

Environmental Remediation of Contaminated Sites
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Lecture – 23
Case Study (Utah) - Contd

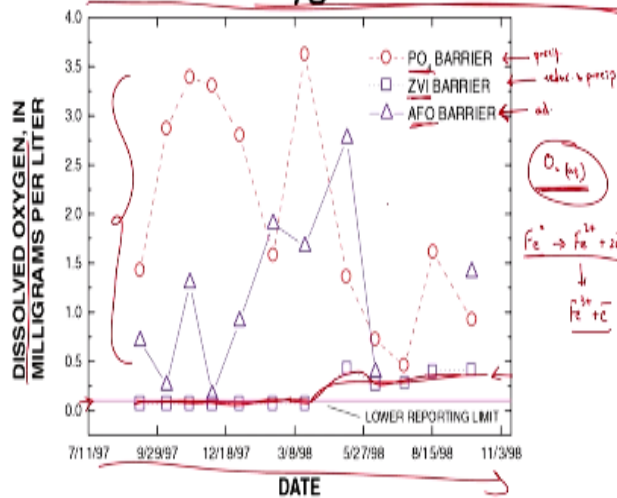
Hello everyone, again welcome back to the latest lecture session, again what have you been looking at; we have been looking at case study with respect to the application of or the initial applications of PRB let us say, right and I think the case we looked at or were looking at let us say was a site contaminated with uranium among other heavy materials, right or heavy metals pardon me.

And since typically, you know we do greater weightage to the one that is of greater part it was, so you know the relevant people were looking at attenuation of uranium right, so in that context as we aware of a; they put in at a field scale or pilot scale let us say after relevant laboratory test, they put in the pilot scale what do we say test, let us say or the emplacement if I can say so, of 3 kinds of PRB consisting of different reactive media.

I mean different reactor media in the sense that they chose 3 different kinds of process, reductive dechlorination; reductive dechlorination, a reduction and precipitation, only precipitation and adsorption right, different kinds and then we looked at the relevant aspects obviously, we need to look at these aspects to understand you know, some of the key aspects here that provide greater or not greater let us say, further knowledge about you know evaluating the relevant applicability let us say or advantages of each of these materials now, right.

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Changes in dissolved oxygen concentration



So, let us move on, I believe we did look at one aspect but we are going to look at that again because it is relevant to some of the aspects we are going to discuss today, so change in dissolved oxygen concentration, so obviously there might be limitations again with respect to the thresholds for the DO levels downstream but that is something you need to consider, right so, on the y-axis we have DO, right and on x axis, we have the relevant date.

And we have the 3 kinds of materials, the phosphate based, zero valent iron based and amorphous ferric hydroxide based, right and this was with respect to the I believe, adsorption was the mechanism here, I think precipitation, right and here I believe it was a reduction and then precipitation let us say, right anyway these were the mechanisms that were supposed to be the case.

Again, as we looked at it not lot of data was presented with respect to validating the mechanism but again if you look at the relevant materials you know it is logical and there is historical data to support this particular hypothesis here, right. So, moving on we are trying to look at DO, so DO, what is it now; oxygen and the aqueous phase, right in the groundwater and typically let us say how would this be affected?

So, oxygen let us say again is an electron acceptor right, so it would be affected let us say or the concentrations would be affected when you have relevant reduction or you know redox process going through let us say that would affect, that would involve oxygen, right so obviously, the 3 of these types of barriers; one of the relevant material is obviously made of a reductive or reducing agent which is zero valent iron, right.

So, obviously if you look at the data that particular data pertaining to the zero valent iron based system obviously, would have lower DO concentrations, why is that; zero valent iron let us say is the reducing agent and even after let us say the first oxidation step to Fe^{2+} pardon me, Fe^{2+} is again a reducing agent and both these particular compounds can react with the oxygen, right which is an electron acceptor.

And I think we looked at the relevant reactions earlier, so we have Fe^0 , which can go to $\text{Fe}^{2+} + 2$ electrons and $\text{Fe}^{3+} + 1$ electron, right so as you see a reducing agent or electron donor and oxygen is an electron acceptor, so right you know you can have consumption of oxygen here right, so that is what you see here with respect to the data pertain to zero valent iron relatively low or you know below the detection limit anyway, right.

So, obviously then we see a slight increase, right a slight increase here, not a great increases, slight increase again, one of the aspects we considered or we hypothesize was that I know you have zero valent iron and over time you have build-up of relevant precipitate let us say on the relevant zero valent iron, so you are going to have what do we say lesser available surface area or the active sites.

