Environmental Engineering Chemical Process
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Lecture - 60
LogC-Pe and Ph Pe- Diagram

Welcome back to our last lecture session I guess. So today we are going to look a couple of what do we say example where anyway I would try to help visualize or help you try to take a holistic view of what it is we have been up to throughout the class. So first we are going to look at one example with respect to Visual MINTEQ. So before we go we do keep in mind that (()) (00:50) process what is it now the asset base what else complex formation precipitation delusion and Redox process they go hand in hand and they are never readily independent of each other in most of the systems.

So here we are going to consider one particular example first before we dig into such holistic view.

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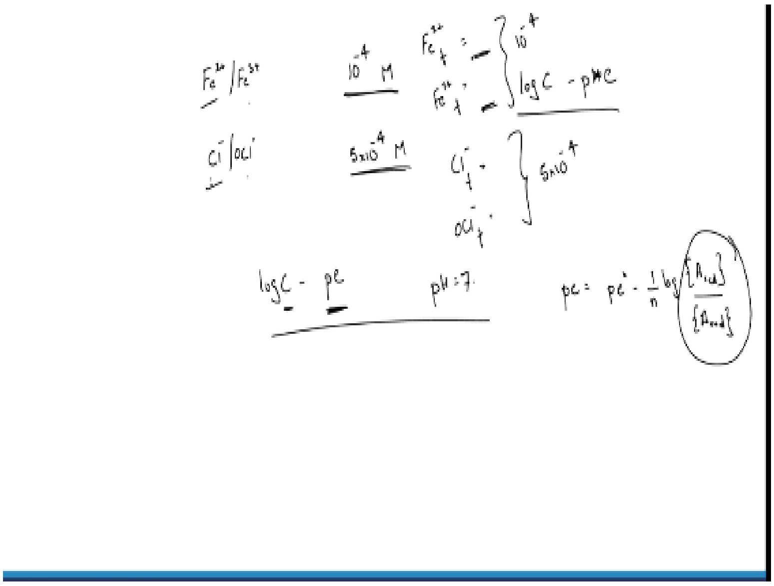

So first example that I would like to look at let say is I am going to look at the Redox couple of Fe2+, Fe3+ and also let say Cl- (()) (01:31). So here let say we are going to look at concentration of total Fe of around 10 power -4 molar total Cl which includes OCL - to be around let say 5*10 to the power -4 molar. So here again before we look at holistic example I would like to let say portray let say or help bring out the reason for such examples.

And for that I am going to look at one particular what do we say scenario where we have two Redox couple. So earlier until now we have looked at calculation of pe values for particular Redox couple, but here we are going to look at obviously two Redox couple and obviously if you have a system out there where you have Redox process going through you will obviously have two Redox couple.

Because you obviously need one (()) (02:20) and never what do you say independent of each other. And the reason being you will never have (()) (02:26) unlike that you can have in the water. So here we are going to plug in the relevant values and look at the systems and so we are going to understand system in terms of the log c ph diagram. So obviously Visual MINTEQ will help cut down on the time.

And here as you see I guess we are going to look at total concentration here as in I can obviously independently plug in the values for Fe 2 total + and Fe 3+ total and Cl--total and Ocl-total independently now such that the sum of these two is 10 power -4 and the sum of these two is 5*10 power -4. But here because we are looking at what do we say couple and it is not log c p diagram we are going to look at log c p diagram.

So we are going to try to draw the log c and p diagram how is the concentration of the various couples going to change with the p values now. So let us see we are going to choose a particular ph of 7 and try to analyze the system at that particular ph. So here the reason why we do not need to give the breakdown with respect to the concentration of the Redox couples is that when it obviously calculates pe you know you are going to have pe= p0-1/n what is it now log of the produced form by the oxidized form I believe.

So anyway even if you give the relevant what do we say independent concentration your individual concentration for a particular p though you will only have one particular ratio of your particular reduced to oxidized forms. So it does not make much difference or any sense rather to at least initially give the Fe2+ and Fe3+ concentration independently and so on. You can but as you see from here for a given p value you will always have particular ratio of that particular oxidized or reduced to the oxidized form.

