then the other type of solid and so on. I mean, mostly only one solid predominates, right. So that is called the controlling solid and that determines the concentration of the metal or the ligand in solution.

So we are going to discuss these aspects in the next classes and see why they are relevant again and, I guess, with that I am done for today and thank you.