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

Lecture – 45
Case Study: In-situ Chemical Oxidation: Part - II

Hello everyone, so again welcome back to the latest lecture session, again a very quick recap of what we have been up to, so in the context of in situ chemical oxidation, we are looking at a particular case study, right and that particular case study, we were looking at a site and I believe South Carolina, right, where you had this US Army or US Marine Corps base let us say and there you have a dry cleaning unit, where they were using per chloro or tetra cholro ethylene let us say, right.

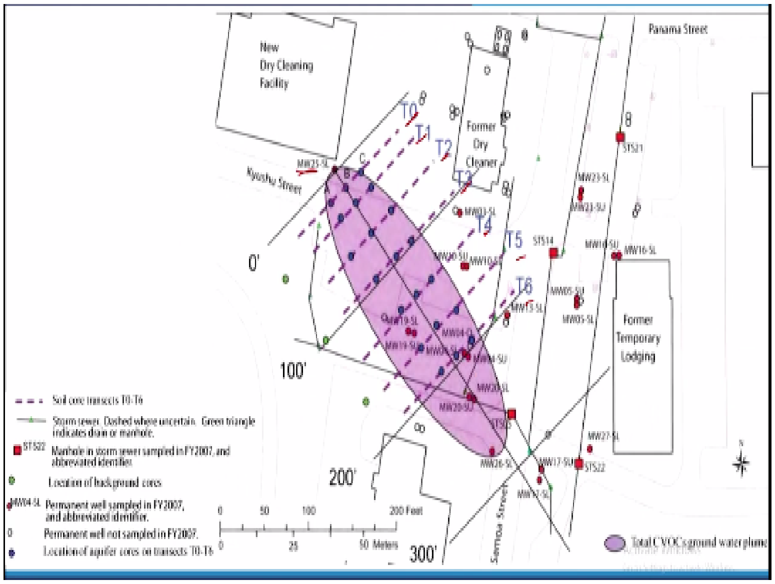
Chlorinated solvent; that is used for industrial purposes let us say, right or is an industrial solvent right and due to a one time release or spill and also due to continuous small releases, you have 2 contaminated zones, let us say near that dry cleaning unit and obviously you are also going to have the relevant by products or degradation by products let us say that you would expect like TCE, DCE and vinyl chloride, let us say, right.

So, the case is that these are hydrophobic compound, so while also being transported by the water, there also be adsorbed on to the soil, so you need to have what do we say some particular case let us say that can remediate both this particular contaminate soil and the relevant water let us say right and this particular site, they looked at application of permanganate let us say and until now we just try to understand the site.

As in what do we have now; we have a shallow region let us say, which here is remarkably hydraulically conductive or has high hydraulic conductivity, right and also deep region which is not or which does not have; has a hydraulic conductivity but nevertheless has some considerable hydraulic conductivity, let us say right and the other aspect was that you know most of the shallow region was of sand let us say.

So, there adsorption on to the relevant soil may be might not be such an important aspect but again as we go further down let us say, I think we do know that around 18 feet or 17 feet, you have this clay layer and thus you know what do we say, a clay again typically has higher organic carbon fraction let us say, right, a fraction of organic content will typically be higher and so you can also assume that you know in that relatively deeper region let us say, the organic carbon content is relatively higher, all right.

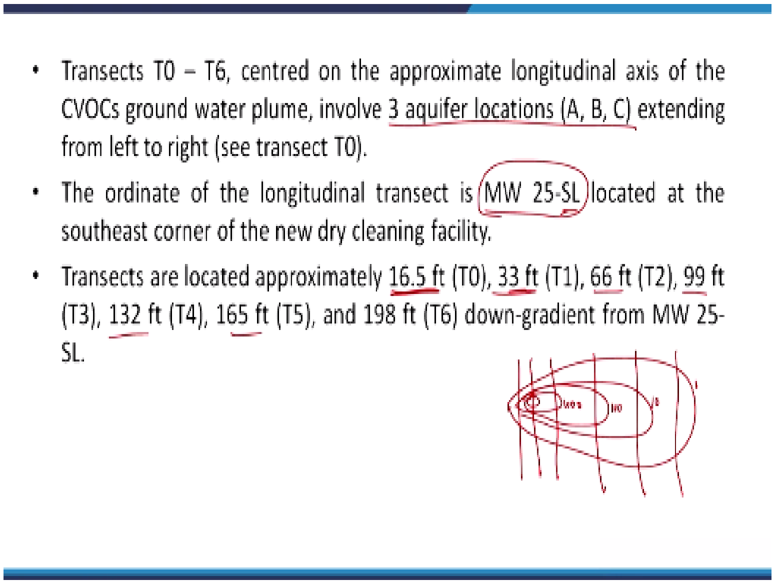
(Refer Slide Time: 02:39)



So that is something I believe we have looked at until now and we started looking at the conceptual model and the people have looked at this particular model and the contaminant is source that this particular location, so there are 2 sources but here we are looking at one particular source, this is the one particular source and keep in mind the relevant name of this particular well which is MSW 25 let us say, right.

And you have soil samples taken along the lateral direction at these locations, right and also let us say, longitudinally too, right, so these are the aspect that we have looked at until now, right, so let us move further.

(Refer Slide Time: 03:09)



- Transects T0 – T6, centred on the approximate longitudinal axis of the CVOCs ground water plume, involve 3 aquifer locations (A, B, C) extending from left to right (see transect T0).
- The ordinate of the longitudinal transect is MW 25-SL located at the southeast corner of the new dry cleaning facility.
- Transects are located approximately 16.5 ft (T0), 33 ft (T1), 66 ft (T2), 99 ft (T3), 132 ft (T4), 165 ft (T5), and 198 ft (T6) down-gradient from MW 25-SL.

