Environmental Remediation of Contaminated Sites
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Lecture - 18
Permeable Reactive Barriers-III

Hello everyone. Again welcome back to the latest lecture session. Again a quick recap of what we have been up to. So in the context of groundwater remediation, we are discussing permeable reactive barriers and I guess we spent considerable time in understanding how to or what are the development aspects we need to look at, when we are looking at PRBs right and what are the different kinds of PRBs right.

And also what are the different types of reactive media that you choose. Obviously how would you choose reactive media depending up on the type of contaminant. So for example if it is hallow carbon or the chlorinated solvents or such let us say which are oxidized contaminants, you are going to choose, a reducing agent, let us say, a zero value item right and if it is let us say acid, you are going to have to provide a base to be able to neutralize that.

So if you have acid and the base you are looking for obviously limestone and similar such aspects we discussed them right and we moved on to also looking at let us say what are some of the cases when this PRB might not work or when the efficiency might be relatively less and we looked at let us say a particular graph right.

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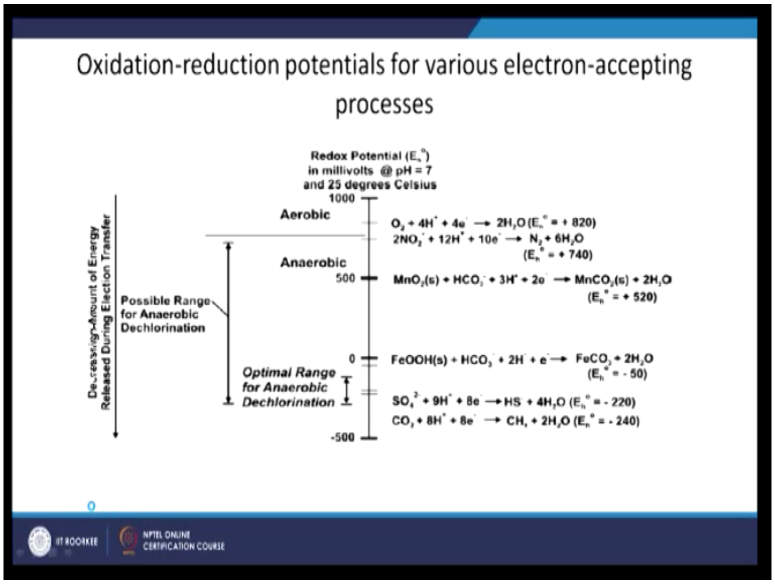

Oxidation-reduction potentials for various electron-accepting processes

Similar to this particular case, yes, we looked at this. So obviously as you see in the aerobic case, yes, the electron accepter preferable electron acceptor would be oxygen and not let us say any of the other compounds that you would have out here right and also we talked about the redox potential briefly right, as in if Eh not is greater than the Eh not or Eh not of 1, let us say is greater than Eh not of 2, let us say this 1 will stay as or will be the reduction.

And the other one will go as or proceed as oxidation as soon as you see the half reactions are written as reduction, yes. So when you say Eh1 is greater than Eh2 and for example let us look at 2 cases here. So this is 1 and this is 2 right. So I what do I see here, obviously I see that Eh not of this particular half reaction is greater than Eh not of this particular half reaction right. So in that case, this particular reaction would proceed as ease and this reaction would proceed in this particular direction yes.

So you get obviously different cases and such, yes and/or you know a better case would be an example would be this rather than this. Hydrogen sulfide, let us say yes and let us say oxygen. So you have let us say oxygen, water some SO4 2- and some HS-, right. So typically I should not look at the standard redox potential. So I need to calculate Eh1 and Eh2, right considering the actual concentrations of O2, SO4 2- and HS- then if Eh1 is greater than Eh2, what would happen?

Oxygen will be reduced by HS-. As in this reaction will proceed in this direction and this reaction will proceed in this direction. As in how is this going to help us let us say, it is going to help us in identifying which particular, what is a half reaction would proceed as oxidation which one would go as reduction as in what was that mean as in which compound will reduce which particular compound yes. So that is what you are going to be able to understand.

So in this context obviously we also looked at the other aspects. Let us say if I had zero- valent iron, and let us say I have both SO4 2- that I want to let us say, reduce to HS- and I also have water in the solution at the same time. Obviously you know the preferable electron accepted would be oxygen, again because greater energy would be released from that particular half reaction.

So obviously if the conditions are highly aerobic, feasibility of zero-valent iron based PRBs or reduction based PRVs are going to be an issue. So obviously you would want anaerobic conditions, right, where it is possible. So obviously we did not know where the Eh not or Eh values fall. So typically we have the relevant optimal range. So that is where somewhere way down out here though right.

So that is something that we can look at to understand the relevant system or look at the feasibility, yes and then obviously the redox reactions. So we looked at this briefly. So we are looking for strong reducing agents right. What is the reducing agent?

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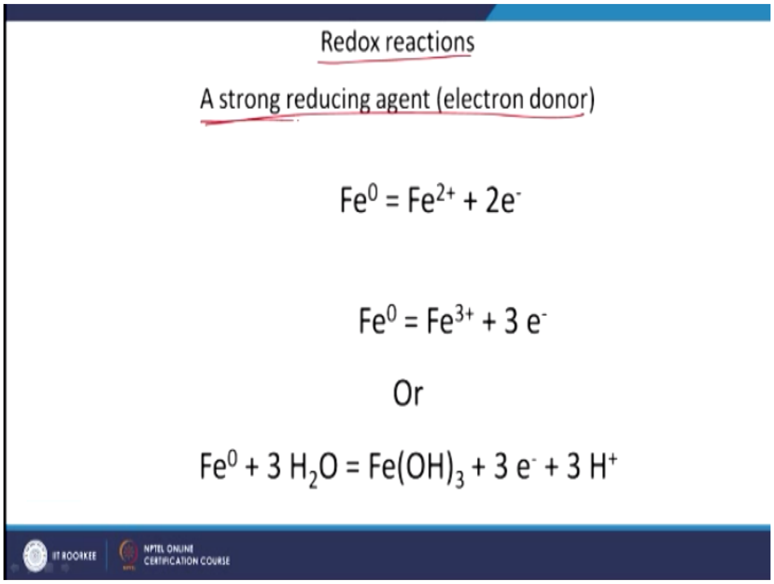

Redox reactions

A strong reducing agent (electron donor)

$$Fe^0 = Fe^{2+} + 2e^-$$

$$Fe^0 = Fe^{3+} + 3\ e^-$$

Or

$$Fe^0 + 3\ H_2O = Fe(OH)_3 + 3\ e^- + 3\ H^+$$

Something that will donate its or wants to donate its electron or an electron. So typically we look at zero-valent iron, right and that can what do we say be oxidized to Fe2+ by releasing 2 electrons or be oxidized to Fe3+ releasing 3 electrons right. So typically though we know that Fe3+ plus will not stay as Fe3+, it is going to precipitate out and that is the relevant reaction that we see here as in this solid that is going to be precipitated out right.