And it does not really need to be taken into account here. So again these are what I am going to plug in as 10 power -4 Fe2+ 5*10 power -4 for Cl- and let us try to understand the system I guess.

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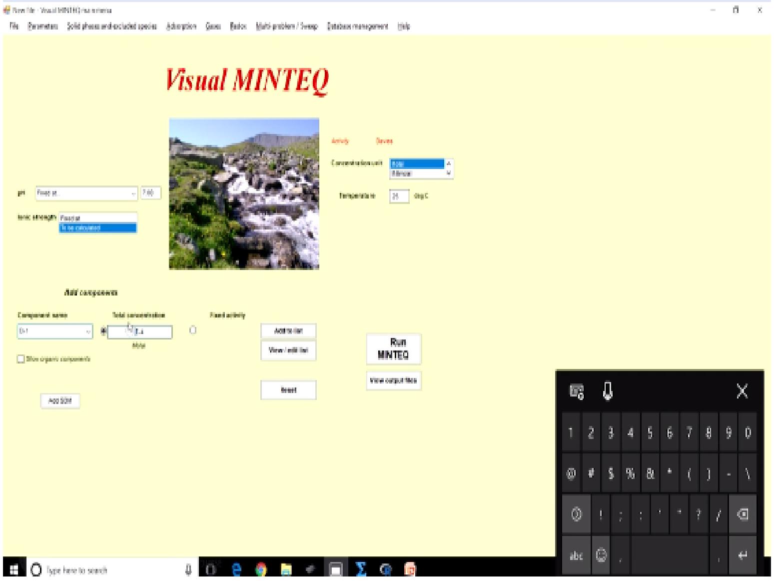

So obviously for that I am going to move on to Visual MINTEQ. So let say here I am going to say ph I am going to analyze it at 7 and then let say I am going to have the Fe2+Fe3+ couple mentioned in times of only the Fe 2 and we have just discussed why. So here I am going to say it is 10 to the power of -4 e -4 add to the list and let say instead of Cl-n I am going to just specify that as Cl- and let the system do its own work.

I think we are looking at example of 5*e-4 right add to the list and obviously now I need to be able to specify the Redox couple and now this option where I say let say limited to those species will not work because I have not mentioned Fe2+n c+ and Cl- and Ocl -. I thus need to look at the relevant couples so I know they are going to be Fe2+ and Fe3+ I need to add that to the system and again the Cl- and Ocl- where that is.

And I am going to add that to the system too. So again back to main menu I will also say there is a possible solid specifies and let say that is very hydride and back to main menu. And now obviously you want to be able to get the graph between the log c and pe. I want to get a snapshot of what the system looks like at different p values because it (()) (06:38) ph. So for that obviously you can do the manual calculation in such, but again that obviously time consuming.

And by now we have a relevant background or understanding of the fundamentals about how to do that but obviously we are going to skip that now and look at it with respect to Visual

MINTEQ. So aspect that we are trying to get it is log c versus pe. So from here let say I can understand at which p would it be relatively more oxidized form of Cl- as and when Ocl – predominates or such.

I want to be able to answer such questions let say or try to understand the system now.

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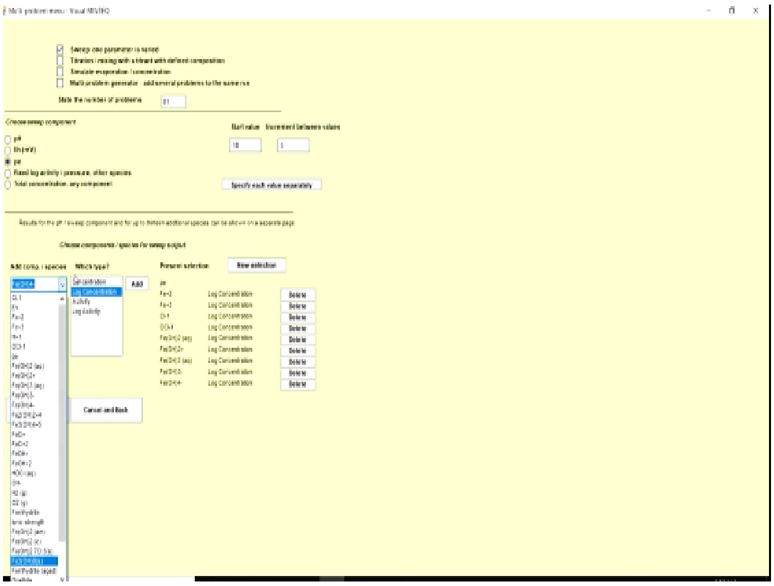