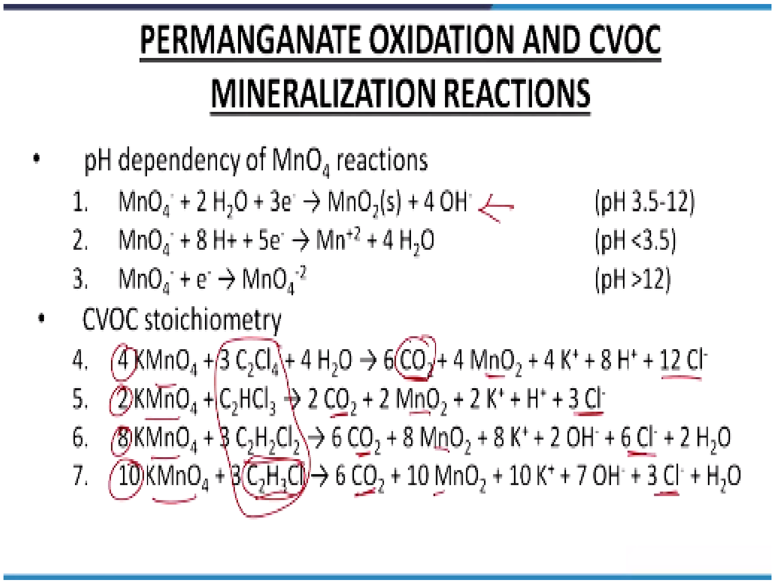
So, as again as I mentioned transects T0 to two 6; T6, pardon me on the longitudinal axis of the CVOC's and also 3 lateral locations; A, B, C right to understand the diffusion and dispersion let us say in the lateral directions, right, so both longitudinal direction to understand the effects of obviously, transport of the contaminant due to advection as in how is the groundwater transporting the relevant contaminant.

Obviously, groundwater flow velocity are relatively less, so thus you will also have advection or dispersion in the x-axis lets us say, saying that here I am assuming that this is my x-axis let us say and obviously, in the y-axis, you have the relevant dispersion let us say, right or diffusion that is what we have out here, right. So, as I mention that we are the source is at MW 25 SL, right, shallow well more or less, right.

And here we have a different transects but the key aspect is initially, obviously let us say, right you are going to have higher concentrations nearer the source, right, so as in if this is my source, let us say, my plume let us say with increasing concentration or decreasing concentrations will be something like this, right, so this one will have let us say 1 ppb, this one 10, 100, 1000 and so on, so obviously, what did they do?

They took samples nearer to each other, initially and then at greater distances that is what you is here, 16.5 feet and then 33 feet, relatively closely spaced and then again uniformly distributed but at you know I think, double the distance between each of these particular transects let us say that is something to keep in mind and what is the reason; obviously, because of this kind of a profile that you would expect now, right.

(Refer Slide Time: 04:54)



PERMANGANATE OXIDATION AND CVOC MINERALIZATION REACTIONS

- pH dependency of MnO_4 reactions
  1. $MnO_4^- + 2\,H_2O + 3e^- \rightarrow MnO_2(s) + 4\,OH^-$ ← (pH 3.5-12)
  2. $MnO_4^- + 8\,H+ + 5e^- \rightarrow Mn^{+2} + 4\,H_2O$ (pH <3.5)
  3. $MnO_4^- + e^- \rightarrow MnO_4^{-2}$ (pH >12)
- CVOC stoichiometry
  4. $4\,KMnO_4 + 3\,C_2Cl_4 + 4\,H_2O \rightarrow 6\,CO_2 + 4\,MnO_2 + 4\,K^+ + 8\,H^+ + 12\,Cl^-$
  5. $2\,KMnO_4 + C_2HCl_3 \rightarrow 2\,CO_2 + 2\,MnO_2 + 2\,K^+ + H^+ + 3\,Cl^-$
  6. $8\,KMnO_4 + 3\,C_2H_2Cl_2 \rightarrow 6\,CO_2 + 8\,MnO_2 + 8\,K^+ + 2\,OH^- + 6\,Cl^- + 2\,H_2O$
  7. $10\,KMnO_4 + 3\,C_2H_3Cl \rightarrow 6\,CO_2 + 10\,MnO_2 + 10\,K^+ + 7\,OH^- + 3\,Cl^- + H_2O$

So, let us move on, so as we mentioned earlier, we are looking at permanganate to oxidise the CVOC’s, right, so there are 2 aspects to consider here and we look at these aspects, right, so one aspect obviously is that it is depend upon the pH and why is that; as in kinetics are depend upon the pH to0 let us say or if not the kinetics let us say even the equilibrium let us say too will be depend upon the pH, why is that?

If I look at the half reactions let us say, I see that OH- is given out or I can understand it as the H+ is consumed let us say, so typically, you would want to have pH in relatively lower or you know acidic conditions and that is what you see here, so there are different half reactions, I believe there are 3 half reactions, so I mean O4- let us say can go to I mean go to the relevant solid, Mn+2 and Mn O42 – let us say.

In each case, different numbers of electrons are accepted, right, so electrons are being accepted by Mn O4-, right, so it is an oxidising agent or an oxidant, it is an electron acceptor and an oxidant is an electron acceptor let us say, it is an oxidising agent let us say, an oxidising agent oxidises the other compound let us say and what are these other or target compound, they are CVOC’s.

So, typically they have different what do we say, ranges for what do we say the different kinds of where, let us say the different kinds of or different half reactions are relatively more, what do we say, a suitable if I may say so, right, 3.5 to 12 < 3.5 because I guess it is 8H+ here and here they say it is around or > 12 let us say typically but again, keep in mind that though the source compound is permanganate, the end products can be different let us say depending on the site conditions let us say, right.

Again, there will be different Pe values let us say for each of these or P0 values let us say which will give you an idea about let us say the amount of energy let us say that can be released from each of these half reactions, when they are degrading different products let us say, right and how are you know; what are they going to degrade as I mention, so this is the tetra chloro ethylene or PCE, right and this is the KMnO4 or permanganate that they are adding.

And what is this transforming into now; let us transforming into CO2 and in this half reaction I guess they are looking at this MnO2, the solid being formed and obviously, what else you see; you see that I guess in this half reaction obviously, I guess, right, 8H+ is being released let us say, right and also Cl-; Cl- what is the source of the Cl-; it is from here now, so what are the aspects here that you need to keep in mind?

Certainly that Cl- will be released, right, why is that because carbon, you are oxidising into CO2 let us say, let us try to understand or calculate the oxidation state here, so here it is 2 times x which is x is the oxidation state of carbon here + 4 times of -1 = 0, so 2x = let us say, 4,s o x = 2 let us say, right, carbon oxidation state is + 2 here, right and what is it out here; so it is x + 2 times of -2, right = 0.