Fe0 oxidized to Fe3+, Fe3+ then precipitating out and the process you see that the electrons are being released and Eh+ is also being released meaning pH will fall right. So typically when we have zero-valent iron, these are the aspects we need to consider as in we can have reduction right of the relevant contaminant and we can also have coprecipitation by the relevant compound being adsorbed onto this particular precipitate of ferric hydroxide right.

So typically you can observe either reduction or coprecipitation in this case of zero-valent iron based PRBs right. So moving on but what is one particular aspect with respect to coprecipitation right?

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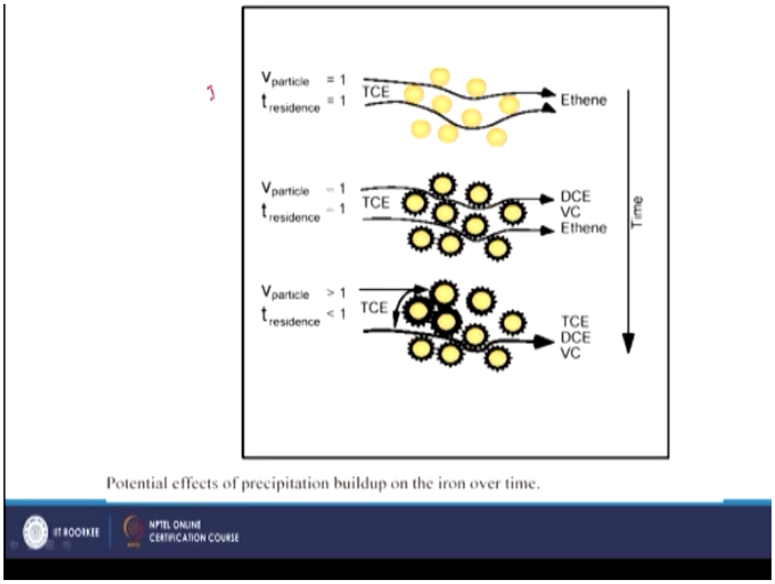

Potential effects of precipitation buildup on the iron over time.

The issue is that let us say this is the initial case and with time let us say, yes I have this particular graph here. So with time this is the changing scenario. So these are my zero-valent iron particles, let us say and I have TCE let us say, chlorinated solvent right, trichloroethylene I believe and so this contaminant is flowing through this particular PRB and coming in contact obviously with zero-valent iron and it is going to be reduced to ethane, okay.

So that is what you would ideally want to have, but over time what would happen right. You are going to have buildup of this particular ferric hydroxide, which we saw would be formed this particular hydroxide would build up over the particular particles yes so you would have buildup of this particular ferric hydroxide precipitates, building you know occupying the relevant surface area are precipitating out on the surface area of the zero-valent iron particles. So what are the relevant aspects that are going to be involved.

So one particular aspect is that, now the time let us say would be less than you would expect or want let us say right. Again why is that the porosity is going to decrease let us say yes and it can decrease much further as you see right. So in this case let us say the particle or the TCE compound would spend more time in the relevant reactor. Here relatively less and here much lesser, I guess yes. So obviously what does that mean that TCE does not have relevant or enough time to react with the relevant PRB or pardon me in this case zero-valent iron molecule right.

So potential effects, so obviously you need to take this into account when you are designing the thickness of the PRB or designing the PRB right.

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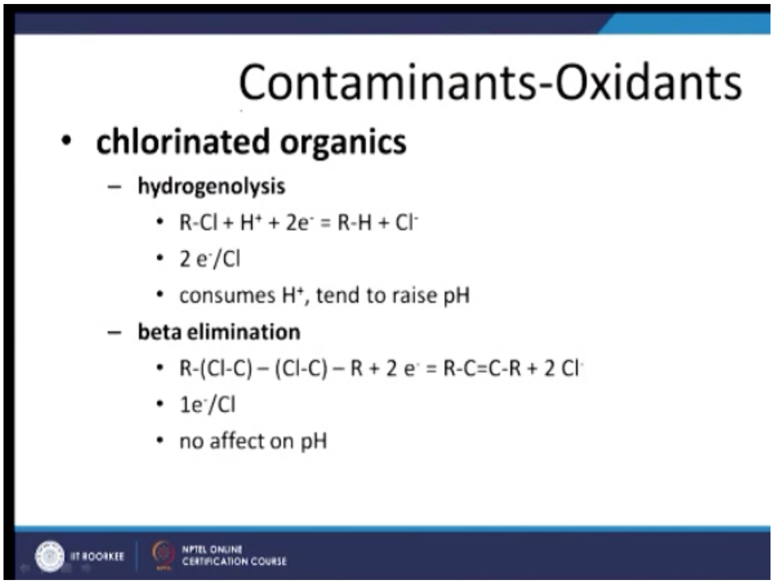

Contaminants-Oxidants

- **chlorinated organics**
  - **hydrogenolysis**
    - $R\text{-}Cl + H^+ + 2e^- = R\text{-}H + Cl^-$
    - $2\ e^-/Cl$
    - consumes H^+, tend to raise pH
  - **beta elimination**
    - $R\text{-}(Cl\text{-}C) - (Cl\text{-}C) - R + 2\ e^- = R\text{-}C{=}C\text{-}R + 2\ Cl^-$
    - $1e^-/Cl$
    - no affect on pH

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So moving on, so what are the other contaminants that we typically look at? One case obviously is that we look at chlorinated solvents, but obviously when you are looking at considering zero valent iron which is what we are going to discuss in greater detail, again why is that because it is widely used. Obviously we are looking for oxidized contaminants or oxidants. So in this case typically chlorinated organics. So here I have chlorinated organics right.

And chlorinated organics, there are two different pathways as in one is the hydrogenolysis and the other is the beta elimination. So let us just look at that and then we are going to move on and understand why we need to look at these 2 aspects too right. So two different pathways for degradation of this chlorinated solvent as is represented here let us say right. So here you have hydrogen being consumed, let us say H+ being consumed and again 2 electrons being accepted.

And then relevant reduction of the relevant compound and then release of this particular CL-. So again hydrogenolysis, yes. Here the key is that for each CL right chloride ion, you need 2 electrons right, 2 electrons per CL and also the case is that it tends to consume pH right, pardon me not consume pH consume H+ as you can see out here what does that mean pH rises right. So pH rises again, what issues would that cause?

It can cause issues with the relevant precipitation right typically at higher pH, you can have precipitation of the relevant metals and so on right. So that is one particular case you need to observe or consider and the other pathway is the beta elimination. As you can see here elimination stepwise, we are going to look at that. So as we see here 2 electrons and 2 CL- being released and here you have the reduced compounds.