And for that obviously Visual MINTEQ has this particular option as we are aware of the sweep option I guess where one parameter is varied and here I am going to vary the P I guess. So let say I am going to go from -10 at 30 p let say so 4 per each 4*20 is 80 and 1 is 81. So I am going to have say number of problems is 81 start value is -10 increment (()) (07:52)-what we say 0.5 okay till 30 so it its two times that is still 81.

And now I guess I am going to have to say what do we say species am I going to look for so obviously Fe2+ and log concentration and why do we choose log concentration obviously because values are going to be relatively less. So if I take the log does not make value it makes for easier understanding of the system I guess. So I am going to have Fe2+ and Fe3+ and also obviously Cl- and OCL- and what else.

And now let say instead of all these are possible specifies, but let us not try to list all these species but let us look at some of the complexes that I know we usually form I guess. So let say with respect to this particular complex and Fe Oh thrice that is respect Fe2+ I am not going to go there so I am going to have this or let me just add the complex. So either Fe2+ or 3+ and I think if you are (()) (09:06) to so let us go back and do that I am going to just add the various complexes and then try to understand the system.

And let say hopefully we have covered most of usually formed complex. So let me have a look here. I still have a couple of complexes out here that I guess we have not included. So now we are going to run the system and then obviously explore these two excel and then understand let say which specifies are predominant at which particular p obviously at a particular ph value.

So obviously I am going to have save and back and hopefully everything is in order and learn this e-4 that is because of the Redox couple that we have specified I guess that is fine ph is 7 so I am going to run MINTEQ and I am going to look at selected sweep results. So from p of -10 to 30 what is what we were looking for, but obviously you know looking at the tabular information and form of a table we know it is difficult to understand what is happening out there.

So obviously need to you know printing that data to excel.

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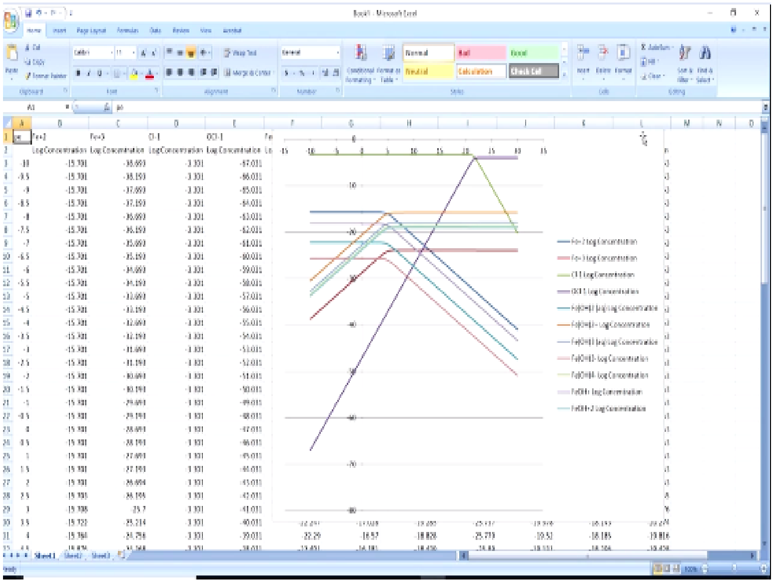

And here we have the relevant columns here Pe and the various what do we say species. So for efficient time management I already have a graph so let us to understand this particular data here. So here keep in mind that the ph is fixed at 7 and then here we have on the y axis log c log of the various concentration, concentration of the various two Redox couple and the complex is based on what our background is I guess.

Some of the complex not all the complexes because if we had all the complexes what do we see the graph would have been too garble I guess and would have been difficult to understand or saturate. So here let us try to understand the system. So here you have Pe here p on the x axis and log c on the y axis. So first let us try to understand the system with respect to Cl- and OCL-.