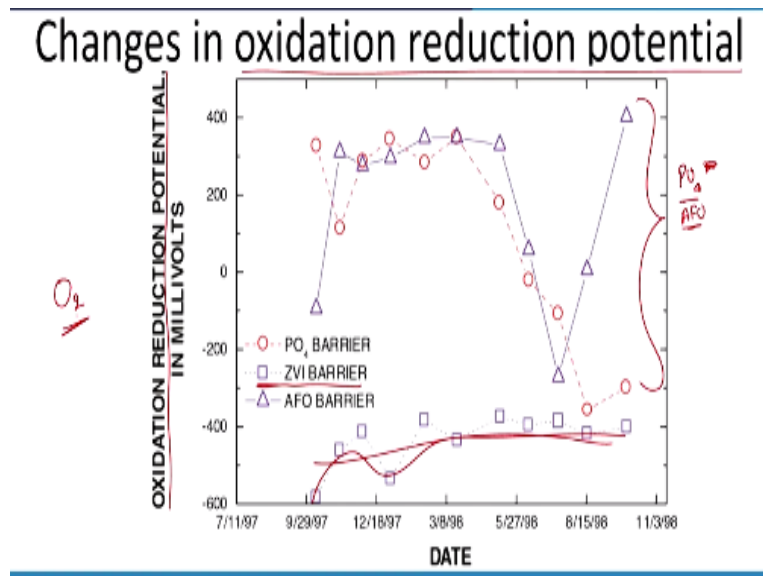
And thus let us say you know the relevant reactions let us say or the retention time might decrease and also the kinetics will be relatively slower in that context right, so that could be one of the two reasons for this increase in oxygen concentration among other aspects obviously, with respect to the other 2 process, I believe they follow different what do we say mechanisms.

But typically let us say there would be if I had the data for the dissolved oxygen concentration of the water coming into the PRB, they would more or less if not mirror be similar to that particular profile and that is what you expect or see out here too, right. Again, moving on so dissolved oxygen right that is something that we looked at and now, we are obviously going to look at oxidation reduction potential or the redox potential, a simple way to do that would be to put in a ORP probe.

But again that is not a great way to go about it but that is what people sometimes typically do so but you should be aware that you know just relying on this particular piece of data which is the

ORP you know measurement let us say to understand your system is not a great idea, we will look at that later.

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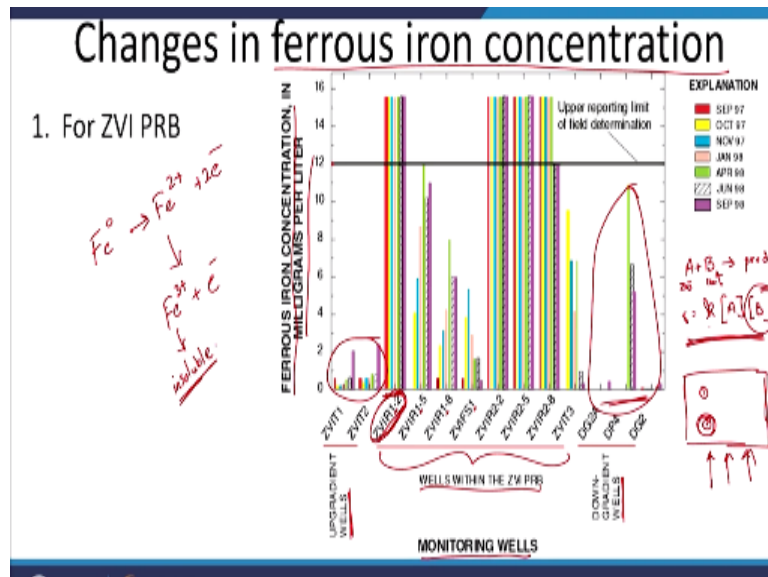


But in this case let us look at that so, again oxidation reduction potential is what we are looking at, let us say right. So, obviously if you have a reducing agent present in that particular solution or that system, what would you expect, you would respect; expect pardon me, reducing conditions to prevail right, so reducing conditions to prevail so, the reduction potential will be relatively less or ORP reading will be less, pardon me.

Oxidation reduction potential; so as expected for zero valent iron, what is the case, it is pretty low, right and not so the case with the other two materials let us say, PO₄³⁻ and AFO, for the phosphate and amorphous ferric oxy-hydroxide let us say, right, so again if you look at the oxygen profile 2 right in conjunction with this data you can understand a system obviously right and the zero valent iron based system obviously, the oxygen concentration is low.

