Environmental Remediation of Contaminated

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Lecture - 43

Chemical Treatment

Hello everyone, so again welcome back to the latest lecture session. Again a quick recap of what we have been up to, right. So in general until now we have discussed let us say quite a few options about how to remediate what do we say sites with contaminated groundwater and then we looked at relevant aspects when or some of the aspects anyway about how to remediate sites with contaminated soil or sediment, right.

So in that context I believe we were looking at certification stabilization and looked at a couple of case studies and then we are going to move on to let us say chemical treatment or you know methods based on chemical treatment let us say. Again keep in mind that chemical treatment rarely is a standalone technique, it is typically let us say used in conjunction with other techniques that we have discussed.

Typically, again as you might have understood looking at some of the case studies really do we apply only one particular kind of a remediation technique to one particular site let us say. Again it obviously depends on the complexity or the simplicity of this particular site or the contamination at that particular site, right. So the more complex it is typically let us say you have various techniques or different kinds of techniques used in conjunction. So in this context we are going to move on to chemical treatment.

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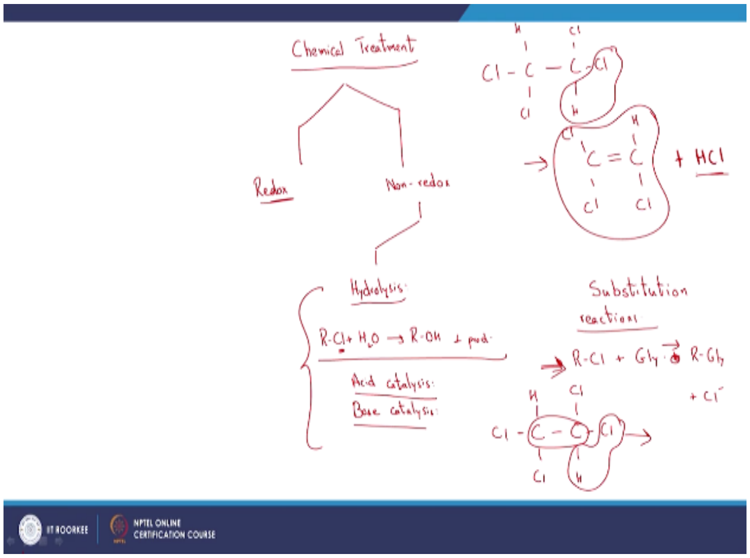

Chemical treatment, right. So in this context we obviously have two classes, one is obviously the Redox reaction based, right, and one the non-redox reaction based. Again Redox reaction what is that about, I guess we did talk about this, so here we typically have more reduced compound and ready to remove oxidized compound and during the relevant reaction, I mean depending upon the relevant redox potentials of these half reactions anyway, we are going to have transfer of electrons let us see.

So the electron donor will typically be the reducing agent and the electron acceptor will be your oxidizing agent, right. So in this context again the aspect to keep in mind is that they need to be in proximity as in let us say in space let us say you cannot have electron donor out here and electron acceptor out here and assume that the reaction or presume that the reaction will go through as an they need to, what do we say, for the electron transfer to occur obviously they need to be in proximity.

So again one other aspect to keep in mind, I think we might have briefly discussed this is that the free electrons do not accumulate out there in the solution, unlike H + let us say so obviously that is one of the reasons or the reason maybe let us say why you need to have the contact of the relevant electron acceptor and electron donor let us see.

Again we are not going to spend a lot of time on this particular chemical treatment but let us just have a quick overview of some of the aspects. Typically let us say non redox reactions we typically come across hydrolysis. So let us say an example can be, right. So typically the CL as we have looked at in the case of either more natural attenuation or certification stabilization, let us say, typically chlorinated solids and toxicity is due to the presence of this particular CL now, right.