So again 1 electron per CL- are required or is required pardon me and as you see H+ is not involved in this particular reaction. So you know pH is not affected here right. So let us look at the relevant compound here.

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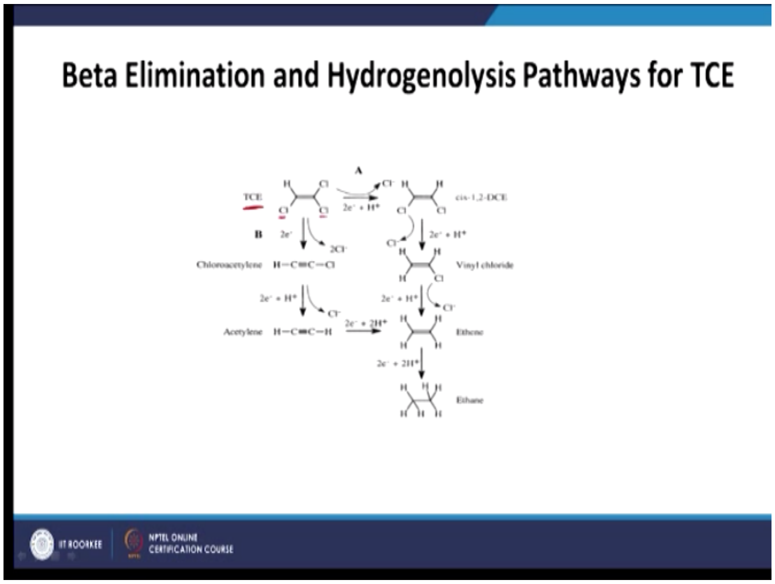

Beta Elimination and Hydrogenolysis Pathways for TCE

So here I have TCE right. So it carbon-carbon double bond, double bond, here H-Cl Cl-Cl right. So I have 3 chlorines here right and so there are 2 different pathways obviously, 1 is the hydrogenolysis which is this particular pathway and the other is the beta elimination which is this pathway. So obviously what do you see here. So 2 electrons and H+ accepted and Cl- is given out. Let us say and that is where now you end up with 2H by 2 hydrogen atoms here.

And again CL right, what is it now? The net effect is that obviously this is a relatively more reduced compound compared to tc and then further degradation or for the acceptance of electrons and H+ and so on and so forth and you end up with relatively more degraded products or reduced products. So here is my initial compound and from hydrogenolysis pathway I first formed TCE, vinyl chloride, ethene and then ethane if the reaction goes to the farthest extent right.

And then the second case is, when I have beta elimination and it goes from TCE, chloroacetylene, acetylene and then ethane and ethane right. So here let us look at that. So 2 electrons are accepted and 2 Cl- is given out and that is what you see out here right and should have 3 out here you now have only 1, Cl-2, CL- are released and then obviously the triple bond here obviously right.

So again the key here is that the aspect to understand again is that here you have 2 different pathways meaning, you can have different kinds of byproducts depending upon the kind of pathway, but why do we obviously need to look at this or understand. The key is that when you are degrading a toxic compound right, depending upon either the extent to which you are degrading it let us say or the pathway, you can end up forming more toxic compounds.

As in as you look at it here, if you follow the hydrogenolysis pathway what we observe, TCE a toxic compound, vinyl chloride which is a carcinogenic and certainly a toxic compound right are formed right, probably a carcinogenic I am not 100% confident, but it is remarkably toxic right. So the key is that depending upon the pathway or the ratio or the rate at which the 2 pathways are carried out let us say right, you need to also consider the effects of these particular byproducts right.

As in you cannot, let us say just say I am going to remove TCE, but end up having a lot of vinyl chloride in your particular treated water right. Why is that vinyl chloride is more toxic than your TCE right. So your design should also be able to take into account further degradation of vinyl chloride into ethane, ethane, or you know the more what we say benevolent or non-harmful compounds or non-toxic compounds pardon right. So that is one aspect to look at.

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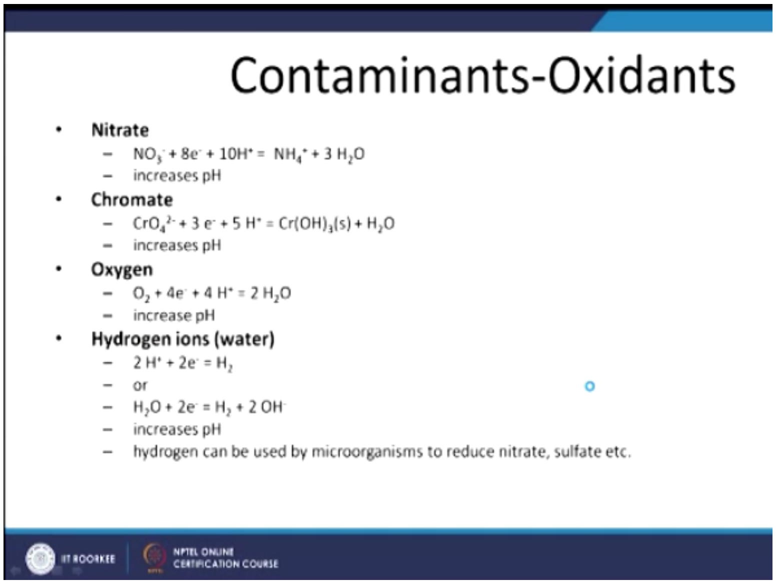

Contaminants-Oxidants

- **Nitrate**
  - $NO_3^- + 8e^- + 10H^+ = NH_4^+ + 3\,H_2O$
  - increases pH
- **Chromate**
  - $CrO_4^{2-} + 3\,e^- + 5\,H^+ = Cr(OH)_3(s) + H_2O$
  - increases pH
- **Oxygen**
  - $O_2 + 4e^- + 4\,H^+ = 2\,H_2O$
  - increase pH
- **Hydrogen ions (water)**
  - $2\,H^+ + 2e^- = H_2$
  - or
  - $H_2O + 2e^- = H_2 + 2\,OH^-$
  - increases pH
  - hydrogen can be used by microorganisms to reduce nitrate, sulfate etc.

So again what are the other contaminants again, as we mentioned oxidants. So typically nitrate again right, methemoglobinemia, I guess right, blue baby syndrome pardon me. So and again it can accept electrons right and you know ammonia is formed. Obviously again the key is that it increases pH. So again electron donor right, so what do you need for that, you need an electron acceptor. What is the electron acceptor, zero-valent iron right?

So that is something you see, nitrate and again chromium. Here as I mentioned earlier the oxidation state is +6 and this states CrO4 2- after the zero-valent iron provides the relevant electrons and you know H+ is consumed let us say you are going to have oxidation state +3 here for the chromium right and that as we know is relatively more insoluble and that is why you see the relevant precipitation here.