So obviously as expected here let see the p0 value is somewhere out here 22 for that particular couple. So here mostly it is in the reduced form when the Pe < Pe0. We expect the reduced form to predominate and that is what you see here Cl- until from -10 to pe value of around 21 or 22 and then let say when p is > p0 and that is when obviously you see that when the Ocl- concentration which gradually keeps increasing is the one that is predominant.

And the Cl- concentration which is reduced species decreases. So again pe <p0 cl- so the reduced species predominates and pe> pe0 you see that it is Ocl- predominate again that something that we have understood from our particular background in the relevant aspects with respect to Redox. So at the same time obviously we need to look at the relevant what do we see so here we have let say Cl- so something that needs to what we say something needs to oxidize it to Ocl- in the real world.

It is not going to go through by itself again because you need a (()) (12:56) here we are having a reduced form (()) (12:59). So we obviously need to look at the Fe2+ and Fe3+ concentration. So let us try to understand where this Fe2+ concentration is so I believe this is the Fe2+ concentration hopefully and the red one here which is Fe3+ concentration. Again here we see that Fe 3 concentration that remarkably low levels.

But Fe OH twice + concentration which is complex is the predominant form of the Fe3+ again that something that we are aware of especially with respect to the metals and thus you see that the free metal concentration especially for Fe3+ is relatively lower and you see that the complex that predominating here is the Fe OH twice +1 charge I guess and that is what you see here.

And hopefully this is the F2+ this is the one looks like Fe2+ but here let say if I want to have complete understand of the system obviously I can add all the other species that I have not included in this particular graph. I can include all the particular possible species and try to have detail analysis now. So that will obviously help and I am digging deeper for a particular scenario as such.

But let see if I am trying to look for let say overview of the system. I am about to get something done, I want to know what the system is, how the system is going to behave at equilibrium at different conditions now. In this case such level of detail what do we say graphics are obviously difficult to understand or disseminate I guess. So thus we can look at what are called the predominant area diagrams which we looked at briefly with respect to our precipitation and dissolution and even our asset based reaction.

Predominance area diagram as in we are going to identify let say in those regions let say for particular compound is predominant we are going to identify only that particular compound. So that will give us a snapshot of what we are going to look at. So obviously if we are going to dig deeper and you want to have all the relevant species Visual MINTEQ and log cph graph obviously at particular ph or such is going to be remarkably worthwhile.

But for snapshot which it is summary of the scenario it would be better to look at the predominance area diagram.

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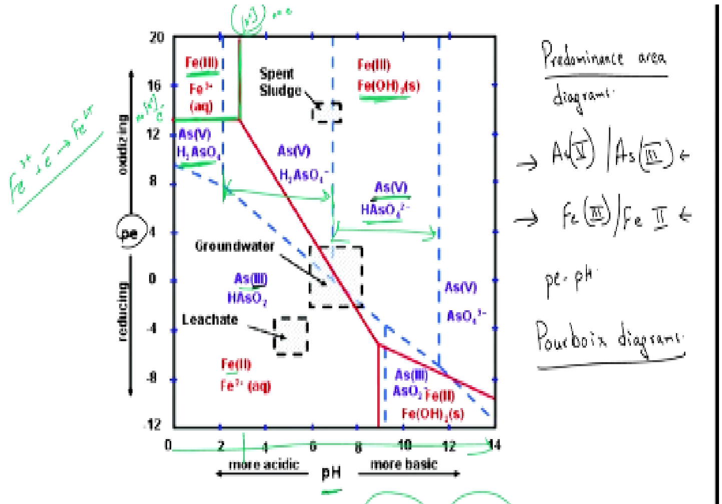

Superimposed predominance or pe-pH diagram of major As(III)/As(V) and Fe(II)/Fe(III) species.

Sudipta Sarkar; Lee M. Blaney; Anirban Gupta; Debabrata Ghosh; Arup K. SenGupta; *Environ. Sci. Technol.* **2008**, 42, 4268-4273.

And here we are going to look at particular predominance area diagram and before we go further I need to highlight that these predominance area diagram. So we have them here for the arsenic and oscillation stage V the two couples are arsenic and oxidation stage III and again with respect to Fe3 and Fe2 and we have the predominance area diagrams for these two couples and here we have pe on the y axis and ph on the x axis.