So again typically want to reduce the toxicity and typically let us say if you can get that CL out, typically anyway right you can end up reducing toxicity but obviously as we saw in the case of 12 DCA or TCNPC depending upon the pathway you can even end up increasing the toxicity but again that is a different aspect here, right. And here we have one particular case. So in the same case we can have, you know acid catalysis, right, and base catalysis.

So these acids and bases let us say they act as catalysts here obviously. If not catalyst they do obviously play a role here, so again hydrolysis these are one particular a set of reaction that we typically come across. And then the other set of reactions being substitution reactions. For example, let us say if you have RCL plus glycol, goes to R-glycol substitutes, right. Okay. So again, substitution reactions are again pretty common, let us look at one example now.

Let us have one example based on this particular substitution let us say. We have I believe; we can have something like the chlorinated compounds here. And then rather than this kind of a substitution we can have hydrodechlorination, so let us look at that particular case. In that context we are going to have removal of this particular HCL and then we are going to have double bond between the carbon atoms.

So let me write that down clearly here, so I have CL carbon - carbon, H, CL, CL and H. So in the context of substitution reactions we looked at the one where glycol played a role and here we are also going to look at one particular subset which is hydrodechlorination, so as we just discussed we are going to have hydrodechlorination, so HCL out here right. And then double bond as we discussed earlier between the two carbon atoms.

So I am going to have this repeated I guess the structure is, the formula is going to be something like this certainly. So HCL, CL, CL, so this is what we end up with a dechlorinated compound and hydrodechlorination. So these are some of the examples for the non-redox reactions, right. So now we look at the other class of reactions that, those are the ones which we actually come across pretty often and these as we discussed earlier are the redox reactions. Let us look at the redox reactions.

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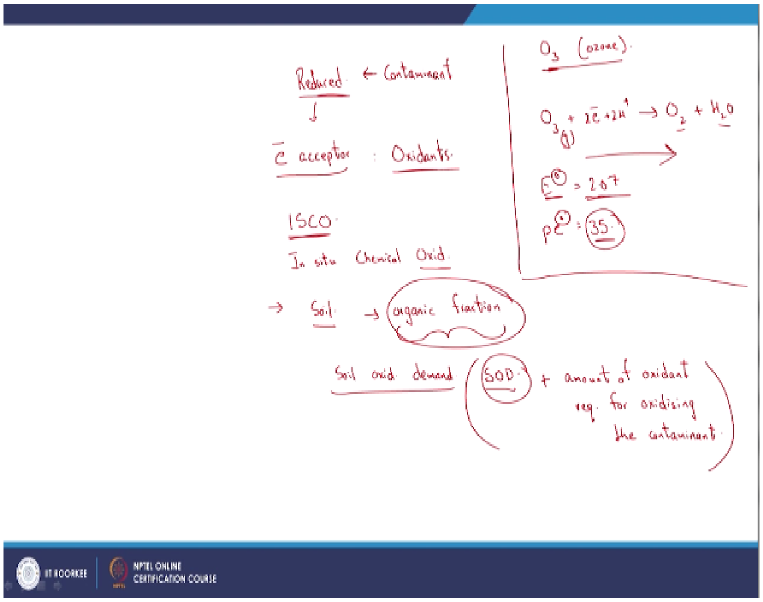

Reduced ← Contaminant

$\bar{e}$ acceptor : Oxidants

ISCO

In situ Chemical Oxid.

→ Soil → organic fraction

Soil oxid. demand (SOD + amount of oxidant req. for oxidising the contaminant)

O_3 (ozone)

$O_{3(l)} + 2\bar{e} + 2H^+ \rightarrow O_2 + H_2O$

$E^\circ = 2.07$

$pE^\circ = 35$

Again redox reactions here depending upon the type of compound or the type of contaminant, you are going to add either the reductant to reduce your contaminant or oxidant to oxidize your contaminant. As we know we can have different types of contaminants. So in the first case we will look at those cases and let us say when your contaminant is oxidized or is in oxidized form. So what do you need to add, it is in oxidized form so you need to give electrons to it or donate electrons to it, so you need to add an electron donor or a reductant.