So, x = +4, now right, so what is happening here compared to this particular state, where carbon is already actually in its more or relatively oxidised forms as in know that the oxidation state of carbon can variably from -4 to +4 so, as you see +2 its already relatively oxidised but it let us say you know because of the type of oxidant that you are adding or type of chemical you are adding, this particular relatively oxidised compound is now being further oxidised to a more oxidised form of carbon.

As in from +2, it is going to +4, now, how will that happen; by donating the relevant electrons and when you are donating the relevant electrons, you also need an electron acceptor, so what is the electron acceptor, you are particular MnO_4 here, right, we can calculate the relevant oxidisation state of manganese here too, right, so here it is let us say K is +1 let us say, this is $+x$ and -8 4 times $-2 = 0$, right.

So, $x = +7$ right, am I wrong here, I guess not and here lets calculate the oxidation state of manganese here let us say, right, as I mention looks like it is going to a solid phase here right that is something to keep in mind, so $x - 4 = 0$, so x is going to +4 let us say, right, so here it was +7, and now, it is going to +4, right , so what is happening; the oxidation state from +7 is decreasing to +4, how can it decrease now; by accepting the relevant electrons let us say, right.

That is how the oxidation state is decreasing, so where is it; what do we say getting these or you know how is this accepting electrons or where is the; what is the source of this electrons now; that is obviously from your chlorinated toxic compound which is the CVOC, right so that is something to keep in mind, so by products are CO_2 and let us say Cl^- because we are going to look at Cl^- as one of the you know, indicators of this particular degradation going through let us say, right.

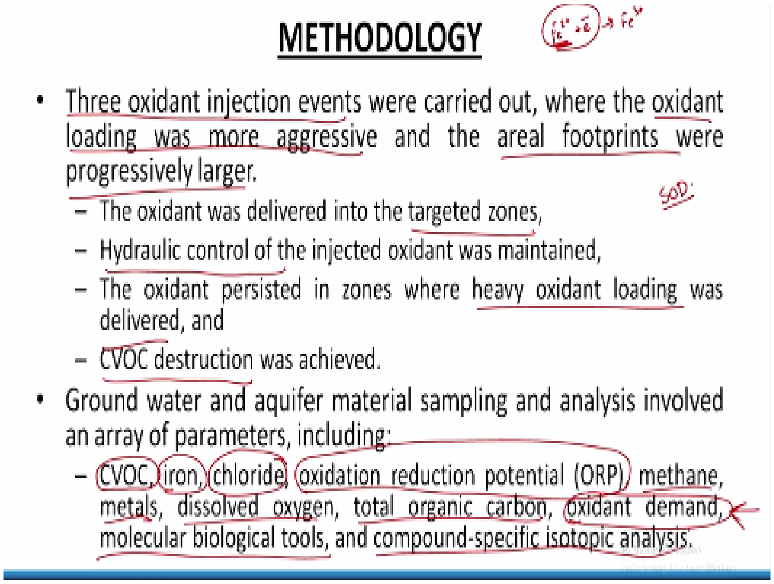
As you can see considerable amount of Cl^- is released out here, right, so let us look at it, so again this is a by-product, this is a tri chloro as you can see 3 Cl^-, right, earlier it was 4 and now 3, again how do we have you know C_2Cl_4 which is what we have initially, as in for dry cleaning they were using this C_2Cl_4 let us say, this is what they were using though, right. So, how do we end up with this C_2HCl_3, let us say, right?

Again, you know in soil let us say, you have reducing conditions typically prevailing, so the compound was reduced to various types of by products and one of those reduced by products was C2HCl3 let us say which is tri chloro ethylene and similarly you will also have di chloro and this is the vinyl chloride again and as we mentioned or discussed earlier, vinyl chloride is remarkably toxic.

But again, as we see with respect to different stoichiometric let us say, KMnO4 can degrade these all these CVOC's at least on paper it can degrade them to or you know it can mineralise them, as you can see CO2 complete mineralisation and typically, for this particular case, they are looking at this half reaction anyway, right, so that is what we see out here and in all the cases, you see that all the Cl- will be typically given out let us say, right.

So that is something to keep in mind, yes, again these are different aspects to look at and go through but again keep in mind that we have a moderately oxidised compound and we are further oxidising it to complete mineralisation, let us say, right and that is what we see here, complete mineralisation to see O2 let us say, right, so that is something to keep in mind, we are adding more stronger oxidant let us say, right.

(Refer Slide Time: 11:49)



METHODOLOGY

$Fe^{2+} + \bar{e} \rightarrow Fe^{3+}$

SOD:

- Three oxidant injection events were carried out, where the oxidant loading was more aggressive and the areal footprints were progressively larger.
  - The oxidant was delivered into the targeted zones,
  - Hydraulic control of the injected oxidant was maintained,
  - The oxidant persisted in zones where heavy oxidant loading was delivered, and
  - CVOC destruction was achieved.
- Ground water and aquifer material sampling and analysis involved an array of parameters, including:
  - CVOC, iron, chloride, oxidation reduction potential (ORP), methane, metals, dissolved oxygen, total organic carbon, oxidant demand, molecular biological tools, and compound-specific isotopic analysis.

So, let us move further, so what did they look at; they looked at 3 phases or 3 intervals they injected the oxidant, right, 3 oxidant injection events were carried out and what did they do or how did they go about it; oxidant loading was more aggressive and also the area was relatively larger each time let us say, initially, the load was relatively less and then the increase the load in second time, third time more amount of permanganate and also the extent of area too that was covered was relatively more.

Again, that is because of based on the relevant data that they got from each of these particular initial injections let us say, right, so let us look at that particular case; oxidant was delivered into the target zones, obviously and also they try to maintain the you know some control of let us say the injection let us say; injected oxidant as in they did not let it flow freely along with the ground water but they wanted to try to travel in the direction that they wanted to.

So, they did try to to maintain some level of control, okay, so the oxidant persisted in zones where heavy oxidant loading was delivered, obviously if I deliver a lot in that particular site you know, that oxidant persisted as in that was stable in that particular case that is one aspect and they mention that the CVOC destruction was achieved, obviously we look at the relevant data let us say, right.