And again as you see H+ is also being consumed that would obviously increase the pH right. So Again oxygen again can act as an interfering compound right. So what do we see here oxygen can consume 4 electrons and again H+ and be reduced to H2O right. Again interfering compound, so again hydrogen ions let us say again the key is that the hydrogen can be used by microorganisms to reduce nitrate sulphide right.

So in some cases when zero-valent iron does not play a direct role, it can play an indirect role by promoting formation of hydrogen let us say, which is required by some microorganisms to promote reduction of nitrate and sulfide let us say, right. Again what is the pathway H^+ being reduced to H_2 here right or a different pathway H_2O I guess obviously I mean just another form of writing this particular reaction right and H_2O will be useful for the relevant microorganisms, right.

So different contaminants and we looked at some of the different cases, but the key aspect is that they are all electron acceptors here right. So moving on, so column tests. Why do we do the column tests, I guess we are trying to look at an idea or get you an idea about the kinetics and once I get an idea about the kinetics what can I decide? I can design the thickness of the relevant PRB right. So that is the case here. So for that I obviously need the rate constants right and that will help me calculate the thickness of the relevant reactive media yes.

So kinetics plays an important role right. So here we are typically talking about redox reactions right, redox reactions right and as we know are people who have some background, redox reactions really reach equilibrium but it is the key aspect that we need to consider in redox reactions is the kinetics or are the kinetics right. Kinetics will give an idea about how fast the relevant process occur right or the rate of change of those particular chemical process.

And equilibrium will give you an idea about how far the system can travel let us say or what is the maximum extent that the system can travel to let us say here right. So typically in redox reactions, we are considering or we need to look at kinetics right.

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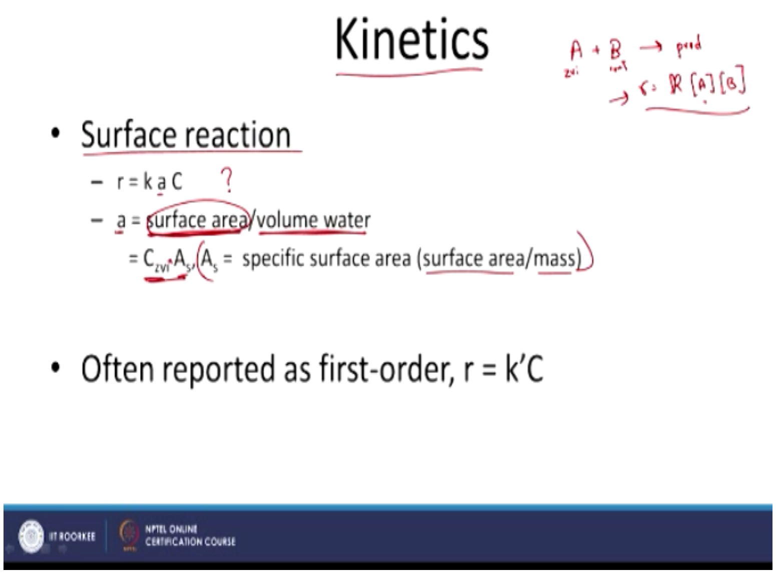

Kinetics

$A + B \rightarrow \text{prod}$
zvi cont
$\rightarrow r = k[A][B]$

- Surface reaction
  - $r = k\,a\,C$?
  - a = surface area/volume water
    $= C_{zvi} \cdot A_s$, (A_s = specific surface area (surface area/mass))
- Often reported as first-order, $r = k'C$

So obviously in this context as we discussed earlier if you have A and B going to products right, the rate of the relevant reaction is the rate constant of this particular reaction K times concentration of A concentration of B right. So here we have zero-valent iron and B is your contaminant let us say and this is my reaction. So but obviously here, the key is that it is a surface reaction yes.

As in you have zero-valent iron right say pellets and you have the contaminant coming in contact, so it is a surface reaction. So the relevant aspect is that rather than concentration expressed in the traditional units, we are going to look at A here which is the surface area per volume of water, surface area of zero valent iron per volume of water right and obviously what will the surface area depend upon.

It is going to be dependent upon concentration of zero-valent iron into specific surface area. As is the specific surface area which will give an idea about surface area per mass right. As in greater surface area of the relevant compound per mass let us say, you will have obviously greater, what do we say, sites for reaction, but obviously way to typically when would that occur, as in when would you have greater surface area for a given mass when the particle size is less.

But obviously we have limitations with respect to size as in if you go for way too lesser sized particles, the porosity let us say or the hydraulic conductivity of your permeable reactive barrier might be less or there might be issues, obviously you can have slurry and such. So you have way too small particles, there are other issues practical issues again with respect to precipitation and then blockage of the relevant pores.

So it is a balance between these 2 aspects right. So here what do we have, we have surface area per volume of water. What does that depend upon obviously the concentration of zero-valent iron times the specific surface area right. So as we mentioned earlier though typically we put in a lot of zero-valent iron right. Typically, it is in great stoichiometric excess right. So this means for all practical purposes, this particular value is constant.

So what can I express this as K dash into concentration of B right. So that what is this, it is first order or pseudo first order, even though it is supposed to be zero order. So it is typically expressed as pseudo first order here right. So that is what we see here. So R=K dash* C. C is the concentration of the contaminant and what is K dash, K Dash is K*zero-valent iron concentration into specific surface area right into concentration of the contaminant yes.

So this is what it is, but obviously most of these are constant and that is why we end up using the pseudo first order rate constant here right. So that is with respect to kinetics and we are going to look at this again later when we need to understand let us say how to design this particular PRB right. So let us move on again. So one aspect here is we come back to this figure, which we looked at earlier.

So if you remember let us say the case was that as I go from this particular case when all the site is available to the zero-valent iron, what do we say having some precipitation on the relevant site and now let us say the PRB material does not hold the relevant compound for as long as it would in this case let us say. So lesser time here and much lesser time here right, so that would affect my kinetics that is one way right.

So the time available is or you know as time progresses let us say I am going to have the relevant particle, the residence time of the relevant particle in the PRB to be relatively less that is something we discussed earlier, but obviously what is one other aspect or how can it also affect what we say the kinetics are the relevant reaction. One way obviously as we discussed was the time itself available for the relevant what do we say compound in the PRB is less.

But what is the second way, as we looked at it earlier, so R is dependent upon this particular specific surface area available right. So here as you see the specific surface area available here right, it is different from what would be available here after certain time T right. As in now initially you had only zero-valent iron and all the surface is available or is active right, but after precipitation of let us say ferric hydroxide or other precipitates on this zero-valent iron.