So in this context obviously you know we are going to look at some of the typical aspects what type of reductants we use, the most common one again this is something we have discussed, there is let us say zero valent iron. Again this as we mentioned in the context of PRBs let us say we have discussed this in great detail so I am not going to go into that great detail again but if you are not, you can go to Fe2+ and 2 electrons, and Fe2+ can be further oxidized to Fe3+, again zero valent iron is used considerably, used quite often now.

And what are some of the applications let us say, for example you can have nitrate or nitrite or you can have chromium and oxidation state 6 which is more toxic and you want to reduce it to chromium in oxidation state 3 which is less toxic and also less soluble, less soluble in the sense that even at relatively low concentrations of chromium 3 in the water chromium is going to precipitate out but chromium 6 is relatively highly soluble and thus more concentrations would be present in or dissolved in the water now, right.

So different cases or examples let us say obviously depending upon the type of contaminants you can have your particular case here obviously you can have chlorinated organics and so on and so forth. So other examples obviously can include Fe2+ but typically Fe2+ by itself let us say is not very effective or has not been seen to be very effective. So in the case of Fe2+ there are different ways to look at reduction by Fe2+, either you yourself add Fe2+ or you know you look at the iron content in the soil.

Typically soil has iron content, again, that is something that we might have seen in the relevant site based analysis or site characterization for the monitored natural attenuation or the natural attenuation based case study. If you remember I think the soil had I think 7 or 5 milligram per liter iron content, ferrous iron right, again the soil typically has iron content, iron out there right. But again as you mentioned, by itself it is rarely been seen to be quite effective.

So it is typically used in conjunction let us say, for example when I say conjunction it means that we have solidification/stabilization let us say. So, we can have this particular ferrous iron as let us say an add mixture let us say and that is going to continue degrading the compound within this particular solidified and stabilized mass. So that is something to keep in mind. Until now we have looked at the case when your contaminants were relatively more oxidized now.

Obviously you will also have the case when the contaminants are relatively reduced forms or in reduced forms, right. So what is you know, what do you need to add here? So the compound is reduced now, right. So let us say, now you want to oxidize the contaminant, right or you want to make it lose its electrons here, right. So what do you need to add, you need to add a compound that can act as an electron acceptor.

Here the contaminant is reduced, so you want to add an electron acceptor so that it can accept the electron from this particular contaminant. So what are we looking for, we are looking at adding oxidants, Oxidizing agents or oxidants. In this context, we typically use the term In-situ chemical oxidization, In-situ chemical oxidization, okay. Again this is a term that is typically used because this is a kind of treatment that is again pretty widely used. So let us look at some of the common oxidizing agents that we typically come across or use now.

So obviously one common aspect or one aspect to consider here is that you know when adding an oxidizing agent, we need to consider that soil as we mentioned earlier has an organic fraction. If you remember when we were trying to analyze different hydrophobic compounds or adsorption onto soil and so forth, the key aspect or the key element here was that soil has some organic carbon that can act as a reservoir for some of these hydrophobic compounds.

That is something that we looked at typically around 1% or 0.5%. So, obviously when you add an oxidizing agent or oxidant, it has different preferences obviously but it will also react with the organic content in the soil. So when we add an oxidizing agent or an oxidant you need to also look into account or take into account the relevant demand from the organic fraction or we are going to call it as soil oxygen demand or oxidant demand let us say.

So this obviously depends upon the organic content or organic fraction of the relevant soil now. So that is something to keep in mind. So whenever you are looking at adding relevant oxidizing agent you also need to take into account the stoichiometry such that you add soil oxidizing agent or sorry, not agent, demand and the relevant amount of oxidant required for oxidizing the contaminant. This is something to keep in mind, right.