So, let us move further, so ground water in aquifer material sampling and analysis involved obviously a lot of parameters as in typically, we do not look at only one particular target compound, we look at what do we say, other indicators too, right, so let us look at some of these aspects, so obviously, CVOC's which are our target compounds irons; why do we need to look at iron and where is this iron coming from?

Typically, in soil you have iron let us say and iron it is Fe 2+ typically, ferrous iron and it can accept an electron and go to Fe 3+, right and so it can act as a reducing agents, so how is this relevant? So, if you have high iron content, it can also react with magnate or permanganate and also consume some of your permanganate , so that is something to keep in mind, it can act as let us say competitive agent here, right.

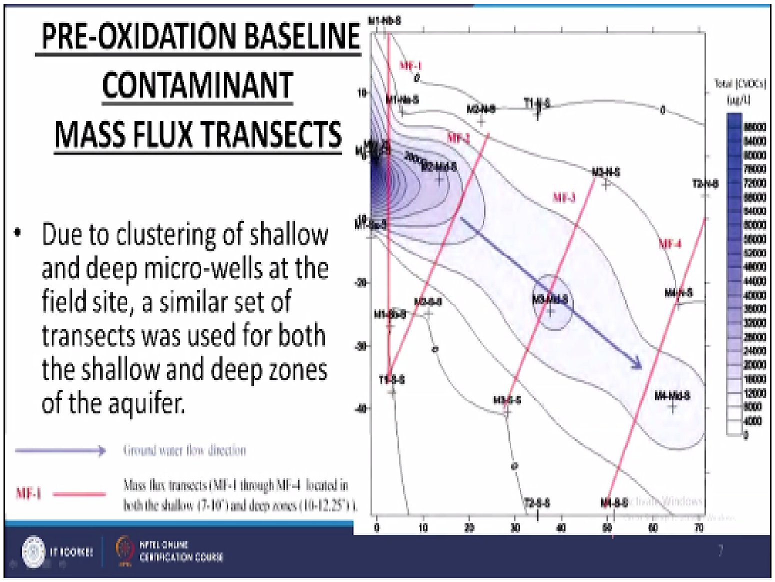
So, iron; chloride, because that is one particular indicator, so ORP readings that will give you an idea about whether typically are reducing conditions prevailing or oxidant what do we say, oxidising conditions prevailing typically, in ground water, reducing conditions will typically prevail because you have no oxygen or relatively low levels of oxygen, right and also because relatively higher content of iron is present typically, Fe 2+ let us say, right.

So, typically you have Fe 2+ which is a reducing agent and other reducing agent let us say and relatively to know oxygen which is an oxidising agent, so typically ORP readings will be negative or low but if you add permanganate and if it is persisting let us say, what would you expect; you will expect ORP to be relatively high, so that is something to look at. So, again methane let us say and different metals to see if there name relatively you know made more mobile or such based upon addition of your particular oxidising agent.

So, Do levels, right, so TOC and again why TOC now; this TOC can also be oxidised by your or you know this organic carbon can be oxidised by your permanganate, right, so what is the issue here; the TOC will also act as an adsorbent for your particular VOC or the containment and also will act as the competing agent for your particular or reagent for your relevant what do we say, permanganate which is your oxidising agent, right.

So that is particular case, so in that context obviously they need to measure this oxidant demand, right, so as we mentioned earlier we soil has its own oxidant demands; soil oxidant demands, so molecular biological tools let us say and compound specific isotopic analysis, again different aspects let us say, right.

(Refer Slide Time: 15:38)



PRE-OXIDATION BASELINE CONTAMINANT MASS FLUX TRANSECTS

- Due to clustering of shallow and deep micro-wells at the field site, a similar set of transects was used for both the shallow and deep zones of the aquifer.

Ground water flow direction

MF-1 Mass flux transects (MF-1 through MF-4 located in both the shallow (7-10') and deep zones (10-12.25')).

So, let us look at the pre oxidation baseline contaminant, right so this is what we have initially let us say for based on actual data, so this our MWS 25 well, where we had the highest concentrations so here we; this is in ppb levels but that is 88,000 ppb or 88 ppm that is remarkably high, way beyond the relevant standards let us say, right and again, keep in mind that these are CVOC's okay but it is the total but I again as we mention vinyl chloride, DCE, TCE and TCE are remarkably toxic compounds with very low what do we say standards let us say, obviously, right.

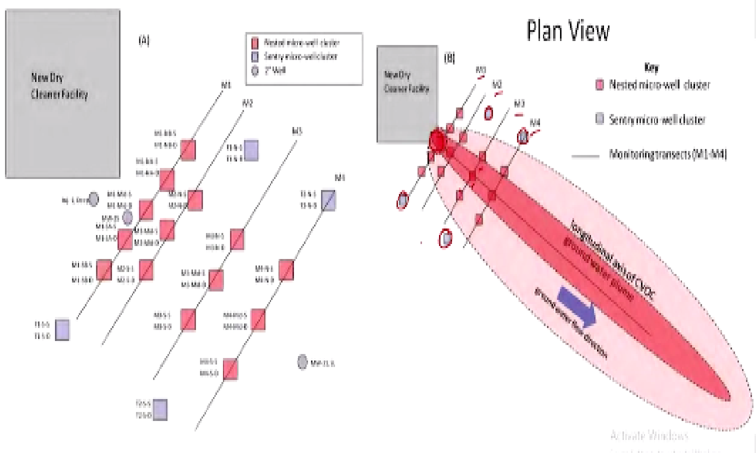
So, you can see the direction of the ground water flow, which is this and the different mass flux transects, where thus calculated the different mass fluxes here, right both in the shallow and deep zones that is something to keep in mind, they categorised it as we saw for shallow; one for shallow, from I think 5 to 7 metres or 8 metres, I believe or 10 meters or feet, pardon me and one from 10 to 14 or 10 to 12, right.

So, they looked at 2 regions, right and 2 different kinds of mass fluxes regions, let us say, right and here you see the different plumes or you know the concentrations out here, right and that is something to keep in mind as in typically, ground water is flowing in this direction and that is why the plume is being contaminant or the contaminant is being transported in this direction and due to diffusion and dispersion, you have some lateral transport let us say, right.