This specific surface area is less, let us say you know or would be less after sometime right. So obviously what would the case turn out to be your K dash*C, which is K times concentration of zero-valent iron times specific surface area times concentration right. So this particular value is or can decrease over time right and thus your particular rate, rate of your particular reaction can be lesser.

So this particular aspect also needs to be taken into account when you are designing for the thickness of the relevant PRB right. So again we are going to move on. So here obviously as we talked earlier, we can have byproducts formed that are relatively toxic or even sometimes more toxic than the parent compound. So here the key aspect is let us first understand the figure.

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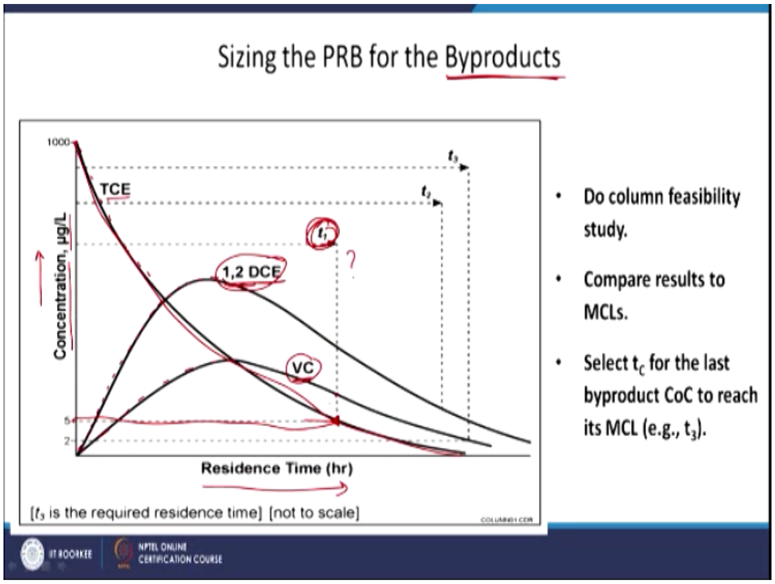

Sizing the PRB for the Byproducts

- Do column feasibility study.
- Compare results to MCLs.
- Select t_C for the last byproduct CoC to reach its MCL (e.g., t_3).

We have on the y-axis concentration and PPB for different compounds and on the x-axis, we have the residence time let us here right and so initially let us say I have concentration of TCE to be 1000 ppb and you know this is the profile that would be for different retention times let us say right and I guess the regulatory standard would be, where is regulatory standard for TCE out here. So this is the regulatory standard.

So if I just you know degrade the compound to this particular concentration, you know which is I believe 5 ppb for TCE, I meet the relevant standard right. So if I go from 1000 to 5 ppb which would require time of T1 let us say, I am fine with meeting the regulatory standard for TCE though, but as you know depending on the pathway right hydrogenolysis or beta illumination, we have these more toxic compounds being formed right. What do you observe here?

As TCE is decreasing, you now have increase of or formation of these byproducts right, which are vinyl chloride and 1 2DCE. So if I stop my particular or design my particular system such that it has a retention time only of T1 what are the issues, I see that vinyl chloride concentration and 1 2DCE concentrations are relatively higher than their relevant standards which seem to be around 2 ppb right, for the vinyl chloride and 1 2DCE.

So obviously by treating 1 problem, I am creating more problems here right. So obviously what do I need to do, I need to look for that particular time or the retention time or calculate that particular retention time that would allow for the relevant standards for all the relevant byproducts to be reached. So here I guess we have T3 where it points out that the concentration of vinyl chloride is going to be 2 ppb, which seems to be the standard vinyl chloride is going to be reached.

So again the case is that am I going to design it for T1, T2 or T3. Obviously I am going to design it for T3 as you see at T3 all the relevant compounds are below the relevant regulatory standards right. So that is something that I need to consider yes. Again how can I get this done, look at column feasibility study and compare the relevant results to the relevant remediation, not remediation, the regulations goals let us say right.

And then you will choose the TC such that the byproduct or contaminant of concern has also been reduced right. That is what we have out here.

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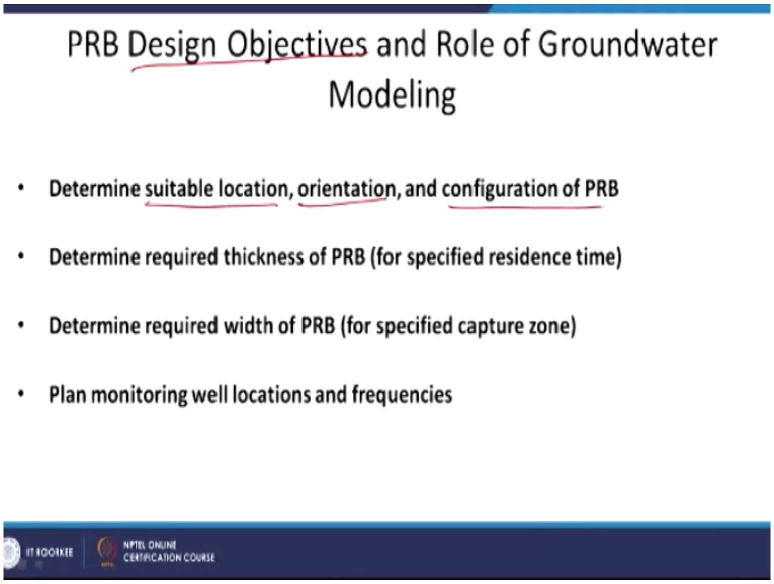

PRB Design Objectives and Role of Groundwater Modeling

- **Determine suitable location, orientation, and configuration of PRB**
- **Determine required thickness of PRB (for specified residence time)**
- **Determine required width of PRB (for specified capture zone)**
- **Plan monitoring well locations and frequencies**

So again PRB design objectives right, what are the objectives obviously. We want to be able to find a suitable location right, suitable location and then orientation is important because obviously of the groundwater flow direction yes. Orientation is important. Configuration are we going for continuous or funnel and gate and obviously PRB thickness that is the major aspect or one of the major aspects anyway and how do I get that based on kinetics let us say.

And the relevant byproducts are such which I would get from the column study right. So first I would get the column study done and then find the relevant retention times right and then be able to reciprocate or replicate that, pardon me in the relevant groundwater right and then obviously width of PRB, width of PRP would typically be dependent upon the width of the contaminated plume right. So again what do we need in this context?

We need what do we say with greater accuracy to be able to estimate the contaminant size and plume distribution right and obviously we will need contaminant what do we say monitoring wells and locations and some frequencies of monitoring right. So typically where are we going to have them? We are going to have them upstream of the PRB, downstream of the PRB, at the sides of the PRB. Why at the sides of the PRB?