Oxygen is an oxidant right, oxidizing agent and that is not present but we have zero valent iron present which is a reducing agent, so obviously the ORP potential will be lower in that particular case, right, what does that tell you; it tells you that the particular system has reducing conditions prevalent in that right, so that can be used to understand let us say or the other aspects of your system with respect either uranium reduction or any other compounds in general let us say, right.

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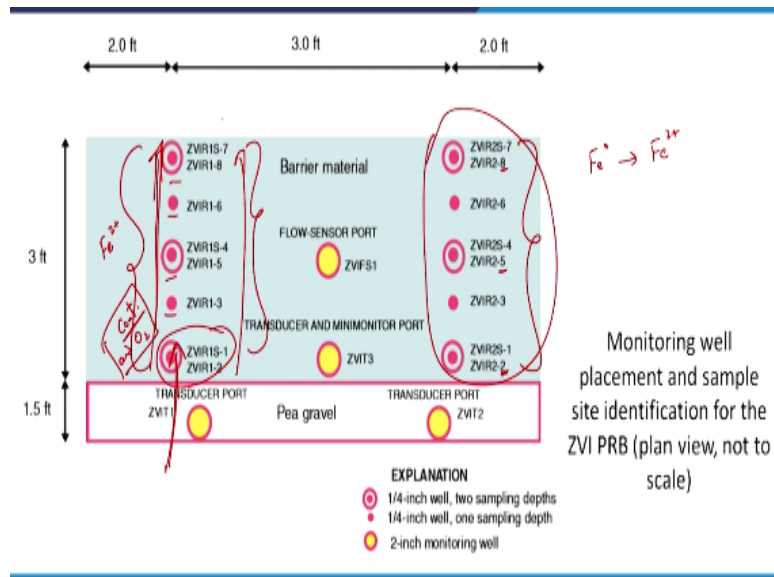


So that is something you can look at to understand, right so let us move on, so here is one key aspect we need to look at so, changes in ferrous iron concentration right, so obviously we have Fe^0 going to $\text{Fe}^{2+} + 2\text{e}^-$, this is one half reaction and if it goes to complete $\text{Fe}^{3+} + \text{e}^-$ and typically Fe^{3+} is insoluble, okay it precipitates out typically in it, right so let us try to understand this system about what we have here.

So, what do we have here; on the y axis, we have the ferrous ion concentration and milligram per litre, right so from 12 to you know 2 let us say, right and here we have different monitoring wells and the particular PRB and what do we have here obviously, 3 cases; one is when upstream of the PRB, downstream of the PRB and within the PRB, right so, obviously you know upstream of the PRB, let us say depending upon the groundwater conditions you are going to obviously expect some ferrous ion present.

And that is one thing that you see here depending upon the method detection limit obviously, you can have a variation here, so you know obviously upstream to you have some particular ferrous iron; iron is present in our soil naturally, right so, again but I guess not at great concentrations or similar concentrations downstream let us try to understand this again later but obviously, you see that within the PRB though, you know the concentrations of ferrous iron are pretty high, right are pretty high.

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Let us try to understand this particular system now, before we go further let us see that there are 2 rows; primary rows of monitoring wells row 1 with the suffix 1 here, right and the second row out here with this one of the suffixes being 2 here let us say, right and then obviously, one particular system out here but this is something we are not going to discuss in detail.

And keep in mind that when we looked at the particular PRB and this is the side view let us say, right and let us say the groundwater level was not what do we say uniform throughout the PRB if you remember that you know, it had a gradient; a considerable gradient either this way or this way, right you know you had that particular gradient and the groundwater, what do we say, a level, right.

Again that is obviously because you know we were or the particular site was very near this particular stream which can act as rather drain or recharge for the relevant aquifer, right, again that was that is something to keep in mind let us see why that is relevant. So, here as you see and the ones are monitoring wells pertaining to the first column of monitoring locations let us say, what do you see that I guess obviously, higher concentrations of ferrous iron and the first set let us see what this is; this particular cell is pertaining to ZV1 R12.

So, this is the first one as in ground water flows in this direction, right and obviously, this is the cell that first comes in contact with your particular contaminated water let us say, right and obviously, you would expect that you know the relevant concentrations are relevant and thus the relevant kinetics of the process are going to be faster initially, why is that? So, the rates are dependent upon let us say if $A + B$ goes to products, what do we expect now, what is the rate?

Rate = the rate constant times concentration of A, concentration of B, right so if I have my PRB this is the top view again similar to the one on the next slide, right and I have one particular monitoring location here and another location here and let us say the water is flowing on this direction, let us say, right so, obviously the greater let us say, this is zero valent iron and this is your contaminant here, right.