So in general obviously the greater the p the greater the oxidizing conditions the lower the Pe the greater the reducing conditions and obviously ph is more basic and the higher the ph more basic lower the ph more acidic. Again for this a diagram I guess I picked one from a publication of my colleague Doctor Sarkar I wanted to look for one particular example let say that would (()) (16:52) or have some practical relevance.

So he was looking into some relevant aspects which obviously we are going to look at so I guess I am thankful to him. So here we are going to look at predominance area diagram and we have the two couples identified and then we are going to try to understand the system in terms of what we see out there in the nature and why it is relevant I guess. At the same time we are now hopefully going to bring into play.

All the relevant aspects we have discussed that is as far. So these predominance area diagrams at least Pe Ph diagrams I guess are also called pourboix. So again a good way to understand what do we say summary or get an overview of the scenario right, but obviously if we are going to look at detail you need to look at the relevant what do you see log cph graphs log cp graphs or such so let us try to understand the system here.

So here on the x axis ph y axis we have pe. And now here keep in mind that we overlaid two particular ph diagram what are they of arsenic III and V and also for the Fe2 and Fe3 couple. So two couple and here let say the red one obviously corresponds to the Fe3 and Fe2 couples and the blue one corresponds to the arsenic form I guess. So let us first try to understand the system I guess.

So when we look at these vertical lines what is that tell us again I guess ph right. So if you remember the way we came up with these predominant area diagram try to look at the threshold or those regions when both would be let say two species what do we say occurring let say or same concentration and try to plot both lines and then to either side of them we will have either of those species predominant.

So that is how we went about our predominance area diagram asset base or the precipitation of dissolution reactions. Again the principle is same so here the additional what do we say information you also have the information you also have the equation for the Pe=P0-1/n log of the reduced by the oxidized species and so on and so forth. So in the same way you can get that done. So again that is not what we are up to here we are only going to try to understand the system now.

So in general this solid line means there is only a change with solid vertical line or vertical line means again with respect to just the Ph so only a change with respect to h +. So similarly let us say a horizontal line let say we have horizontal line here there is one right here means change with respect to electrons here, but no hedge + are involved here in that particular transformation as in with respect to the equilibrium between Fe3+n.

We know the equation is just Fe3+ electron goes to Fe2+. So obviously no hedge+ involve here that is why you see a horizontal what do we say horizontal line and obviously here again I guess it is between Fe 3+ and Fe OS thrice and it is just again h+ involve no electron. So that is why in vertical in general would correspond to let us say the involvement of h+ and no electrons I guess.

So in such I guess you can understand the relevant aspects involved. So first let us try to understand the system with respect to the ph I guess. So obviously at acidic conditions you know that Fe3+ or the free metal will be predominant but it should be remarkably what we see acidic conditions and in most of the greater range of the ph as you can see as you can see here from as I move from what do we say ph0 to 14.

So from Ph3 to 14 it is the solid if you are thrice that is predominant and not the free metal anymore and maybe a few complex that too and again if we look at it with respect to arsenic here and what do we see here. Here it is H3AS04 and in this zone between here and here you see it is H2AS04- and between the ph of 7 and approximately 12 it is HAS04 2-and from around 12 or 11.8 to 14 it HASO043-

So again this is nothing but the appreciation with respect to the disassociation of the proton I guess so H3AS04 or so if the Pk was around I am assuming it is around 2.2 or something like that. So it obviously deprotonates and when the ph is greater than pk which is the pk line corresponding to this obviously and in this region you end up having the deprotonate form H2ASO4.

So pka2 I guess is around 7 and thus when the ph> pK2 you will again see the other deprotonate form HASO4 2- when ph is> pk3 you see that the most deprotonate form predominates.