So that is something to keep in mind, these are the actual concentrations more or less let us say, right and due to the clustering of shallow and deep micro wells at the filed site, looks like they use the similar set of same set of transects for both the shallow and the deep zones of the aquifer, right, so that is something particular aspect I guess, so right.

(Refer Slide Time: 17:22)

WELL AND MICRO-WELL NUMBERS AND LOCATIONS



So, now let us look at the well and the micro well locations let us say, right, so where is this MSW 25; this is the source location let us say and they looked at different monitoring wells and so on I guess, you can understand these aspects so, typically along the central lines let us say and also laterally let us say, right and obviously they have wells outside the particular contaminant plume to be able to understand the relevant base line aspects or uncontaminated aspects let us say, right.

And where was the contaminated site earlier; it was somewhere out here, I believe right, so plan view; this is their particular model as we discussed earlier, so based on the relevant data let us say that they came up with, so initially they had just the model and then once they looked at the relevant data, they were able to come up with this particular aspect, right, again here is the source, MSW 25, different transects where they will looking at flux, different monitoring locations and so on.

And this entry or these control wells outside the contaminated plume, so that is what we have out here, right.

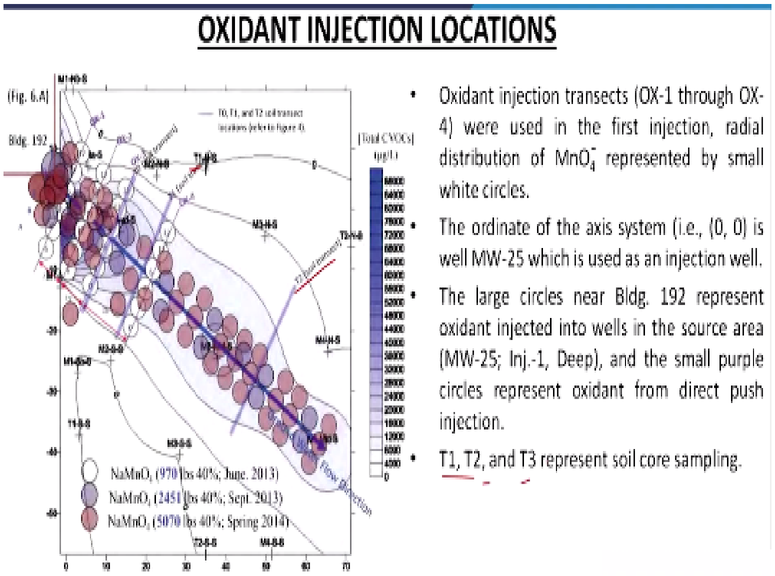
(Refer Slide Time: 18:24)

Construction of flush-mounted paired micro-wells (i.e., shallow and deep)

So, let us move forth, so construction of flush mounted paired micro wells let us say both for shallow and the deep, this S indicates shallow and this the deep let us say, these are for more or less typically, monitoring let us say and again, keep in mind that even though we are calling them wells, keep in mind they are micro wells and that they are paired micro wells as in nested or cluster, right, both for shallow and deep let us say, so that is what you see out here let us say, right.

So, for deep and for shallow let us say, right, these are you know obviously pretty compact now, right, so let us move on.

(Refer Slide Time: 18:57)



OXIDANT INJECTION LOCATIONS

- Oxidant injection transects (OX-1 through OX-4) were used in the first injection, radial distribution of MnO_4^- represented by small white circles.
- The ordinate of the axis system (i.e., (0, 0) is well MW-25 which is used as an injection well.
- The large circles near Bldg. 192 represent oxidant injected into wells in the source area (MW-25; Inj.-1, Deep), and the small purple circles represent oxidant from direct push injection.
- T1, T2, and T3 represent soil core sampling.

So, oxidant injection locations, let us try to understand what we have here, so keep in mind that the oxidant was injected in 3 different phases, right, so 3 different phases as an initially, certain quantity and then more and then much more later on and also over a wider area, so let us look at what we have here, so one injection was in June 2013, September 2013 and spring 2014 let us say.

So, initially around 1000 pounds, 1 pound or 2.2 pounds is typically = 1kg, right so, from that you get an idea about the amount of this permanganate being put in and looks like it is 40% concentrated and now, 2451 and then again double around 5000 let us say right, so white circles initially right, so they put them along these 3 transects typically or 4, pardon me, 3 transects initially now, right.

Initially, only along these 3 or 4 transects, pardon me, right and then obviously, you see a lot more of these blue coloured what do we say, circles and that is obviously indicating that now and the second injection, they; where they injected greater amount of the oxidant, they also covered a wider area as you can see, right, greater amount of a wider area and the third one obviously, they covered obviously a lot more area.

And also what do we say injected more of this particular contaminant not contaminant, oxidant into the source location let us say, right or if not the source location where they; the location where they looked at or measured maximum concentrations of these CVOCs, right, so that is what you see out here, right. So, oxidant injection transects, right as I mentioned earlier, they have looked at 4 transects.

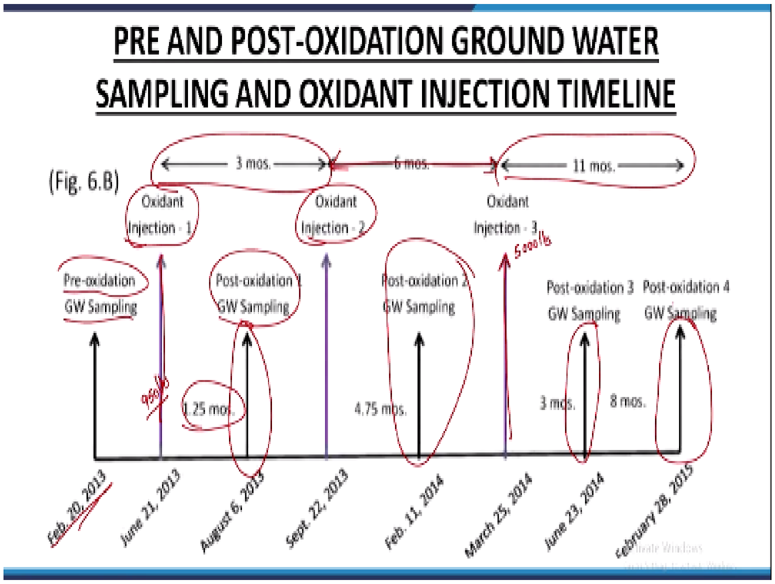
First in; were used in the first injection, radial distribution of NO; MnO4 is represented by the small circles as in so if I injected here, the assumption is that this is the radius of influence of that particular permanganate as in this whole area was covered by that particular permanganate let us say, right or the radial distribution let us say, right, so here that is one particular radius of influence and here it is relatively greater or higher radius of influence let us say, right.