So at which particular location will you have greater concentration of your contaminant; obviously, out here right, so you would have obviously greater rates at that particular location which was or is ZV1R12, right so and thus what would you expect; you know if you look at the stoichiometry and the rates let us say you would expect that more of the zero valent iron would be transformed into ferrous iron, right.

So that is something maybe you can look at that or understand that from that point of view, right that is one particular case and then obviously, as you move further up or you know as the groundwater flows through what do I see though, the relevant kinetics if not the kinetics you know the concentrations of this particular contaminant, right are going to decrease as I move through the relevant reactor, right.

So, the kinetics you know at this particular case are going to be low or in the first case there is not just enough contaminant for the relevant reaction to proceed even if the kinetics is fast let us say and if it is we consider that we have an irreversible reaction more or less right and you still need the relevant contaminant for the redox process to go through but if most of the containment has been degraded in this particular cell though, right what would that mean that you know the there is not enough contaminant for the redox process to go through, right.

Redox process means transfer of electrons, so here zero valent iron is your electron donor, so if you do not have an electron acceptor though right, the redox process will not go through and that is something yet you see obviously, the case is that we have both the contaminant and oxygen to be our electron acceptors so that is something that needs to be considered but obviously, we do not have the data for oxygen concentration as we go through the relevant particular PRB, right.

But that would be interesting to have that and here though we see that it is a slightly different profile for the ones in the second column of wells that the concentration of ferrous ion is pretty high, right ferrous ion concentration, the cells are 2, 5 and 8, so I think 2, 5 and 8, right so this is what we have and compared to the; this particular location, the concentrations in these particular locations of ferrous iron are pretty high now.

Why is that? So, this again we need to go back to the relevant aspects of the site characterization, if you look at that we saw that the influent concentrations let us say were not uniform across the particular PRB, right, so that particular locations they are pretty high at particular locations they were not and also we had a gradient with respect to the groundwater table let us say, right.

So, it depends upon the amount of contaminant that is actually coming in contact with your relevant PRB let us say, so looks like more of the containment is coming in contact with the relevant PRB in this particular section or half if I can call that and thus you know more of the zero valent iron is you know oxidized to Fe^{2+} , let us say right but lesser of the contaminant is coming in contact with this particular section of the PRB.

And thus you have lesser concentrations of Fe^{2+} in this location right, so that is what we see out here, so in this particular cells let us say as you can see in these locations concentrations of Fe^{2+} which would indicate let us say, reduction let us say are the action of reduction if I can say that you know but if I assume complete reduction assuming that the kinetics are pretty fast, you know this would give an idea about how much contaminant is coming in.

And obviously, here you see greater concentrations of Fe^{2+} , right, so again this comes back to or points at the relevant influent concentrations of uranium coming in contact with these cells but again keep in mind that you know there are some loopholes with respect to this hypothesis and in we know that Fe^{2+} can be further oxidized to Fe^{3+} and electron giving out and Fe^{3+} is insoluble, it will settle out let us say.

So, it could as well be the case but again we do not have as much data at let us say or do we do not have the historical data either that Fe^{2+} has been further oxidized to Fe^{3+} and this particular set of wells, right, set of wells as in column 1 but a typically has when we looked at

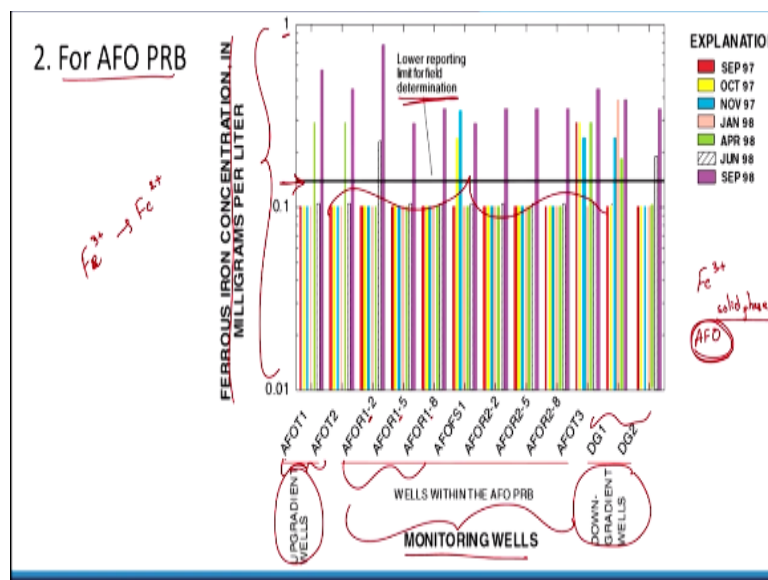
the site characterization data or if we look at it in more detail let us say we will see that you know it is because of the variation in concentration and it is not due to this reason.

