Environmental Remediation of Contaminated Sites Prof. Bhanu Prakash Vellanki Department of Civil Engineering Indian Institute of Technology- Roorkee

Lecture – 16 Remediation of Contaminated GW Permeable Reactive Barriers

Hello everyone, so again welcome back to latest lecture session a quick recap of what we have been up to. We have been discussing how to remediate contaminated ground water we looked at containment pump and treat and very briefly discussed source controlled right and look at the relevant aspects there and then we very briefly touched upon the do a relevant option called permeable reactive barriers right. So let us dig further.

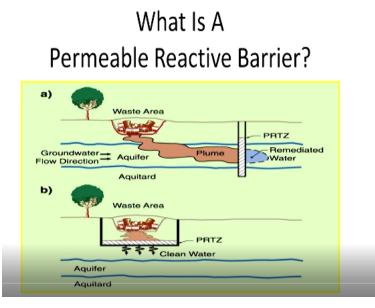
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So what do we have here we have permeable reactive barriers? The key is that the we term them barriers they are permeable and reactive right and the context that you want to you know see to it or facilitate the relevant ground water to flow through this particular barrier that you are going to construct subsurface or being the surface right and you are going to have reactive media or the relevant reactive media and that particular barrier right.

So that you will have the removal or degradation of the relevant contaminant. So let us look at the relevant aspects here.

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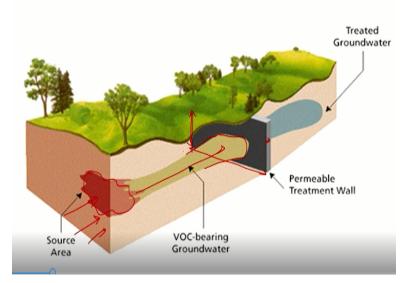
So again to make it clear or to help you visualize it let us see here we have a side view so do you have the containment of waste let us say you do not think of this as a landfill let us say and let us say the liner or the collegiate costumed system failed and now you have the leachate you know coming through and then permeable through and reaching the ground water and then being transported over a considerable areas let us say considerable extent now let us see.

Now what is the PRB here where is the PRB here. Here I am going to have the PRB here this is obviously the side view right and as the groundwater flows through this particular barrier or reactive media you are going to have the relevant reactions out here and the water coming out is going to be the treated water here right. So again this is your PRB out here so the key aspects of that we are going to have what do we see it constructed subsurface.

Obviously and perpendicular to the groundwater flow right and again the relative and porosity of the relevant barrier is going to be real to less than the relevant surrounding media. Why is that obviously you want the water to flow through the barrier and obviously if you have the porosity greater than the relevant porosity of the media and the water is going to take the path of least resistance and flow around the barrier right.

So again this is the relevant aspect so obviously there are many technical aspects relevant here. We will look at those aspects later but let us look at some of the general piece of information here right. So one way obviously here to is to treat the groundwater and the other way is let us say if you identify the spill relatively early you know you can have this kind of a mechanism to treat the relevant leakage that you know coming through or the spill that is you know permeating through before it reaches the ground water right.

Again just two different cases, so again what do you say different what do we say view here. (Refer Slide Time: 03:18)



So here is my contaminated a what do we say zone and how ground water flowing through right and obviously here and now as you can see here the thickness this is the thickness of the relevant PRB but aspects to be considered carefully are the length and the width or the height of the relevant PRB right. Because if you do not estimate your contaminated plume accurately as in this is my contaminant plume let us say right accurately.

And if I do not obviously you know place or you know a calculator relevant length and height of the PRB I am obviously going to miss the plume let us say and the plume can flow around relevant PRB so these are aspects that need to be considered again we will look at those in greater detail later on right. Again at relevant reactions occurring within this particular PRB and then you have the treated a contaminant coming out of the PRB right.