So that means, they injected with greater pressure let us say at that particular location let us say or with greater control, right, as we look at the diameter out here and the diameter out here, right and let us look at that. The ordinate of the axis system as I mentioned is at this particular contaminant site which is MW 25 that is the source as we mentioned, it seems thus MW 25 itself was also used as an injection well, right.

So that is something to keep in mind and as I mention the larger circles let us say represent the oxidant injected into the wells into the source area, right so, in the source area obviously these larger circles represent what do we say injection of the oxidant into the source area itself, right and the others circles typically from the direct push injection now, right that is something to keep in mind.

And where did they take the soil coarse samples let us say, right that is also relatively relevant T1, right and I believe we had T2 to T7 and so on, so T1, T2 and T3 out here, right, so different soil coarse out here let us say, right.

(Refer Slide Time: 22:12)



PRE AND POST-OXIDATION GROUND WATER SAMPLING AND OXIDANT INJECTION TIMELINE

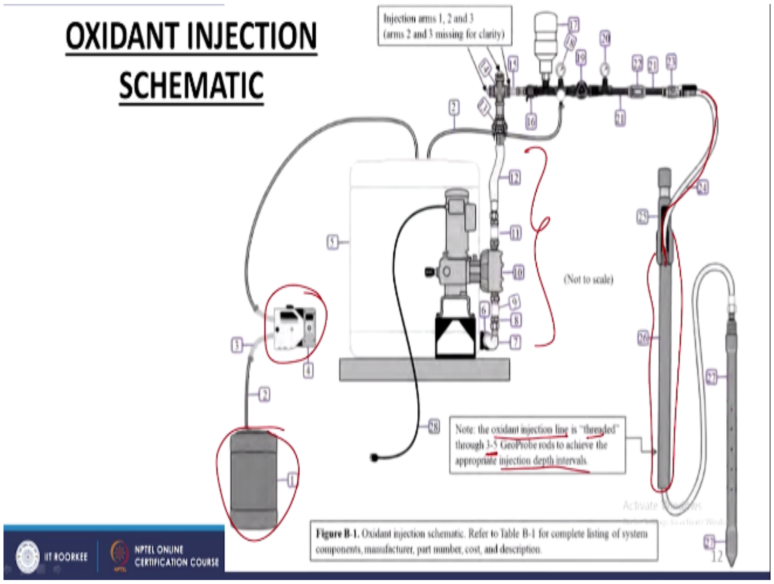
(Fig. 6.B)

And let us look at the pre and post oxidation groundwater sampling and oxidant injection timeline, so this is the first pre-oxidation ground water sampling, let us say in February 2013, then after a few months let us say they put in the first oxidant ground water that around I think 950 pounds let us say, right and then after a 3 month gap and then relevant data being collected let us say after some time which is around 11/2 months after the first injection.

They took some data and then from the first injection after 3 months, the put in the second injection, again they collected the data after certain amount of time around 5 months this time and then after a total of 6 months from second injection, they put in the third injection, I think this time around 5000 pounds, right and then again they monitored it for almost a year let us say, right, a year let us say, right.

So, what do we see here; obviously, monitoring and different levels of injection as in typically, obviously, you do not just dumped everything in one go or in 1 trail, again it is a protracted process right, so you are going to put some stuff in let us say based on your particular model at the different locations, then you look at the relevant behaviour let us say which we are going to look at and then based on those results, you are going to take the sampling further based up on your particular change in the plume shape and distribution let us say, right.

(Refer Slide Time: 23:39)



OXIDANT INJECTION SCHEMATIC

Injection arms 1, 2 and 3 (arms 2 and 3 missing for clarity)

(Not to scale)

Note: the oxidant injection line is "threaded" through 3-5 GeoProbe rods to achieve the appropriate injection depth intervals.

Figure B-1. Oxidant injection schematic. Refer to Table B-1 for complete listing of system components, manufacturer, part number, cost, and description.

So that is what you can see or understand out here, let us move on, so let us look at the schematic let us say how are they injecting that this is the actual what do we say, injected that they used source for KMnO4, a controller here and then the relevant pump and the relevant assembly let us say and let us look at what they have here, you know how did they injected the oxidant injection line, this is the oxidant injection line is threaded as you can see it is threaded through 3 or 5 such geo probe rods.

These are these geo probe rods let us say and depending upon the depth towards they had to inject, they chose different number of these geo probe rods let us say towards this particular oxidant injection line was threaded let us say and then a proper injection depth intervals, you know they could injected through this particular probes let us say right, so depending on the relevant depths obviously, they change the relevant; what do we say probe length let us say right.

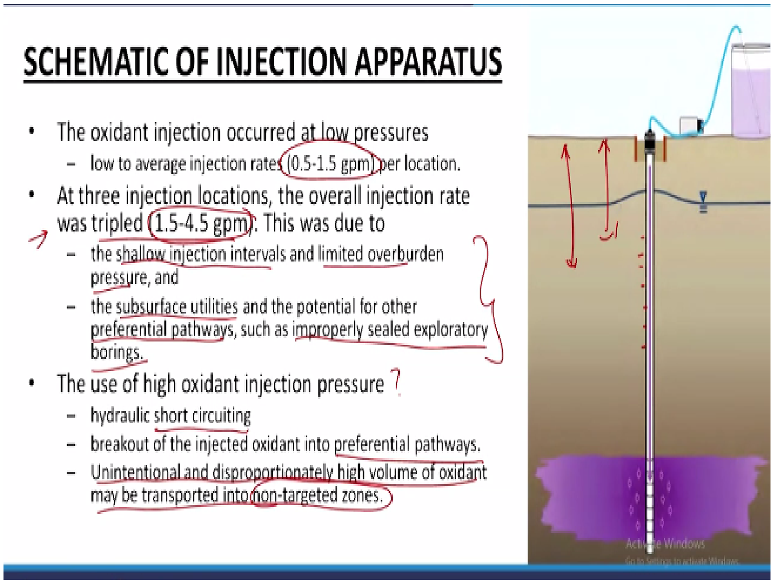
(Refer Slide Time: 24:34)

So that is what you see out here and this is the actual operators I guess, right, again as you can see, you know, permanganate injection let us say and that too at relatively shallow depths, so again it is relatively compact assembly right and it is not humongous task but the data collection, the analysis, the modelling does obviously take considerable time and obviously without that you do not know where to inject, how much to inject and so on.