But it could as well be that this particular aspect of Fe 2+, whatever Fe 2+ is formed is again reducing the relevant contaminant and transforming to Fe 3+, so that is one reason why you could not or might not see this particular concentration in here and this particular column of for monitoring wells right, again this is the one in the middle right I think that is points to the shift between column 1 locations and column 2 locations, right.

And then down gradient I guess right, obviously depending upon the season right, you have different concentration of oxygen which is a competing electron acceptor and you also have different what do we say concentrations coming in, so obviously you see some effects of seasonal variation but again that is some variation but not a lot right that is something to keep in mind again, right which is indicative of the reductive process going through right.

How can I you know be sure that the reductive process is going through by obviously looking at the by parts which are let us say in this case Fe 2+ and also oxygen concentrations and ORP potentials and so on, right so, we need to look at the system holistically and moving on.

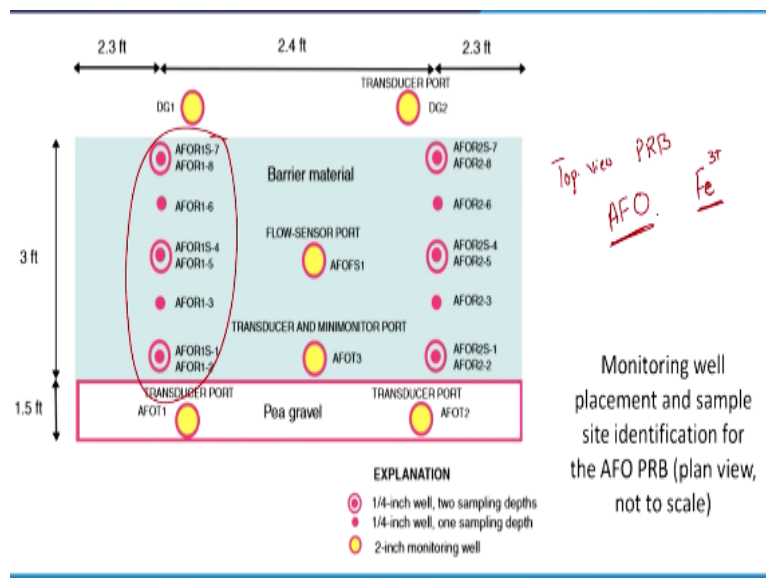
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And for the amorphous ferric oxy-hydroxide, so here again here we have ferrous iron concentration in the y axis or on the y axis and in the x axis we have the monitoring wells and again I believe these are the ones above or up gradient or upstream of the PRB, downstream of

the PRB and within the PRB, right and I think one again pertains to set of columns let us say on the left hand side.

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I think I have data here again to this particular set of monitoring wells again, what is this do; this is the top view of that particular PRB and what kind of PRB are we talking about here, this is the amorphous ferric hydroxide, again the key is that iron here is present as Fe^{3+} right, amorphous ferric hydroxide right, again as we mentioned Fe^{3+} is relatively insoluble, right most of it is present in the you know, again the concentrations of Fe^{3+} in equilibrium with the solid phase are going to be relatively less as in what does that mean, Fe^{3+} is typically insoluble, right.

Again, this acts as a good adsorbent, so what do we see here though, I and again down gradient obviously, the first case is that you know this is the lower reporting limit and the one aspect that needs to be looked at when we try to understand this data is that because we just looked at the data for the zero valent iron base PRB and what we see there that the concentrations were you know varying depending upon the relevant situation.

So, obviously when we try to look at the relative comparison you need to keep in mind that here we the scale is different as and the maximum here is one milligram per litre and out here we had around you know this is 12 milligram per litre, so one would be somewhere out here right, so you need to understand that the axis are different and thus you know when you cannot make for straightforward or make straightforward relative comparisons, right.