To see if any particular contaminant plume is escaping the relevant PRB and also within the PRB to see if the relevant rates or kinetics are being held as you would expect let us say right. So we are going to look at some of these cases later right.

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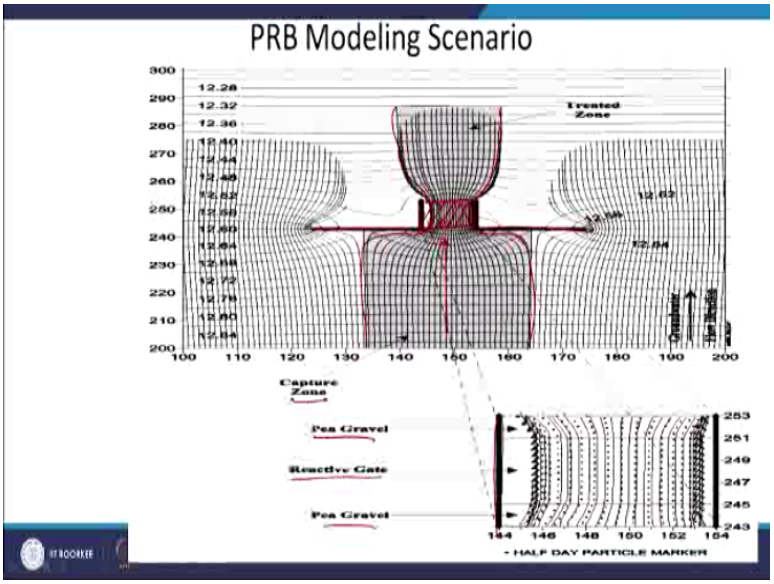

PRB Modeling Scenario

PRB modelling scenarios, so here we have a funnel and geared system right, you know different models out here and the contaminated plume is flowing through the PRP that is what we see out here, contaminated plume or which is the capture zone for this particular PRB anyway I guess right. It is a capture zone and as it moves through this particular PRB, this is the top view obviously you have the treated water, you know that is coming out.

And here we have the relevant PRB I believe. So pea gravel, reactive gate and pea gravel again general cases not worth spending way too much time here, but it will help you understand that.

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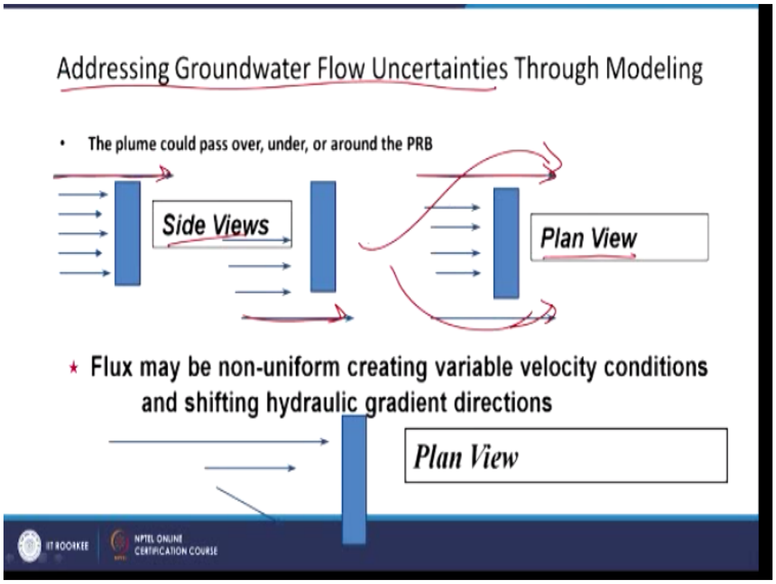

Addressing Groundwater Flow Uncertainties Through Modeling

- The plume could pass over, under, or around the PRB

★ Flux may be non-uniform creating variable velocity conditions and shifting hydraulic gradient directions

So obviously the case that as we talked about is that we need to address groundwater flow uncertainties right. So again as we looked at it earlier a case when we had recharge of the relevant aquifer and then the plume shifting shape and direction and thirst PRB performance you know not being optimum or failing right. So obviously what is the key you need to be able to look for uncertainties. So side views what are you concerned with?

The ground water flowing above or below the PRB. So that is something you are looking at, plan view, you are concerned with the plume flowing around the PRB right. So this is the top view and earlier we looked at the side view. So this can be different cases as in the porosity of this particular reactive media let us say or your particular PRB is let us say lesser than the aquifer let us say and what would that lead to.

Then you would have either what we see not either pardon me your water trying to take the path of least resistance and would prefer to move around the PRP right or let us say this can also be the case let us say the PRB there has been considerable time let us say a few years and now the PRB or the relevant zero valent iron has precipitation let us say and now the porosity is lesser than what was the case earlier and then again you have you might have failure of the PRB.

So that again needs to be taken into account when you are designing for the porosity of that particular PRB right and obviously let us say if you did not accurately estimate the width of the particular contaminated plume, the plume obviously might flow around this particular PRP right and obviously let us say the flux may be non-uniform as in you might have different strata creating variable velocity right.

As in here velocity and then shifting hydraulic gradients to I guess right. So that can lead to hydraulic gradient. So there are different cases but again the key aspect is to be able to understand how the contaminant moves and what does that translate to how does groundwater you know flow I guess right.

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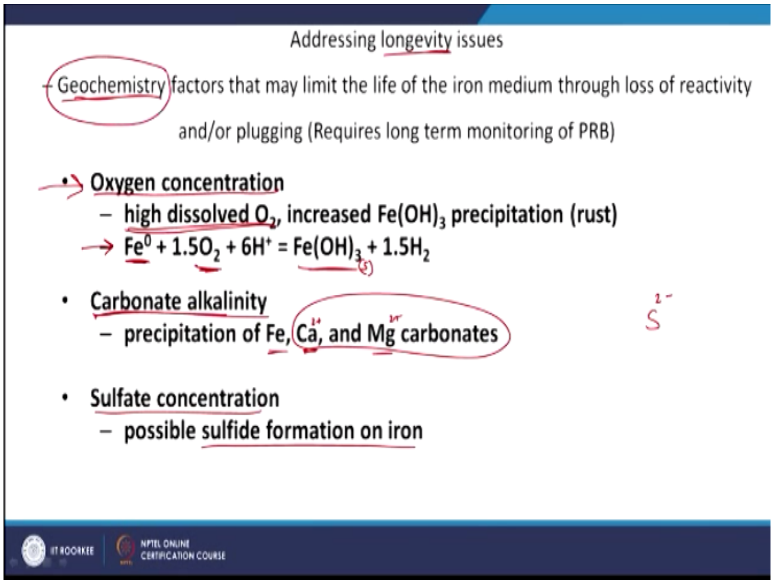

Addressing longevity issues

Geochemistry factors that may limit the life of the iron medium through loss of reactivity and/or plugging (Requires long term monitoring of PRB)

- Oxygen concentration
  - high dissolved O_2, increased $Fe(OH)_3$ precipitation (rust)
  - $Fe^0 + 1.5O_2 + 6H^+ = \underset{(s)}{Fe(OH)_3} + 1.5H_2$
- Carbonate alkalinity
  - precipitation of Fe, $\overset{2+}{Ca}$, and $\overset{2+}{Mg}$ carbonates
- Sulfate concentration
  - possible sulfide formation on iron

S^{2-}

So moving on, so addressing longevity issues what are the issues obviously as we mentioned geochemistry and something that we need to look at. As in what are the typical aspects we need to look at oxygen concentration. Why is that, if you have way too high oxygen concentration, you are going to have relevant, what do we say degradation of the zero-valent iron right in the presence of oxygen, which is an electron acceptor and then you are going to have the precipitate being formed or rushed or rushing in this case as you can call it right.