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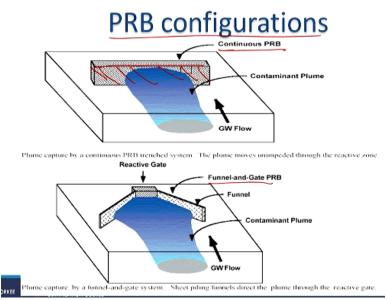
And here typically obviously I did mention that you know PRB is widely used as you can see here we have we are looking at fuel installations either for full scale or pilot scale for volatile organic carbon right typically in industrialized nations let us say or industrial areas you have contamination of the soil and groundwater by volatile organic carbon right or volatile organic compounds right and they are typically toxic let us say hydrophobic right.

And the key here is that they are hydrophobic right so as you know pump and treat not really a good way to what do we say address ground water contaminated with the hydrophobic compounds right. So in that context obviously the PRBs are going to be remarkably worthwhile or you know are going to facilitate the remediation greatly. Let us look at why later on as you can see typically the east coast of US relatively more industrialized.

And you see many installations there and again western coast California and such again it will take European union are such typically this is the picture you see that you know there are many PRBs installed out there again as I mentioned in the Indian context not many are to my knowledge none like us right. But again that is because of lack of transfer of knowledge and maybe the complex complexities inherit in the Indian context.

Or the type of soil in the Indian context I guess right. So again obviously if we know what are the options you can obviously choose whether the relevant option is worthwhile or suitable to you or not right so again we will move on.

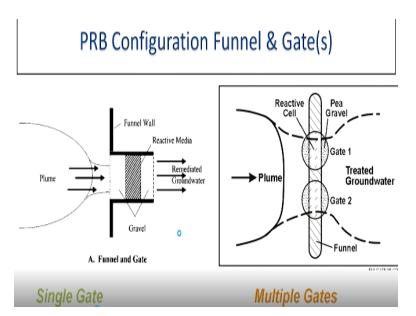




So here there are two types of PRB configurations so one is the continuous one is the funnel and gate. Continuous as in I have the reactive media throughout the relevant PRB and the width of this particular PRB is greater than the width of this particular contaminated plume right. So continuous PRB now so final gate obviously as the name indicates and as you can see here you have only a part of this particular system to contain the containing the reactive media.

And then you have impermeable let us say gates if I can call them right that would channel the groundwater towards this particular reactive and permeable zone right. So two cases what is it now the continuous PRB and the funnel and gate system but typically where the funnel and gate though you obviously need to be able to very accurately estimate the plume shape and size right. So typically I believe most people try to go for the continuous PRB right.

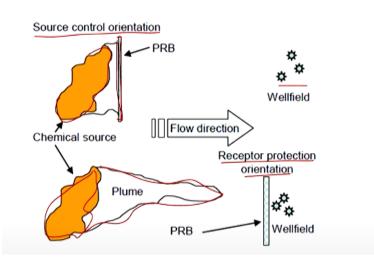
So as an even if there is a change in the shape of the particular contaminant plume you know this particular continuous PRB can address the relevant issues right. **(Refer Slide Time: 06:51)**



So here again I have the top view with respect to funnel and gate right. So plume coming in let us see and then being channelled towards my particular reactive media and then I have the remediated groundwater after the relevant reactions within my particular reactive media right and also obviously here we have what we see multiple gates let us see. I have multiple gates or multiple zones yes again depending upon the site conditions.

Let us see you can have multiple sites particular cases so again even within funnel and gate keeping in mind that we can have different gates out here yes.

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PRB receptor protection configurations

So the PRB again installation where do I install the PRB now right so obviously two aspects need to be concerned if I know the shape of the relevant plume and its distribution pretty accurately or am relatively more confident based upon my monitoring network out there I can try to address the issue at the source right. I can try to address the issue at the source by installing the PRB so that it catches the contaminated groundwater plume right.

But let us say that is not the case and maybe there are the extent is too huge let us say the extent of the contaminant is too huge and what do I do in that case the let us see. Then I can install the PRB near the receptor locations as in let us say I have a village out there and the I know the locations from where they are let us say drawing the water or withdrawing the water. So I can try to look at you know the particular location.

Where let us say the installation of PRB would you know see to it that only the treated groundwater would reach the relevant extraction locations for that particular village right. So here again as we talked about one aspect with respect to source control orientation so you have the plume here and the PRB tries to capture that particular source and the well field is out here. But let us say the second aspect is the receptive production orientation.