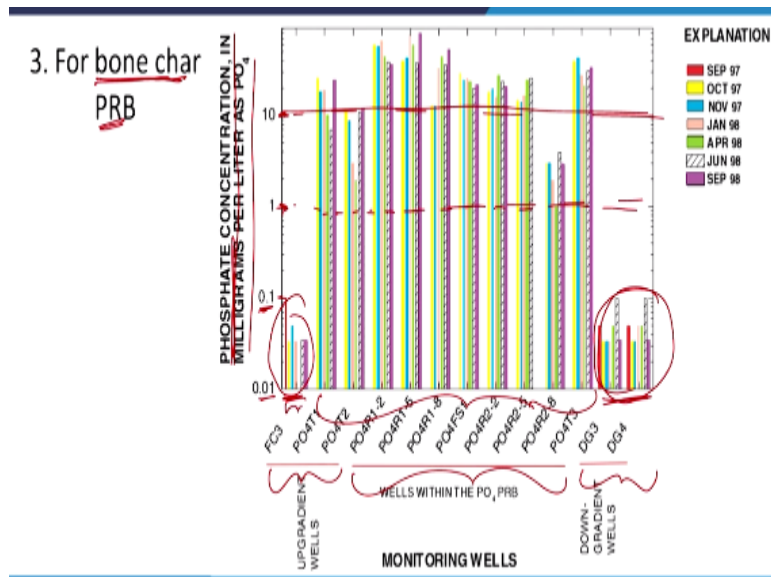
So, again what do we see here, so if you look at that the up gradient wells or the water coming in has some ferrous iron as expected, right and again when it as the water passes through the system though is there any source of Fe^{2+} coming into play here, not really why; because you have the Fe^{3+} in the solid phase let us say which is the amorphous ferric hydroxide or oxy-hydroxide in the solid phase let us say, right.

And here how is the uranium being removed, I believe it is or by adsorption onto this particular solid phase, right you have this amorphous ferric hydroxide, amorphous is the state let us say I mean, gives you an idea about the structure more or less, right here either crystalline, amorphous and so on again that is something aside though you know, I digressed again, so we have the solid phase material you know in which iron is in the form of Fe^{3+} and uranium contaminated water flowing through.

And we presume that its adsorption that is occurring and again keep in mind that there is no obviously transfer of electrons involved in this place or in this particular context and even then let us say for Fe^{3+} to be reduced to Fe^{2+} , you need a; what do we need now, for Fe^{3+} to be reduced to Fe^{2+} , you need a reducing agent or an electron donor and obviously that is missing out here too, right.

So, obviously what we are trying to hint at is that you would expect no ferrous iron to be formed in this particular or within this particular kind of PRB, why is that because here we have Fe^{3+} based system that is acting as an adsorbent here, right and so that is why you see that the concentrations of Fe^{2+} throughout the system both upstream and downstream and within the PRB are you know more or less pretty low, right that is something that we see here.

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So, moving on and here though for bone char based PRB, right and I think phosphate was the issue here site, so we are not looking at ferrous iron here we are looking at the phosphate concentration and milligram per litre, okay and keep in mind here that it is not the scale here is logarithmic scale 0.1, 1, 10 and so on right, so what does that mean let us say if I look at this particular case you know, this more or less means that the concentration here is 10 times what is it here; what it is here, so this is more or less negligible compared to this particular case, right.

So, again what are we looking at; we are looking at the phosphate concentration here, right again the hypothesis was that for this particular kind of PRB material that you know it will have uranyl phosphate you know uranium precipitating out in the form of a uranyl phosphate and such, right and that is something we looked at they I believe the relevant molecular formula and so on, right.

So, obviously one of the aspects that we looked at though was that when we were evaluating this material or when the relevant people who are evaluating the material and we looked at this particular data, we saw that some of this particular bone char material was you know leaving this particular system and traveling downstream right, I think that is something we looked at as in we looked at the filter and unfiltered samples.

And we saw that with respect to there was a particular deviation with respect to the relevant what do we say, concentrations right, why is that because some particulars collides were leaving the system let us say, right but obviously, again we looked at the data and we saw that these

collides were being again entrapped within the soil, so again but there is still an issue, so let us try to look at that or understand in terms of this system.

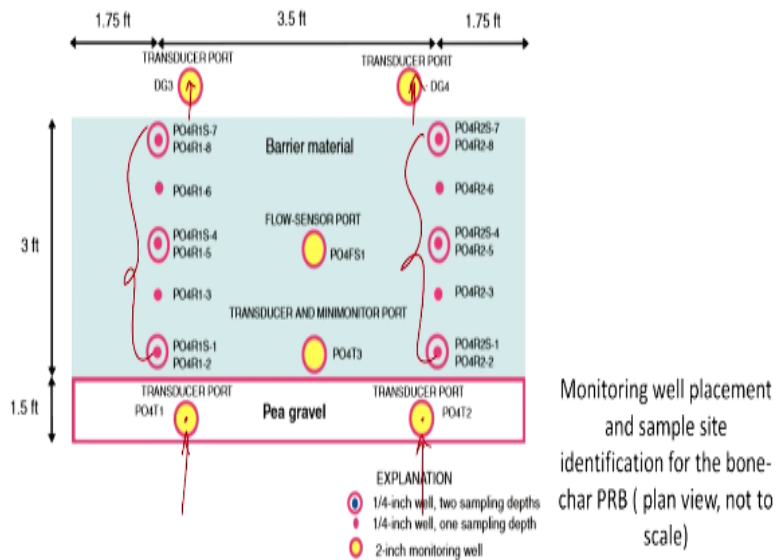
So, up gradient within the well and down gradient, though right and let us look at the data so initially, we have relatively low concentrations of phosphate pretty low right, 0.1 to 0.01 milligram per litre, obviously it varies with season but something that you would expect right but obviously, within the PRB across all the particular, almost all the particular monitoring locations within the PRB, you see that you know the phosphate is you know release let us say or you know you have phosphate in the particular aqueous phase, right.