And this is going to obviously lead to relative inefficiencies in your PRB right or carbonate alkalinity again right that can lead to precipitation of either Fe2+ Fe3+ Ca2+ or Mg2+ and so on right. You can have calcium and magnesium carbonates being formed or you know precipitating out right and that can again you know clog up your PRB right. So you need to be looking at alkalinity and also the relevant calcium and magnesium concentrations.

And again sulfate concentration because sulfide formation on iron is something that can lead to that can be led to as in you have SO4 2- reacting with zero-valent iron, you can have sulfide formation let us say right. So that is one case sulfide formation again ligand S2-. So in the presence of any other metals or such let us say it can precipitate out. Again there are such issues. These are the issues that you look at when you consider the geochemistry of that particular site, which would determine how long the system can work finally, let us say. So let us move on.

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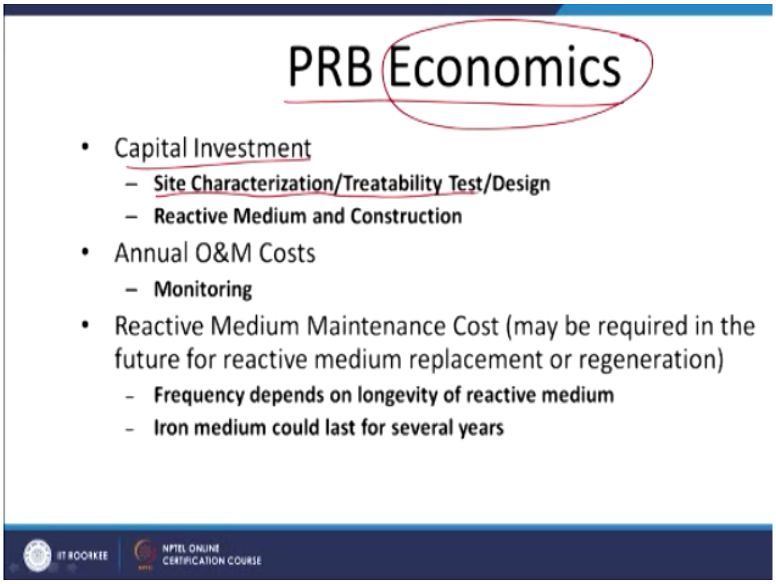

PRB Economics

- Capital Investment
  - Site Characterization/Treatability Test/Design
  - Reactive Medium and Construction
- Annual O&M Costs
  - Monitoring
- Reactive Medium Maintenance Cost (may be required in the future for reactive medium replacement or regeneration)
  - Frequency depends on longevity of reactive medium
  - Iron medium could last for several years

So what are the aspects that are you know driving, the driving factors behind choosing for PRB, obviously it is the economics right. Typically, capital investment is less, but you need to spend considerable amount though or you know major fraction of it and site characterization, treatability test and design. Again more importantly in site characterization as in you want to be able to capture the plume direction, groundwater flow direction.

And you know uncertainty is there and the aquifer characteristics considerably right or accurately and then obviously and getting the reactive medium and construction. So we are going to look at the relevant data in the context of what do we say the relevant aspects of the case study. As I mentioned we are going to look at a case study later and then we are going to look at all these aspects in greater detail and typically obviously, you need to look at some monitoring cost for your PRB right.

I mean you need to look at the monitoring cost for the groundwater right and these are some aspects but obviously not major aspects though and then if required let us say if you think the reactive medium needs replacement or regeneration that needs to be looked at by typically most people or you know most scenarios would not require that particularly as in if you need to regenerate or remove and replace your reactive medium.

So obviously the frequency at which you do that will affect the longevity of your or will be dependent upon how long your particular zero-valent iron can say has enough active sites or such yes, but typically as we discussed earlier that is not required and typically iron medium could last for several years right. So moving on again PRB economics, what are the issues that are driving it so no annual operating requirements right.

So once I put it in, it is just a passive technique and only monitoring cost. So unlike other cases you know there are no annual operating requirements, a major aspect pardon me our major advantage in Indian context is no above-ground structures, so especially when you have groundwater contaminated in relatively high population density areas PRBs depending upon obviously the site let us say and the extent of depth of contamination is going to be something worthwhile.

And again obviously you do not have any other waste streams being generated above-ground. As in I am not pumping water out right and I do not need to have a treatment train for that or now be concerned about the waste from that particular treatment train right. So it is again passive, everything is happening below the subsurface. So these are the major benefits obviously right and monitoring.

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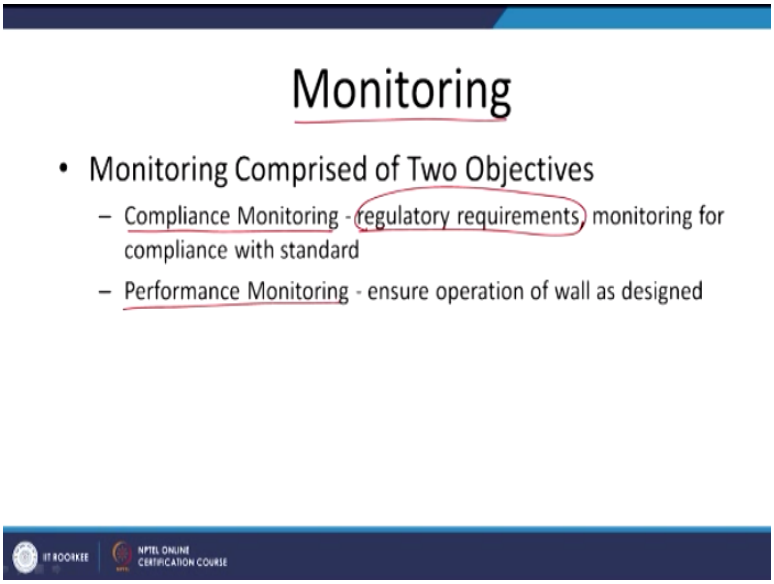

Monitoring

- Monitoring Comprised of Two Objectives
  - Compliance Monitoring - regulatory requirements, monitoring for compliance with standard
  - Performance Monitoring - ensure operation of wall as designed

We also obviously need to look at monitoring. What are they? First to look at let us say 2 cases, as in am I meeting the regulatory standards or not, secondly to understand is my PRB working as I designed it to be right. So let us look at what we have here.