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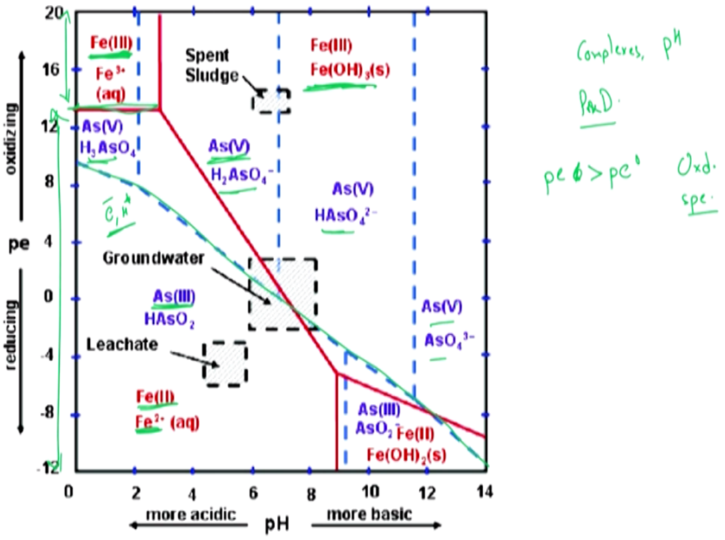

So let me just look at again figure here. So here again we have some background with respect to acid based relevant chemical process and here we have some with respect to Fe3, we have some background related to our complexes which are obviously ph dependent and precipitation and dissolution. So now let us try to understand system with respect to the vertical axis or the y axis. So let us say let us look at it here respectively.

So obviously Fe3+ when pe is what do we say > p0 and I guess looks like p0 is somewhere out here when pe is> p0 we know that the oxidize species typically predominate. So in this region you see that the oxidize species or Fe3+ predominate are in this region you see that the reduced form of the Fe2+ predominates. So that is what you see out here but obviously as you shift the ph it is not the equilibrium between Fe3+ or Fe2+ but the equilibrium between Fe3+ Fe2+ so that is what you see here as you shift the ph.

But for a broader what do we say range of pe and ph value you see the equilibrium is between Fe OS thrice and Fe2+ but only at very low ph and high p value would you have any Fe3+ and again same case here, but with respect to arsenic let us understand the system. Here we have a particular threshold I guess so obviously a slope line what does that mean now? It means that the equation has both the electrons and H+ electron transfer and H+ involved in the particular reaction unlike just the vertical or the horizontal lines.

So here let us say this is the line that gives us the boundary let say the arsenic 3 and arsenic 5 forms. So here in this region we have arsenic in 3+ oxidation stage predominant and above it obviously is arsenic in 5+ oxidation stage predominant and obviously again as you vary the ph you see that H3AS04 H2ASO4 and so on. So with respect to one particular example we did at this particular aspect as in if you want to remove arsenic by an exchange process. So what form would you want to predominate here.

As you see here in most of the ph if it is reduced form as (()) (24:56) HASO2 would be neutral. It has no charge. So will that be suitable for removal by exchange, but let us say if I consider the more oxidize form let us say arsenic in oxidation stage 5 I see that even at ph from 2.2 or something like that it has a charge and at neutral ph it is either HASO4 – HASO42-. So the component has charge on it.

So obviously if it starts at neutral ph it is relatively obviously amenable to be removed by the ion exchange process and this is one example we have looked at, but this gives us an understanding of it. So again we have taken considerable time in understanding the relevant aspects. So now let us try to see the practical relevance I guess.

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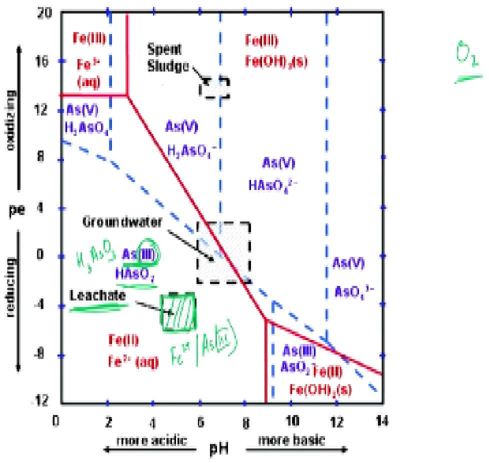

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So here we have let say regions that is supposed to confirm to the ground water now. So I guess here the ph is we are saying it is going to be between 6 and 8 and the p values for ground water typically I guess. So in this region let us try to understand which forms of either arsenic or what do we say the iron are going to predominate now. Here as you see let say here let say in this region which form predominates now arsenic let say an oxidation stage 5 mostly HAS04 2- iron which form predominates its Fe OH thrice.