This is the phosphate obviously in the aqueous phase and that is something you know that hints at the change in phase let us say and you see that the concentrations are pretty high or remarkably high, right and that is something that you need to make sense of in the context of understanding that I know these particular what do we say compounds or the barrier material pardon me seem to be mobile let us say.

But typically, you want your PRB material to be immobile so that is something that we need to look at or consider, right and obviously you have; you can have dissolution of the relevant material of this particular bond char or phosphate base PRB but as you see though downgrade; the down gradient, the concentrations are not that high though they are higher or relatively higher maybe compared to the upstream but down gradient they are not.

Again why is that; the reason lies in that we have collides being formed and let us say you have soil and now this collides are traveling along with the groundwater after they left the PRB, they are traveling along with the groundwater but again you have size, it can be entrapment or adsorption onto a soil, what this shows though is that even the; even though the relevant PRB material has or is mobile and leaving the system let us say or has the potential to leave the system, it is not traveling a great distance downstream though.

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So that is something that we can understand from this data right, obviously you know coming in; water coming in concentrations of phosphate are relatively low here, right and then we saw that the concentrations at these wells of phosphate are pretty high but we see that down gradient though the concentrations are not that high, right so let us move on here.

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ACTUAL COST AND DURATION OF PROJECT PLANNING		
Project phase and approximate duration	Tasks	Cost, in U.S. dollars
Phase I March 1, 1996 to March 15, 1997	<ol style="list-style-type: none"> 1. Project planning and Site selection 2. Laboratory testing of reactive materials 3. Selection of reactive materials 4. Regulatory permitting 5. Site Health and Safety Plan for site characterization 6. Site characterization 	\$280,000
Phase II March 16, 1997 to August 15, 1997	<ol style="list-style-type: none"> 1. Design of permeable reactive barrier structures 2. Design of monitoring network and Logistical planning 3. Analysis and awarding of subcontracts 4. Development of Health and Safety Plan for construction phase 	\$148,000

So, obviously until now we looked at the relevant aspects how did we go about that let us just summarize this, we looked at or they looked at rather you know uranium contaminated site among other heavy metals also being present, right and they looked at the case of conducting what do we say, field trials, again keep in mind that this was I believe one of the initial cases for what do we say field trials and then full-scale emplacement of PRB's.

So, obviously extensive background work was required, so initially they tried out a lot of materials for batch systems let us say and see whether they worked or not based on that they screened them down let us say to 3 kinds of process and then from those process, they chose different materials or materials that would you know followed those types of process, what were those process?

One was precipitation, one was adsorption, one was reduction and then precipitation, right so in this context they chose materials and then conducted the column studies, right looked at adsorption, desorption and equilibrium or breakthrough what is the case, why is desorption relevant let us say, if all the uranium is removed, you still have the PRB there and then the contaminated groundwater; uncontaminated or the pure groundwater comes in contact with this PRB, if the relevant uranium again is desorbed into the groundwater that is an issue.

Obviously, in that context the relevant data was looked at, we looked at or analysed that moved on and then chose one particular material for these 3 materials or such and then we analysed the relevant data, so as you see as we looked at let us say from you know, all these sets of data or you know humongous amount of information that is available, we see that zero valent iron based PRB at least for the one that they chose let us say you know was much better in almost all the aspects with respect to reduction and precipitation of for uranium let us say, right.

There was no breakthrough let us say and the concentration was less or is almost 0 or negligible of uranium anyway, right and again zero valent iron was not mobile or such, yes that is something that we see or no too, yes but obviously dissolved concentration is low but I think that is balance our trade-off that is acceptable here right, so obviously we looked at the relevant aspects.