I have the contaminated source here how the plume here right but here the key aspect is that I am trying to protect the relevant what do we say withdrawal sources let us say for the relevant receptor right so two aspects moving on.

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Again different kinds and different ways of what we say constructing PRBs typically constructing the PRB is what we say maybe in the Indian context the challenge because I guess we have not or we do not have much experience. But it should not be a complex because however what do we say construction or the relevant what do we say companies are remarkably competent I would say in various fields and those should not be an issue.

But again keep in mind we have different kinds let us say powdered I think here we have fine grained and in b coarse grained is being laid in a trench to this is the trench. I believe continuous PRB and they are placing the coarse grained zero valent iron. ZVI is the zero valent iron that is being placed here in this continuous trench here right and third one is microscale zero valent iron a slurry this is a slurry that is going to be injected here right and again installation different methods of installation here right.

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Application

- Unclear location of source (s)
- Slow contaminant release from the source
- - Tailing and Rebound
- + Large volumes of contaminated soil \leftarrow
- Built up areas

Application I guess in which particular cases or context would this be more applicable now right so think of this now the key aspects are that its subsurface let us say and there is no active maintenance or such required right other than monitoring the plume before and after. So the key aspect obviously is that here you are you can treat the volatile organic carbons let us say they are those hydrophobic compounds or NAPL which you cannot buy a pump and treat.

Let us say right again there are different applications for PRB depending upon your site conditions. But obviously one particular aspect that comes to mind is because is the NAPL or the VOCs because we just looked at or discussed those aspects in the previous couple of sessions right. So obviously what was the case earlier so you had the relevant compound adsorbed onto the soil right absorbed onto the soil are present as NAPL.

So even though you treated pumped out the ground water and treated that groundwater you again have released out the containment from the soil or from the NAPL into the groundwater again contamination right. So obviously this active mechanism of trying to pump the water out and treat it you know was failing in that context. We looked at the relevant numbers too so here this particular case PRB obviously passive technique.

So have the PRB in place say as and when the relevant contaminant from the relevant soil or the NAPL is released into the groundwater and groundwater comes in contact with the PRB is going

to be treated right. So that is one particular case obviously we are at a you know greatly applicable so let us look at some of the other aspects here. So when my location is not clear let us say or the location of the source pardon me is not clear.

That is one particular aspect and obviously slow contaminant released from the source right and thus again leads to tailing and rebound. Different cases stratification, NAPL, adsorption so on and so forth and then let us say the contaminant is again relatively less soluble right. Again for hydrophobic compounds let us say solubility is relatively less but high enough such that it is above the regulatory standards right.

So in that context what do you I have I am going to have or end up absorbing this tailing and rebound right and obviously of the contaminated soil is volume of contaminate soil is way too high and its not feasible to have either exit or in treatment of the relevant soil let us say. What can I go for I can have this passive technique as in I place these PRB set strategic locations capture the plume and then you know let the what do we say PRB do its job now right?

So and moving on and this is an aspect that is remarkably relevant in the Indian context. So let us say I think we looked at a case of Ghaziabad let us say where obviously they were looking at pump and treat and also by putting in engineered microbes I believe let us say if not engineered microbes non-native species into that particular case or remediated site to reduce chromium from 6 to 3 and so on and remediate the site.

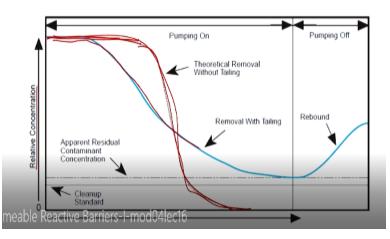
So again the key aspect there is now they had to occupy a whole part let us say whole as in I guess a huge park right and that particular location which Ghaziabad again keep in mind the land area again the costs are remarkably high let us say. Population density is high and again keep in mind also the relevant park is being deprived of its natural or you know the people are deprived of usage of that particular park right.