As in without the relevant concentrations, you do not know how much manganese to inject, right because you know the stoichiometry and as is only if you know how much contaminant is present and from that you can calculate the amount of permanganate required, the amount of soil oxidant demand out there and taking into this account in a factor of safety, you will be able to inject the amount of required permanganate, right.

So, obviously these are the aspects that come into play and this is one such particular aspect out here or one particular pump up out there, right.

(Refer Slide Time: 25:25)



SCHEMATIC OF INJECTION APPARATUS

- The oxidant injection occurred at low pressures
  - low to average injection rates (0.5-1.5 gpm) per location.
- At three injection locations, the overall injection rate was tripled (1.5-4.5 gpm). This was due to
  - the shallow injection intervals and limited overburden pressure, and
  - the subsurface utilities and the potential for other preferential pathways, such as improperly sealed exploratory borings.
- The use of high oxidant injection pressure ?
  - hydraulic short circuiting
  - breakout of the injected oxidant into preferential pathways.
  - Unintentional and disproportionately high volume of oxidant may be transported into non-targeted zones.

So, let us move on, so this is the typical schematic, so this is the source obviously as we discussed, this is the simple schematic and so through the pump, they let it go through and at that particular location due to the pressure and the relevant control that they are trying to maintain, it is going to spread and let us say this is what I was calling was the radius of influence let us say, right.

So, depending upon their particular priorities, they let it what do we say, spread to a particular radius of influence let us say, right. So, let us see what we have; see oxidant injection occurred at low pressures, right and low to average injection rates per location, they looked at low to average injection rates which is 0.5 to 1.5 gallon per minute, 1 gallon is approximately = I believe 3.7 litres, right.

So, you will get an idea about that so, around let us say, 1.8 litres per minute let us say, right which is obviously not a very high rate, so that is what they are referring to here. So at 3 injection locations, the overall injection rate was triple, they increased it and why is that again, we are looking at some of the practical aspects out here, right because let us say the shallow injection intervals and limited over burden pressure let us say.

So, let us say at the shallow regions let us say, right it seems they looked at limited, what do we say, close the space injection intervals let us say and also let us say because of limited over burden as in the over burden was relatively less out here in the shallow region, right that is why they you know increase that to 1.5 to 4.5 gallons per minute and also looks like the subsurface utilities like say the pipelines and so on.

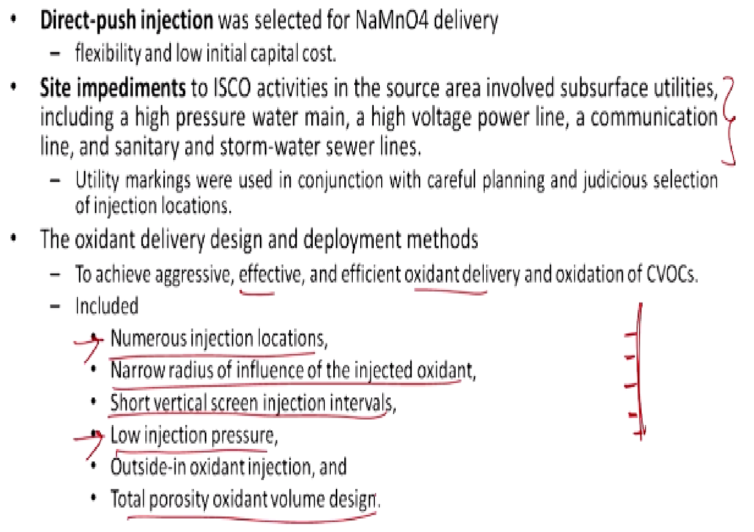
And the potential for other preferential pathways such as improperly sealed exploratory borings as in there were some exploratory borings, right and that again act as let us say involuntary or additional pathways for transport of this particular permanganate let us say, right and use of high oxidant injection pressure is not worthwhile, why is that though; again keep in mind that they typically, maintained low.

And only at a few locations, they increase that due to various reasons, right and why is that let us say, if I pump it out big time let us say, big time as in at higher rates let us say, pump the relevant permanganate at higher rates, what can happen now? Typically, you want to have uniform distribution of the permanganate within that particular radius of influence let us say but if I pump it at remarkably higher rates let us say, so you are obviously going to have short circuiting let us say, right.

And what is that obviously, going to lead to now; it is going to have break out of the injected oxidant into the preferential pathways let us say, so it will try to find the path of least resistance right, rather than having a uniform distribution let us say or leading to uniform distribution, it will yet as in the oxidant which is pumped if it is pumped at a higher pressure let us say will try to find the relevant pathways where it faces the least resistance and take that pathway.

And thus unintentional and disproportionately high volume of oxidant may be transported into non targeted zones, the key is that you might end up going or the contaminant might go; end up go into the non-targeted zones, right, so that is why typically too you do not want to have high oxidant injection pressures though right.

(Refer Slide Time: 28:41)



- **Direct-push injection** was selected for NaMnO4 delivery
  - flexibility and low initial capital cost.
- **Site impediments** to ISCO activities in the source area involved subsurface utilities, including a high pressure water main, a high voltage power line, a communication line, and sanitary and storm-water sewer lines.
  - Utility markings were used in conjunction with careful planning and judicious selection of injection locations.
- The oxidant delivery design and deployment methods
  - To achieve aggressive, effective, and efficient oxidant delivery and oxidation of CVOCs.
  - Included
    - Numerous injection locations,
    - Narrow radius of influence of the injected oxidant,
    - Short vertical screen injection intervals,
    - Low injection pressure,
    - Outside-in oxidant injection, and
    - Total porosity oxidant volume design.