Now let us move on to the typical oxidizing agents, one aspect that maybe we might have used in the relevant example was that of ozone. Ozone, so you have ozone which is one of the most strongest or one of the more stronger oxidizing agents out there and this can oxidize or indiscriminately oxidize most of the relevant compounds out there. Again Ozone is a very strong oxidizing agent. So let us look at the relevant reaction here, O3, Ozone again typically in the gaseous Ozone and it is an electron acceptor.

And it typically goes to O2 and H2O again to balance this out we need to have 2H + out here. Again I believe the redox potential, let us say standard redox potential and the P knot values; again what do these two typical parameters give an idea about? Let us say how strong or how strong an oxidant is or how strong a reducing agent is. Typically, the higher the value the better and I think the values for E knot and P knot are around 2.07 and 35. I think 35 anyway.

So I think that can be checked out here. Again these are the standard redox potentials, keep that in mind, redox potential and P knot obviously gives you an idea about the activity of the relevant electron let us say. Again that is a different aspect. Again the P knot values as you can see are remarkably high, that typically means that ozone is very strong oxidizing agent and reaction will go in this particular direction let us say for most half reactions out there.

That is something to keep in mind. So let us move on to the next type of contaminant. So let us look at the next kind of what do we say oxidizing agent let us say we are going to look at.

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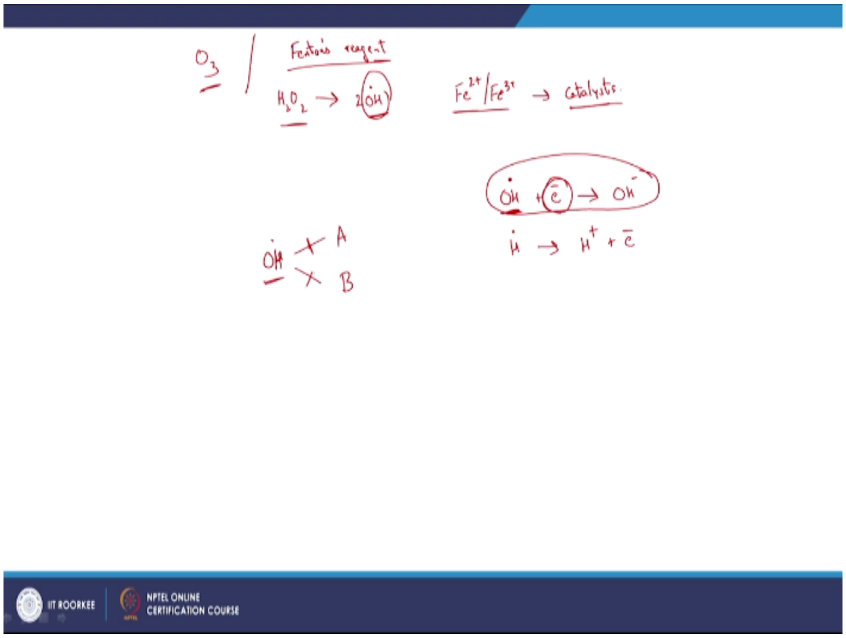

And this involves addition of hydrogen peroxide, again this uses some of the constituents in the soil like ferrous iron and also Fe3 + if present. But these act as catalysts. And this is called the Fenton's reagent and we end up forming something called a hydroxyl radical. Again we have something maybe relatively new, I am not sure if we covered that particular aspect in this particular class. So we are looking at something called radical, here it is a hydroxyl radical.

What is the unique aspect about this hydroxyl radical or any other radical? Typically, electrons are paired but in this particular, or in these radicals you have an electron that is unpaired. So for example that is the reason that why we have this particular simple out here, let us see if I can say so. And this is an unpaired electron, or represents an unpaired electron, so what does this compound do, wants to do,

Let us say it strongly want to accept an electron and moved to its stable state which is OH-. Similarly, you can also have strong reducing agent, so what does this hydrogen radical want to do? It wants to go to it is more stable state H+ by donating and electrons but again in this context we are looking at radicals or the oxidizing radicals and in this context we are looking at hydroxyl radicals. These radicals are probably in general the most, even better than oxygen, or not oxygen pardon me, Ozone in the context of what is the potency of their oxidation or oxidizing capabilities. So let us look at that.