So here at least in the Indian context where you have built up areas let us say and land is a precious source or resource pardon me you know having PRBs is let us say it is going to be remarkably worthwhile or you know an option that certainly should be considerable let us say.

Why is that you know as you see a subsurface the footprint let us see is going to be remarkably less.

You just need a couple of monitoring wells let us say at this strategic locations right but obviously you need to be able to understand the relevant plume size and distribution accurately right. So again these are the aspects again we did look at this particular case earlier tiling and rebound.

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Tailing and Rebound

As we know theoretical case would be this as an if its only in the dissolved phase I will be done with removing the contaminant when I pump out that contaminant plume. So that is why I see that the concentration of the what do we say compound that is being pumped out relatively constant and once all the plume is let us say pumped out the sharp fall and then you know what would you expect nothing out there.

But for slow contaminant release hydrophobic compounds, NAPL desorption or absorption on the soil and so on you will have Tailing again what does that do increase the time required and also rebound which makes it impractical for most pump and treat options right. In this case obviously the PRBs are pretty good option now right.

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Advantages Of Permeable

Built up area

- Barriers
 Treatment occurs in the subsurface ←
- No above ground structures or routine day-to-day labor attention required
- Allows full economic use of a property
- Typical treatment in(passive) ←
- Potentially lower operation and maintenance costs
- Monitoring can be focused

So moving on so what are the advantages of PRBs right. Soo let us look at some of these aspects so treatment occurred subsurface that is something s we looked at because you know let us say if you have considerable built up area right and if the land costs are relatively high again that is going to be remarkably worthwhile in that context treatment occurs in sub surface again operation and maintenance costs are relatively low or remarkably low.

Because the passive techniques and again no above ground structures are required and no labour costs or such right and then again most of these aspects related to what we say the use of that particular built up area now right. Full economic use of a property and again as I mentioned earlier the treatment is passive right again coming back to the lower passive more or less relates to lower operation and maintenance costs yes.

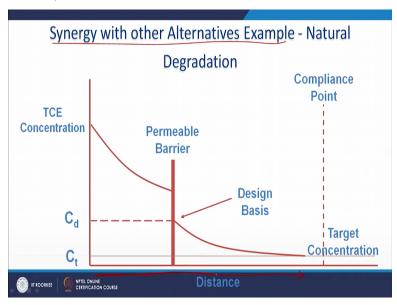
And the key here is that unlike other particular techniques let us see pump and treat containment or size right you need to obviously monitor the relevant plume right. But in this context let us say of permeable reactive barriers you will need to only look at let us say a few areas that need to be or few locations that need to be monitored for pump and treat let us say you need to have a wider monitoring network let us say.

Right or for national attenuation let us see or so you will need to have a wider monitoring network but for PRB let us say I need to have what do we say typically what we say the

monitoring wells or locations before and after the PRB and let us say inside the PRB and beside the PRB right beside because I want to see if the plume is escaping the PRB before and after to look at the performance inside too obviously for the same reason right.

So here again the costs are going to be relatively less yes.

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So moving on the key aspect is that as I mentioned earlier you know it can be used in conjunction with other alternatives now right. So here let us see we have a particular graph here so here we have the plume traveling with distance here let us see this is distance on the x axis and the y axis. So I have this trichloroethylene let us see here right TCE here at this particular concentration.

Obviously, you know it is going to decrease because of adviction and diffusion you are going to have dilution of the relevant compound and so if I take the sample along the centre line I am going to see a decrease and also natural attenuation as in if the microbes have the relevant electron donor here or I think yeah its a donor here right. You know that should serve the purpose right.

Again you will see some decrease maybe but not at the rate that you want to and here is the target concentration and maybe here you have let us say the source of different wells. So that is

why I have that as compliance point. So from here let us say your village withdraws water and so by here or by this location I need to go beyond this or below this particular standard or regulatory limit let us say right.

So what can I do let us see I know that natural attenuation does take place but it is not fast enough to be able to meet the relevant standards? So what can I do I can design the PRB here let us see right and at particular distance and that of as the ground water comes in and it moves out it is going to be decreased to a particular value depending obviously upon your thickness? So here again we have the PRB.