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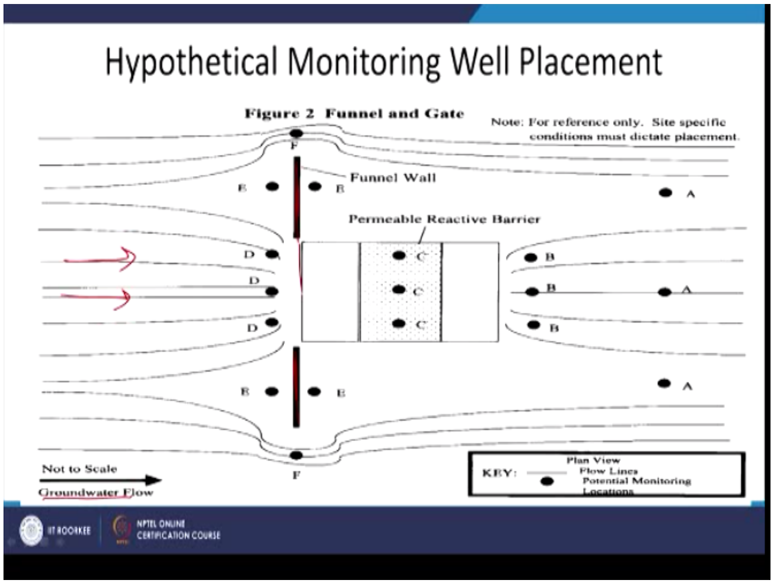

Hypothetical Monitoring Well Placement

Figure 2 Funnel and Gate

Note: For reference only. Site specific conditions must dictate placement.

So this is one particular hypothetical case. So groundwater is flowing I believe in this direction right yeah. Groundwater flow is in this direction. So have funnel gate right, I have funnel walls here, and the gate here. So I guess pea gravel here relatively more porous and then I have my reactive media here right. So this is the capture zone, that is flowing in. So obviously I need relevant monitoring wells here.

And I also need monitoring wells at the sides of the PRB to understand if any contaminated plume is flowing around the PRB right and obviously at the funnel walls too before and after and more importantly I will also need them inside the PRP. Why do I need them inside the PRP, as I mentioned to understand the performance of the PRB as in I do not want to understand that the system has failed after it has failed.

I will need to be able to predict the performance let us say. So for that let us say I need to have relative monitoring wells or relevant monitoring walls within the PRB too and obviously I will need monitoring wells downstream and far downstream right. So let us look at another case in actual case if I am not wrong okay.

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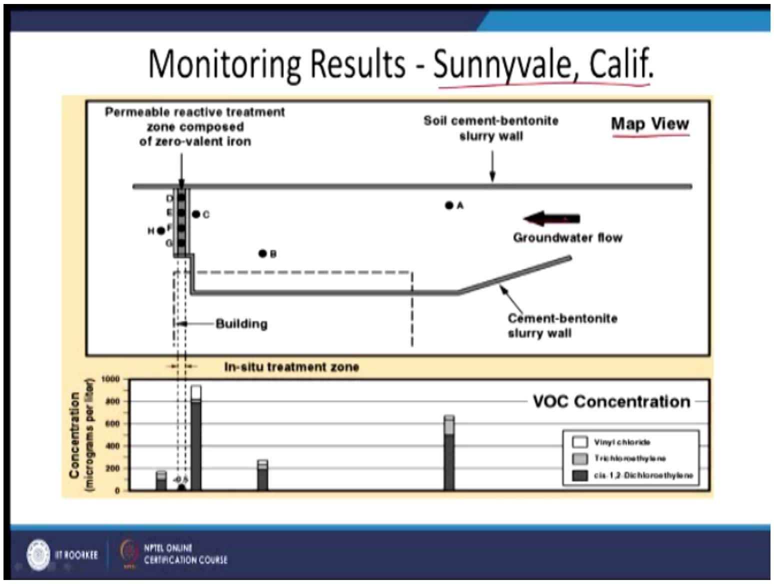

Monitoring Results - Sunnyvale, Calif.

So this is an actual case and this is from Sunnyvale, California okay. So here let us look at what we have here. This is the plan view right. This is the plan view or top view. So ground water is flowing in this direction. So here they have used a funnel and gate system if I can call that but keep in mind that the shape of the funnel and gate can suit your particular site conditions. So this is a good example here.

As in this is my funnel right or the impermeable layer and what is that made of soil, cement, bentonite, slurry wall let us say impermeable layer here. This is the top view obviously right and again similarly a funnel here right. So this channels the groundwater flow towards my particular reactive media. So here I have a particular monitoring well location another monitoring well location out here, which is slightly away from the centerline of the flow path.

And then right before the PRB and right after the PRB and obviously within the PRB. So again as you can see in this case, which is an actual site condition. They had a building out here right and obviously with this type of structure, you need not obviously keep these above surface clear right of built-up area. You can have built-up area above the surface. So that is what you see out here. So now let us look at the relevant concentration profile here right.

So concentration microgram or PPB on the y-axis and this is the distance corresponding to this is at A, this is at B, this is at C and this is within the PRP and this is outside the PRP. So obviously at A, you have the concentrations of the relevant compounds to be relatively high, what do we have, we have TCE, trichloroethylene and also vinyl chloride and 1 2DC right. So that is what we have here.

Most of it is present looks like as 1 2DC, some as TCE and very little as vinyl chloride right. So again B but slightly off the centerline of the flow, groundwater flow that is why you see relatively less concentration, but C gives you see a better picture of the true concentration that is entering the reactor and that is what you see out here. Concentrations are remarkably high right. So obviously as you see the concentration within the PRB is relatively less right.

And this is the concentration outside the relevant PRB or as it exits the or after the relevant treatment right. So before treatment C not and after treatment CT let us say right. So again simple case when we can understand the relevant system based on the relevant monitoring, that is right. So I guess I have spent enough time on this session. So in the next session we are going to look at the relevant technical aspects as in how do I design the relevant PRB right.

So we are going to look at let us say the plug flow model as in what is a plug flow now. Again we are going to again look at what is a plug flow and what are the different types of reactors and then apply mass balance and then model, not model pardon me design the relevant thickness of the PRB right and then we will move on to looking at the case steady, right and I guess again as I said I am out of time and thank you for today.