So again as I mentioned earlier we have a Fe2+ and Fe3+ playing the role of catalyst and you have this particular H202 being added. And you have the hydroxyl radical that is produced and as we see here that is a very strong electron acceptor as in it wants to take in the relevant electron and then it is going to, in the manner let us say in this manner oxidize the relevant contaminants now.

Obviously, one aspect that needs to be kept in mind when we are looking at all these aspects with respect to ozonation or such or even maybe addition of hydrogen peroxide or such is that the system needs to be, or the site needs to be porous or permeability needs to be relatively high. Location wise obviously addition of this particular hydrogen peroxide or the relevant agents is going to be a tricky aspect.

So obviously permeability needs to be relatively high. But obviously in the case of ozone, even the bladder ozone you can add or try to bring about degradation with Ozone even in the bladder ozone but obviously for hydrogen peroxide and such you need to have the relevant moisture or water now. So that is something to keep in mind. So we have looked at ozone and then we look at Fenton's reagent.

Typically, we mentioned that hydroxyl radical is a better oxidizing agent than ozone, but obviously what do I mean by let us say greater oxidizing or better oxidizing agent let us say. Typically, I am talking about the potential now. But one other aspect also to keep in mind is kinetics as in how fast the reactions have occurred. Typically, Ozone and hydroxyl radical both degrade their relevant contaminants pretty fast or their targets pretty fast. The kinetics are typically fast, but one disadvantage in this context is that they are indiscriminate.

So if there are compounds A and B and if it as I mentioned here ozone or the hydroxyl radical, A and B, there are two particular targets and this is indiscriminate typically now. But let us say with the kinetics of hydroxyl radical reacting with B are faster than you know, Hydroxyl radical reacting with A, so what is going to happen, this reaction is going to be predominant now, right.

And thus obviously the relevant, I mean depending upon the rate constant and so on, let us say this reaction is going to be relatively slower let us say here, right. And thus here, you are going to have what you say, relatively less removal of A compared to B now, right. So depending upon the mixture of compounds and such, you know that is going to be an issue, right. As in selectivity is an issue out here, right.

So another aspect is, let us say, as we mentioned, you know the kinetics are very fast. So let us say you know, they do not have long half-lives now. They are going to find something to react with, and you know react with them. Let us say, right. So, that is something to keep in mind. That is a slide disadvantage, so you know introducing the relevant system and maintaining the relevant conditions is the key. Why is that? They are very strong oxidizing agents, and they react very fast, right.

So being able to take use of these two aspects is something that is of relevant aspect here. So let us move on to the relevant, you know, other typical oxidizing agents that we use.

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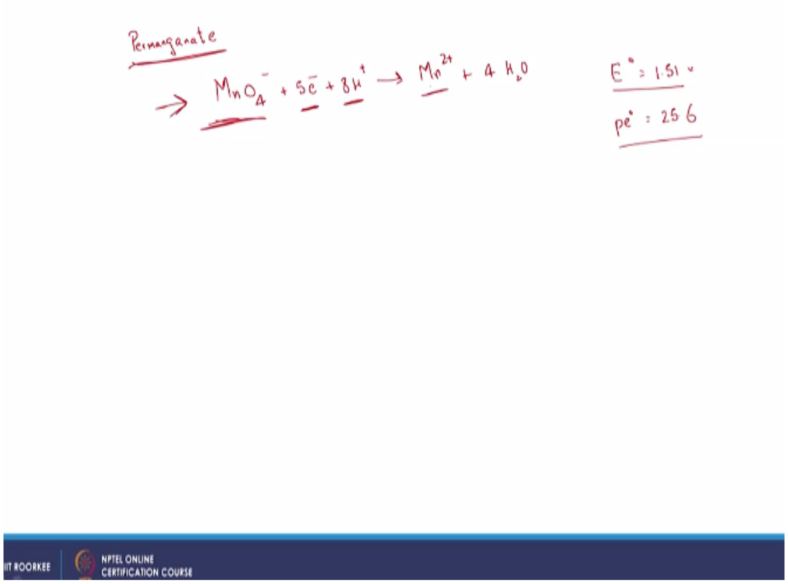