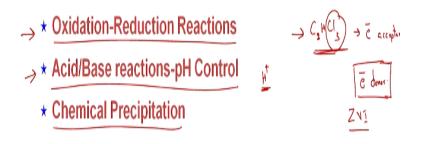
And that is going to you know let us say act in conjunction with natural degradation or natural attenuation right. So typically you have what do we say the microbes is doing their job you know as they do out there in nature they you know obviously look for sources of what do we say energy in terms of electron acceptors and donors right again that is something we are going to discuss later.

But let us say that is not good enough to do the job let us say what can I do I can augment this particular natural attenuation by you know putting in a PRB. So as you see here you know the influent water at this particular point or in this distance is it relatively high concentration after the PRB again it comes down to the relevant design value let us see. And how do I come up with this design basis.

Estimating that you know natural attenuation let us say takes place at a considerable right not considerable at a certain rate. I can you know try to look at the design value which would allow the microbes to do their own job and by the time pardon me by the time not say the distance let us see after traveling a certain distance and the plume reaches the relevant receptor you know the relevant concentration is below the relevant standards right. So again that is something we can look at.

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Treatment Mechanisms



And again what are the treatment mechanisms right is it only redox process or it is only sorption or in which case is this applicable and so on and so forth. Let us look at that obviously one widely used treatment mechanism is the redox process oxidation and reduction so what are these oxidation and reduction what do we say reactions about now right. Well they are discussed I am sure widely right.

But a quick recap should you know have those people who have relatively less background in this regard let us see. Redox reactions typically deal with what is it the transfer of electrons right so typically I think we looked at thus C2HCL3 I think TCE right trichloroethylene right so as you see here this is an oxidized compound right I mean you can try to look at or try to calculate the oxidised state of carbon here

But again as I know that we have CL here let us say and typically from that we can understand that this is an oxidized component and typically the presence of this CL imparts the toxicity to your particular compound here. So what do I want to do I want to remove that CL now how is that going to happen or again through what do we say reducing this particular compound? As in this is an oxidized compound so I need to reduce it.

Or I need to provide a source of electrons right so this compound is an electron acceptor right. So I need to provide an electron donor once I provide that let us see and if this is my contaminant in

the groundwater and I provide an electron donor typically let us say as we saw earlier zero valent iron widely used right. Zero valent iron is a reducing agent it provides the relevant electrons right we are going to again look at these aspects later on.

So I need to provide an electron donor right. So again why is that required obviously because this compound is an electron accepted TCE and I once I provide the relevant electron donor perhaps reaction is going to take place and you are going to have reductive dichlorination of relevant compound and thus let us say you know the toxicity is going to decrease depending upon the pathway anyway right.

So what are the other aspects again so acid base reactions again typically use for pH control let us see you have acid mine drainage and there let us say the relevant pH an issue let us say right again you have can have the subsurface systems there are again other treatment techniques for acid mine drainage but you can help pH control by PRB. So depending upon let us see if you want to have increased the higher what is increase the pH or load the pH.

But typically in acid mine drainage you typically want to increase the pH you can have the relevant media to be what do we say a limestone or such right. So again we will move on chemical precipitation so here let us see I am treating the component or degrading the compound typical in redox process and it can also lead to precipitation of the relevant degraded product or by-product.

Acid based reactions exchange of H+ or typically H+ is involved here right and chemical precipitation right. So again in the case of Ghaziabad 2 what did we look at let us see the example that we have been referring to considerably. So they were trying to change the oxidation state from chromium 6 to chromium 3 right chromium 6 remarkably toxic chromium 3 slightly toxic or relatively less toxic.

But the key aspect is chromium 3 is insoluble right. So insoluble in the sense that the concentrations the equilibrium concentrations or the solubility gives you an idea about the maximum concentration at equilibrium let us say the solution can have let us say. So if the

solution or the compound is relatively insoluble what does that mean the compound would what do we say precipitate out right.

So again you can have reactive barrier media pardon me that would help facilitate this particular chemical precipitation of the containment right and then adsorption reactions as in you can have compound let us see that can act as a site for a what do we say at this particular contaminant to be absorbed onto right. So typically a these are the four major chemical or physio chemical process.