But now we are going to look at let us say the other important aspect which is the cost let us say which are the cost, right so initially, let us say I think the estimate was for around 2 lakh 50,000 dollars or a quarter of a million dollars, right again if we compare that to other process let us say pump and treat or such for a year or 2 years let us say considering capital cost and such it will be around 7 million.

Million means I believe 10 lakhs, right or 70 lakh US dollars compared to let us say quarter of a million or 2 lakh 50,000 dollars, so you can understand the relative cost here, right but again

this data is obviously for let us say a field scale emplacement and I am comparing the data for maybe a full-scale pump into each system, so we cannot compare that we cannot have direct comparisons.

But you can still understand the degree of what do we say, difference in the cost right, so here let us look at the final cost for this particular PRB and let us see what are the major aspects that you know increase the relevant cost let us say, so here we are going to look at the initial phase right, obviously project planning and site selection is an issue, yes and laboratory testing of reactive materials, this was the one for the batch studies or column studies, right.

Selection of reactive materials again from column studies, regulatory permitting obviously people need to deal with relevant regulations and the relevant cases, right so that is something out here and site health and safety plans for site characterization as in to see to it that you know it is relatively safe for operation and obviously, the major aspect would have been site characterization.

You know cost were understanding you know or you know analysing the particular site or site characterization, so you see that it is around quarter of a million or 2 lakh 80,000 dollars and phase 2; we have obviously the design of the PRB that is something we know how to do the thickness we can get that if you have all the relevant data, design of obviously the monitoring network in logistical planning, typically monitoring network is key here, right.

And analysis and avoiding subcontracts minor issues with respect to their management and again development of health and safety plan again, the cost here though again because they are mostly what do we say office relevant or blue-collar type jobs and the relevant work, so you know you see the costs are relatively less, right but typically, site characterization is relatively costly and that is what would have contributed to the cost here, right.

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Project phase and approximate duration	Tasks	Cost, in U.S. dollars
Phase III August 20, 1997 To September 4, 1997	1. Purchasing and shipment of material, supplies, and equipment	280,000
	2. Excavation of trench	150,000
	3. Installation of monitoring network	246,000
	4. Placement of reactive material and backfilling/ re-contouring operations	
Total		<u>\$674,000</u>

So, again we looked at two phase and obviously, the third phase is purchasing shipment and so on, excavation of trench maybe not that costly but so adding to the relevant cost, installation and then placement of the PRB or you know constructing the PRB, if I can say that and recontouring operations, so that you know the site is not affective that again adds up to about a quarter of a million.

So, what did we have for phase 1, I think around 2 lakh 80,000 dollars and for phase two, I think 1 lakh 50,000 dollars, right and you can see how the costs add up, right to around what do we say 6 lakh 75,000 but still you see that it is pretty less than what do we say what you would consider for any other kinds of treatment systems but obviously for PRB, the site condition should be suitable, the type of contaminant and so on.

But again in this case we do see that you know what that its typically economically feasible and we see what are the major aspects here again, the costs are what do we say cover all the aspects as in the logistical cost with respect to purchasing shipment of material and such again, zero valent iron is relatively cheap, bone char too and amorphous ferric oxy-hydroxide is cheap too.

So, again these materials are not costly and again, obviously that adds value to your particular project, right.

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CONCLUSION

- PRBs are an efficient and financially viable means of remediating uranium contaminated groundwater.
 - Attenuate other contaminants. ←
 - The results of this project have wide applicability.
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So, in conclusion what can we you know decide though, we can decide that PRB's are in efficient, right and more importantly, financially viable means, right of remediating uranium containment groundwater or any other groundwater contaminated with let us say the relevant type of contaminant obviously, in this case we looked at uranium containment groundwater but obviously, it is applicable to you know different aspects that is something we looked at in great detail earlier, yes.

And obviously, you know as we just discussed you know it can attenuate other contaminants either by reduction or by even for acid mine drainage we mentioned that if pH is the issue, we can have a barrier or reactive media that let us say acts as a base let us say to neutralize that particular acid that is something else, even heavy metals let us say you can have reduction and precipitation let us say, right.

Or you can have barrier that just increases the pH such that the heavy metals are precipitated out yes that is various applications and again keep in mind that this project was one of the initial projects let us say and as you can see then they have wide applicability, right again what are the aspects though, if we looked at some of the pictures let us say you know structures have subsurface, monitoring is pretty limited let us say, yes before, after and at the sides.

And then you know you can get your relevant analysis done, right so, I guess with that I am going to wrap up the permeable reactive barrier based aspect and we are then going to move on to the relevant aspect which is natural attenuation and also bioremediation within that context in the next session, right and I guess I am out of time and thank you.