Permanganate

$\rightarrow MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

$E^\circ = 1.51\,v$

$pe^\circ = 25.6$

I believe I have that listed here. So it is permanganate, right. People might have come across this in their laboratory experiments; again as you see, now, again, you know it is an oxidizing agent, so thus takes in relevant electrons. Obviously, keep in mind that, this particular reaction, even the one with, I believe ozonation is, you know, consumes H+, right. So, thus, that will lead to an increase in pH, so that needs to be looked at or that increase in pH needs to be looked at, let us say for possible issues or such, let us say, right.

If required you might have to control that particular aspect, let us say, right. So again, as we see here, the redox potential and p0 values, again p0 is still you know pretty high again, that something to be expected again because as we mentioned earlier, let us say, right, you know, permanganate here is again one of the more stronger oxidizing agents but maybe not as strong an oxidizing agent as your particular Ozone or Hydroxyl radical.

Again when you are choosing the relevant oxidizing agents or even reducing agents, obviously one aspect to keep in mind is that, you did not want to let us say introduce a compound, let us say, that ends up increasing the toxicity of the side, right. So that is some aspect to keep in mind. So here then, in that particular aspect let us say, obviously this stoichiometry is of importance.

As in, even for Manganese, let us say there is going to be a threshold, let us say, right. You cannot have lot of manganese, you know dumped out there in your particular side, let us say. So you need to look at those thresholds, or the standards for the relevant, what do you say, products to, right. So that is something to keep in mind. So let us move on. So, Persulfate, again S2O 8 2-, 2H+, 2 electrons and HSO4-, right.

So one aspect here is that, let us say, you know, Persulfate works in two ways. Either by itself, acting as a strong oxidizing agent or let us say.

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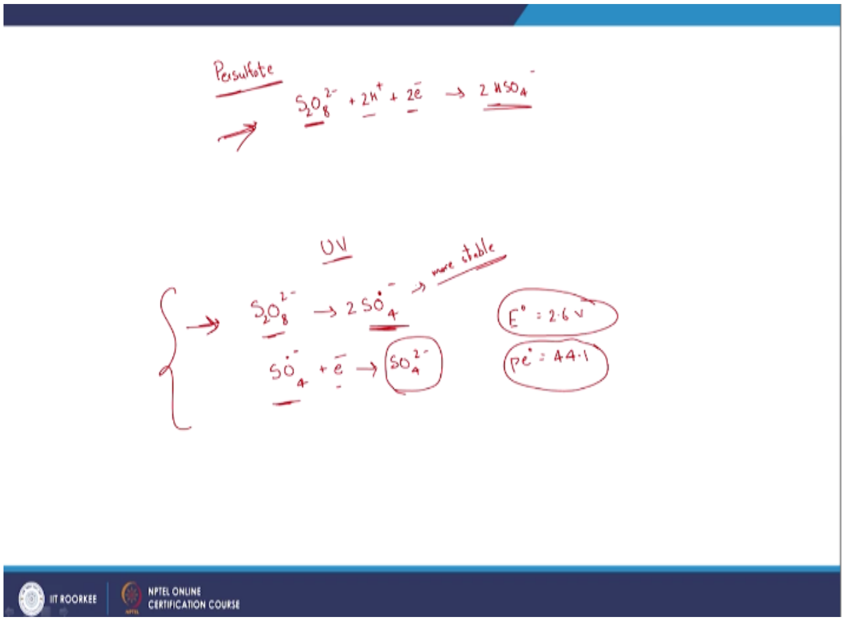