And then you can also have media that would promote let us say the biological process yes you want to attenuate let us see or you know try to increase the effectiveness of the biological process for that again you can probably grant to an accept or donor again right.

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Oxidation-Reduction Reactions

$$\begin{split} 3Fe^{0} &\rightarrow 3Fe^{2+} + 6e^{-} \\ C_{2}HCI_{3} + 3H^{+} + 6e^{-} \rightarrow C_{2}H_{4} + 3CI^{-} \\ 3Fe^{0} + C_{2}HCI_{3} + 3H^{+} \rightarrow C_{2}H_{4} + 3Fe^{2+} + 3CI^{-} \\ \bullet \text{ Reductive precipitation of hexavalent chromium} \\ &\rightarrow CrO_{4}^{2-} + Fe^{0} + 8H^{+} \rightarrow Fe^{3+} + Cr^{3+} + 4H_{2}O \\ &\rightleftharpoons (x)Cr^{3+} + (1-x)Fe^{3+} + 2H_{2}O \rightarrow Cr_{x}Fe_{(1-x)}OOH_{(s)} + 3H^{+} \leftarrow \end{split}$$

So we are going to discuss oxidation reduction reactions in relatively greater detail and typically we come across you know the zero valent iron in the context of PRBs now right. Most of the relevant compounds typically let us say the organic solvent let us say or the water organic compounds are typically oxidized and you want to reduce them. So in that context we place zero valent iron and typically what do we have the process involved are redox process right.

So let us look at what we have here so this is zero valent iron right zero valent iron and what can that transform into let us see so it can what do we see its an electron donor as I mentioned earlier or it is a reducing agent right it is a reducing agent electron donor. So it is donating the electrons and now you have Fe2+ here right for asylum. Or okay there is another case that I want to look at but we will come back to that later.

So these electrons that were released by are donated by Fe0 or the zero valent iron can then be accepted by this TCE right and you know also change in pH I guess and then you can have that relevant degradation to more simpler compounds C2H4. So here it is more oxidized and you are here as you can see it is reduced form right and here you see that the CL- is released and typically this particular compound is either can be further degraded.

Let us say if you want to or you can let the microbes do their own what to say do their job right. So again what do we have here we have an exchange of electrons so zero valent iron is electron donor and the relevant contaminent which is the TCE here is the electron acceptor and in that process it leads to degradation of the relevant compound here right and here let us see this is the what do we say these are the half reactions right.

And this is obviously the relevant reaction so obviously you see that the pH and H+ is going to be taken up so the pH will increase. So that again needs to be considered in that particular system obviously right so moving on so reductive precipitation of hexavalent chromium this is the example that I was referring to earlier. So I have CrO42- oxidation state is +6 here for chromium right. How do I calculate the oxidation state of chromium here?

So if I assume that the oxidation state of chromium is X+4 times oxidation state of oxygen typically -2=-2 and solve for x. I see that it is +6 here right. And here again I have zero valent iron right as I know there from here it is electron donor. So it is providing the relevant electrons right and then again in presence of you know it takes in H+ let us say it is oxidized or Fe0 is oxidise to Fe3+.

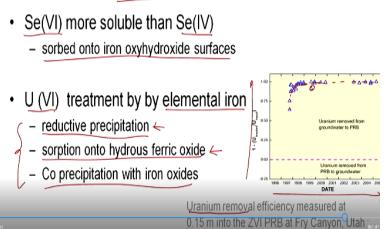
But CrO42- is reduced to Cr3+ how can I say it reduced. Earlier the oxidation state of chromium was +6 and here as I can see the oxidation it is +3 right so it has taken in 3 electrons let us say as you can see here right +6 to +3 and here as I know we mentioned earlier Cr3+ is again relatively to insoluble and you are going to have the relevant precipitation right. So again why is this particular background relevant.

Now because obviously only if you have an idea about let us say the relevant component and its relevant chemistry can you design the relevant reactive barrier let us say and also you also need to look at which media to obviously put in right. So these are the aspects we need to be aware of. And here I guess here I have the relevant equation here right Cr3+1-x F and so on the generic equation anyway right.