So what does this, how does this what do we say effect the system now. So as you know let say a solid is formed FE3+ precipitates at this particular range of p and ph what do we say also allows for co-precipitation of this arsenic phi makes sense hopefully. If the pe, ph ranges within this particular area let say we know that ferric iron is going to precipitate and similar to what we had looked at with respect to our coagulation and flocculation one of the aspects we looked at was co-precipitation as you have these particular what do we say few or twice solid particles.

Upon which you can have upon which you have absorption of thus co precipitation of various other components. Thus let see whenever in this particular region I guess the arsenic will be removed by co precipitation on this ferric hydroxide, but obviously it is in this particular range though what is going to happen we see that in arsenic three form and also that its iron in Fe2+ form so it is relatively more mobile.

And as in here it has no charge arsenic has no charge and Fe2+ as we know mostly stays as Fe2+. So here let us say if this particular ground water conditions fall within this zone of pe and ph we see that arsenic three form is going to predominate and also Fe2+ and arsenic three is going to stay in solution. Unlike the other case when we had F2 OS as thrice and arsenic five.

We saw that co-precipitation is going to occur so the arsenic concentration in the water is going to be less or negligible obviously depending upon the amount of precipitate that is available or being formed. So again that particular understanding with respect to estimating let say the concentration or arsenic carcinogen toxic compound and saturate in your particular system.

So now let us see one other aspect is let say in your leachate from your minds let us see. And here looks like the relevant pe and ph range is within this particular area now. So what do you see here now. In this particular pe and ph range which corresponds to leachate let say from your minds you see that arsenic stays as As3 in its oxidation form of 3+ . It can also stay as

H3AS or 32 not just HAS02 but both the oxidation states are arsenic are still 3+.

So here though you see that it is Fe2 and arsenic in its three form. So what does this mean now arsenic again as we have seen in our case with respect to our ground water arsenic concentration is going to be present in if any arsenic is present arsenic is going to be present in the ground water or the water itself. It is going to be dissolved and thus it can transport over a greater distance or let say or the (()) (39:47) can travel greater distances.

Depending again on the pe and ph conditions leading to contamination of wider area so that is one particular aspect, but let say if you are particular leachate or such has been in equilibrium with the atmosphere as in with respect to oxygen. So then obviously your pe value will be relatively higher so that is why let say for the spent sludge the ph range is somewhere out here.

So again for the spent sludge we are trying to understand it what form or what are the issues let say for arsenic is present in water and pe and ph ranges and we then if it is leachate which we usually see in acid mind drainage e let say and it is in spent fludge let say which is in equilibrium with our atmosphere what would be the case let see. So if it is spent sludge it is going to be in equilibrium with your atmosphere or with oxygen.

So obviously more oxidation conditions prevail that is why you see that the pe and ph range is somewhere out here and obviously what do we see here right now at this particular range of pe and ph we see that arsenic predominates and at the same time you have what do you ferric hydroxide precipitating. So again you are going to have co precipitation of arsenic on this ferric hydroxide rate.

And thus removal of arsenic from your sludge or at least from the water here. So thus if I just filter out the relevant if I use right filtration techniques I can remove what do we say ferric hydroxide and rather co precipitates of arsenic on this particular ferric hydroxide and thus what do we say relatively treated water. So again this hopefully gives you an understanding about which species predominates at which particular Pe or Ph and why they are relevant.

So here that is one particular case where this example is relatively worthwhile as it in ground water which species would predominate and if it is in the oxidized form or let say oxidizing conditions prevail. We saw that arsenic can be removed from ground water because it can precipitate out along with Fe OS 0thrice. So again hopefully this particular example give you snapshot or overview of all the process involved as in we have looked at complications, we have looked at acid based chemical process and Redox process so on and more importantly tried that up to what it is that we expect out there in the nature.

So again I guess with that I am going to end up chemical process related course. So this hopefully was intellectually challenging for most of you guys out there. And hopefully what do we say enjoy the homework too I guess and thank you for your time and again I guess I thank you my advisor Dr. (()) (32:24) from whom I have learnt all these relevant aspects and again thank you all for taking this course.