Persulfate

$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^-$

UV

$S_2O_8^{2-} \rightarrow 2\dot{SO}_4^- \rightarrow$ more stable

$\dot{SO}_4^- + e^- \rightarrow \boxed{SO_4^{2-}}$

$\boxed{E^\circ = 2.6\ V}$

$\boxed{pe^\circ = 44.1}$

In the presence of typically UV, let us say or you know such other, what do you say, external source of energy. Let us say, you have this Persulfate radical let us say, right. You have the radical being formed and again see that, it has an electron, what do you say, unpaired electron. So obviously, what does this particular radical want to do? It wants to accept an electron and go to its more stabler state of SO4,2-.

And here again, as you see you know, p0 is pretty high, right. And similarly E0 obviously, but again these are at standard conditions. That depending upon this side characteristic, let us say and so on, they are going to slightly vary, let us say, right. So that is something to keep in mind. Again, two ways, how is that now? Direct pathway and indirect pathway, but in the presence of let us say some source of energy, if not UV, there are other, either heat, let us say or such can be applied obviously you cannot have UV sub surface.

But again, one way that, or one aspect, or in, example, when you might have come across this particular Persulfate, let us say or its application is that, in the TOC machine, let us say or the total organic carbon machine let us say that you might have to measure TOC let us say, you need a strong oxidizing agent, right. So this is the pathway again that is used, either UV S20- or such path ways, you know the combination of those two aspects are used now, right. Again a quick example out there, right.

So again, the direct path way and the indirect path way, right. But one advantage for this, of this Persulfate radical is that; let us say, you know, it is relatively more stable. In the sense that unlike the Hydroxyl radical, let us say, which has very low or less, low half-life let us say, very short half-lives, pardon me, right.

You know, this particular sulfate, what do we say, Persulfate radical is relatively more stable. So in which context is this going to be helpful to you, right? So this is going to be helpful to you in this context, let us say, we have lot of organic carbon in the soil, let us say right. Or let us say when you want to introduce your particular compounds, right. But they are not reaching the relevant target, let us say, right.

As in, they are being consumed during the relevant transport with in the soil, let us say or sub surface. So you want a more stable compound, so in that context let us say, this Persulfate radical is of you know greater advantage, let us say, or gives some particular added advantage, right. So that is something to keep in mind, right. So again it is relatively more stable, compared to the Hydroxyl radical. Relatively more stable.

Keep in mind that again radicals are relatively unstable, right, because they are, they have this unpaired electron, they want to either get rid of, or you know pair up with, let us say with another electron. So that is something to keep in mind now, right. So we have looked at you know different types of chemical methods, let us say, right.

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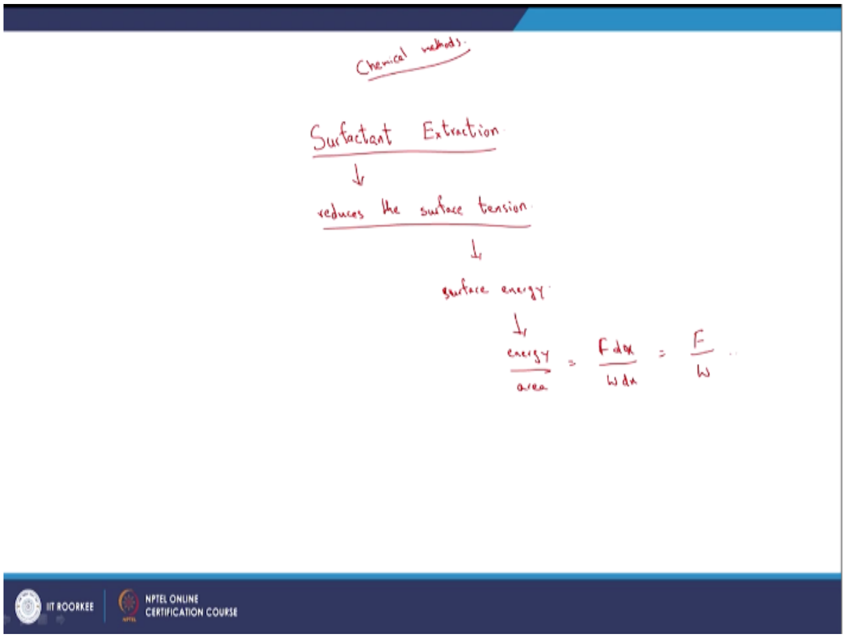