So, let us move on, so direct push injection was selected for permanganate delivery, so again flexibility and low initial capital cost, you looked at the kind of equipment required obviously, right and site impediments, what were the practical aspect that you know were hurdles, or served as hurdles let us say, right, involved subsurface utilities as in they had pipelines, power lines and so on underneath right and also high pressure water main, high-voltage power line communication lines.

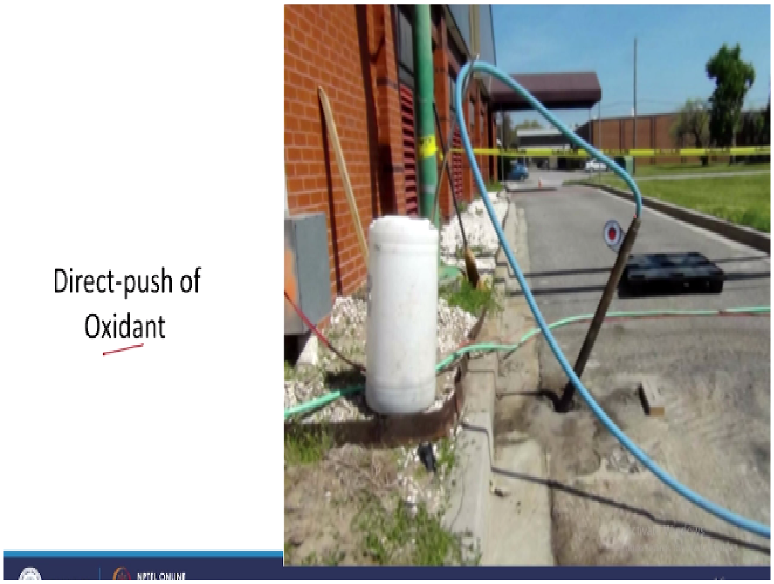
All these are subsurface utilities, so you know obviously, you need to take these into account the practical aspects, we are digging a lot of wells, you are trying to inject a permanganate a slurry, it was in the form of a slurry not a solid not a liquid, right, so you are injecting a slurry but you will obviously have to see to at that it do not damage the utilities and so on and also the sanitary and storm water sewer lines as in you obviously, do not want to you know burst these or you know, damage these or lead to leakage of these particular storm water lines and so on.

Again that is one particular aspect or you know, this was the major hurdle in this particular you know, site remediation let us say, right, so utility markings were used in conjunction typically though you know in US, they have utility marketing alliance let us say for power and so on for use in conjunction with careful planning let us say, right so, again oxidant delivery design and deployment methods what would they?

To achieve effect to oxidant delivery, what did we do; so we looked at rather than just pumping everything through a particular or a few locations and at high pressure, they chose many locations and at low pressures let us say, right, so that is something to keep in mind, so a smaller radius of influence for the injected oxidant, right, short vertical screen injection intervals as in let us say if this is below the subsurface the probe.

The distance let us say was relatively less let us say right, they did not have try to look at you know greater depths between injection towards intervals let us say, right and obviously as I mentioned earlier, they maintain it at numerous locations, low injection pressure than you know less number of locations with high injection pressures, right, obviously outside in oxidant injection and total porosity oxidant volume design based on the total porosity, right.

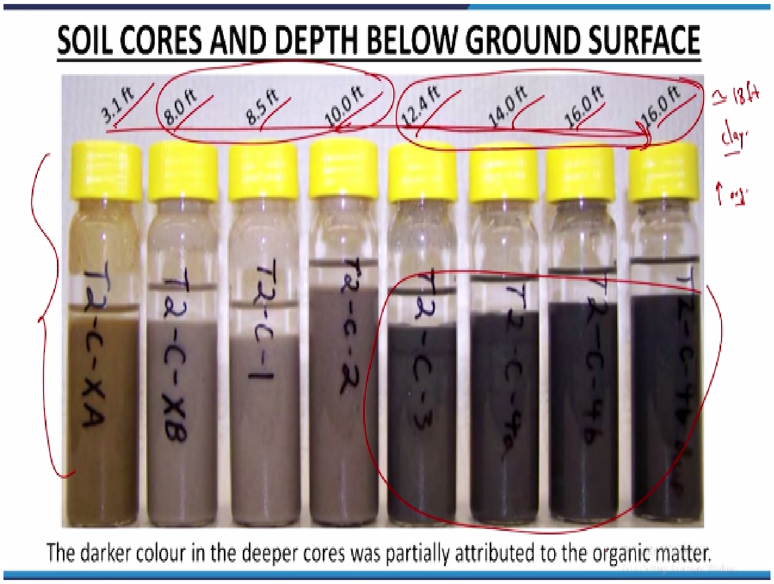
(Refer Slide Time: 30:55)



Direct-push of Oxidant

So, direct push of the oxidant, so this is what they have here, earlier there were 2 cases; one in the source location where they had particular set up and then they were trying to pump it out and this is the direct push of the oxidant as you can see it is remarkably simple, then we looked at the schematic earlier right, so here as you can see it is remarkably simple and relatively compact, right, so that is something to keep in mind here.

(Refer Slide Time: 31:17)



SOIL CORES AND DEPTH BELOW GROUND SURFACE

The darker colour in the deeper cores was partially attributed to the organic matter.

So, soil cores and depth below the ground surface, so they took different samples at different depths, right and obviously, why do you want to do that again, as we can see the colour is darkening as you are going from the relatively shallow regions to the deeper regions, again keep in mind about 17 or 18 feet, you had a clay layer, so typically that means higher organic content right.

So that typically could be this particular transition as you can see from 12 to 16 feet, you see relatively or progressively darker coloured soil and also if you remember, the porosity was very high in this region not porosity, hydraulic conductivity and it was relatively though it was high, it was relatively low in this particular region again, why is that obviously, one reason could be that you know, increasing percentage of clay or the fine sand so on, right.

So, the darker colour in the deeper cores was it seems due to obviously, the organic matter let us say, right, so I guess I am again out of time, so I guess I will need another session or 2 may be too be able to finish this aspect but again, you know this is one of the particular sites where I was able to get let us say, lot of worthwhile data, so it is again worth spending time on this particular site.

Because here we are also looking at contaminant transport and also the other variables in how to understand them in relation to your particular site remediation let us say, right. So, I guess with that I will end today’s session and thank you.