Again you have complex of iron and chromium being formed and again are the precipitate I guess right again different ways. So here is the reduction from Cc+6 or chromium +6 to +3 and here you see the precipitation I guess right. That is why we call it the reductive precipitation of hexavalent chromium yes okay.

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Reduction, sorption, and precipitation of redoxsensitive oxyanions



Moving on we looked at reduction and typically sorption and precipitation of redox sensitive oxyanions. Let us look at some of them so selenium 6 looks like is more soluble than selenium 4 so what do I want to do or promote surfaces say sorbed onto iron oxyhydroxide surfaces right

and uranium treatment by elemental iron let us see and what is the process again it is not clear but it looks like it is reductive precipitation.

And also let us say or could be sorption onto hydrous ferric oxide let us say you know when you iron and let us say you have what do we say it being oxidised let us say right. You are going to again have formation of the relevant oxides here right. You know you are going to have complexes are being formed or relevant what is it precipitate of that particular ferric or saturation right.

And again you are going to have now sites for adsorption of the relevant compounds and so here it can either be reductive precipitation of this particular uranium or sorption of uranium onto the hydrous ferric oxides or co -precipitation along with the iron oxides as I mentioned. As in this Fe2+ you know is oxidised o Fe3+ and as that precipitate that provides site for your particular contaminant to again precipitate upon or adsorb upon.

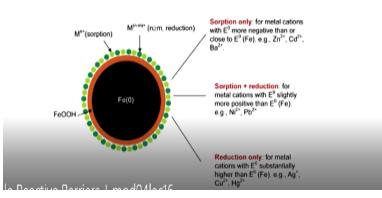
And that is typically referred to as co- precipitation right. So I believe I have one particular data set here we have time on the x axis and here we are looking at uranium removal and the key aspect is that its zero valent iron PRB was used in Utah I guess right and here we have on y axis the relevant concentration let us see. That is you know the higher the data here obviously as you can see from this particular metric the better.

So let us say they are measuring at 0.15 meters or 15 centimetres into the PRB. Typically the PRBs are not many meters thick let us say. Typically less than a meter thick yes and as you can see here the efficiency increased and then it held well for considerable period of time and again the relevant mechanisms could be any of these three mechanisms either reductive precipitation, sorption or co precipitation right.

Again this is from a what do we see a real life scenario in Utah I guess right okay and the next aspect.

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Conceptual model for metals removal from water using NZVI



So again we looked at sorption mechanisms let us look at you know tried to understand these aspects here. So three cases we are going or we are going to look at sorption only. Sorption and reduction and reduction only right. So again as I mentioned here iron let us say can act as a reducing agent iron as in zero valent iron can act as a reducing agent right either it can donate 2 electrons and be oxidized to Fe2+.

Or you know more further what do we say oxidation to Fe3+ and donate 1 for the electron right. Or it can also what do we say lead to reduction and sorption such that Fe3+ let us say an precipitate out or will precipitate out depending upon the concentrations and then that can act as a site for a co precipitation or absorption let us say. So that case we see sorption and reduction or depending upon let us say.

If the compound cannot be reduced by the relevant Fe2+ or zero valent iron it can just act as a site for adsorption. So let us look at some of these aspects obviously so here we have the E0 I guess we will look at this in greater detail in the next class because we are almost out of time all right. So here depending upon the E0 value let us say you can understand let us say you know well Fe2+

I mean zero valent iron while being transformed into Fe2+ and or Fe3+ be able to reduce the compound or not. We are going to look at some background about that in the next class. Again in

the same cases I have what do we say copper mercury and so on and so forth which can be reduced by iron right and so these are the different ways or mechanisms by which zero valent iron the most widely used reactive media for PRB let us say, can lead to removal or degradation of your relevant containment right.

So again what is it typically now redox process, redox and precipitation or adsorption right. So again we are going to continue this and you know looking at the relevant technical aspects in greater detail from the next session right and for today that is it for me and thank you.