Chemical methods.

Surfactant Extraction

↓

reduces the surface tension

↓

surface energy

↓

$$\frac{\text{energy}}{\text{area}} = \frac{F\,dx}{W\,dx} = \frac{F}{W}$$

So now we will move on to other methods, let us say, you know, based on the physical properties of the relevant, you know contaminant or the site, right. So if you remember, let us say, one of the aspects, when our pump and treat let us say or other such techniques would not work or as we demonstrated by the relevant calculations would not have been feasible, or when let us say you have soil and let us say you have hydrophobic materials adsorbed onto these particular soils now, right.

So how do you or what are some of the ways let us say, that you can, you know, try to address such particular site, let us say, or immediate such particular sites, right. So, maybe, you know, maybe if I can give this particular example, let us say, you have your hand and let us say it is stuck with you know, you have it greasy now. Let us say you are working with grease and now you have grease all over it.

So washing it with water, let us say, right, typically is not useful now, right. Obviously water is polar and your grease is non polar. So obviously you cannot you know, get this grease off your hands, at least certainly not efficiently with water now. So what do you do now, right? So, if you think of it, typically we use soap, let us say, right and what is the role of this particular soap now, right. So it is a surfactant, right, more or less it is; not more or less, it is a surfactant, right.

In that case it decreases the surface tension, let us say or forms an interface between your hand and this particular grease let us say. There by letting the grease move away from your particular hand, let us say, right. So, it is going to form either an interface or decrease the surface tension, depending upon the relevant, what do we say, mechanism out here, right. So similarly here, when the soil too, let us say, we are going to add a surfactant.

So, the next kind of method that we are going to look at is based on surfactant extraction, right. And what are the properties of a particular surfactant now right. I have just mentioned that typically reduces the, or works in such a way that it reduces the surface tension now, right. Typically let us say reduces the surface tension now, right. Again now we have another term, surface tension.

What does this give you an idea about, let us say, right. Its more or less surface energy, right. Or let us say, energy per area, energy per area let us say, right. So if it is Fdx into or divided by Wdx, its nothing but force per unit length, let us say, right. Again these are aspects that we are going to look at later, but again what is the key aspect here? We are trying to form a particular surface, let us say, or decrease the surface tension or form an interface between two different kinds of what do we say phases here, right.

That something we will look at in the next class, because I am running out of time. Again, this is something this as in surfactant extraction, is again something that is used pretty wildly, not wildly pardon me, widely, right. So, one of the key aspects obviously is side conditions as in obviously it needs to be relatively porous and relatively more permeable right. So only then, you can add the surfactant and then pump it out.

So it is maybe in a way similar to pump and treat, but instead of water, your going to add the surfactant let us say, which decreases the surface tension, let us say and let us the relevant NAPL, let us say, be squeezed through two soil particles let us say, right or it also forms a different kind of face called micelles let us say, within these micelles these NAPL or hydrophobic compounds can be absorbed and when you pump out this surfactant these micelles also going to remove the contaminant, right.

Again, this is something that we are going to look at in the next class. And I guess that is it from me today and thank you.