Environmental Remediation of Contaminated Sites
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Lecture – 47
Surfactant Extraction: Part - I

Hello everyone. So again welcome back to the latest lecture session. So in the last couple of sessions we have been looking at or we looked at a particular case study let us say with respect to in situ chemical oxidation right and now we are going to move on to the relevant topic that we discussed briefly maybe a few sessions ago right that was surfactant extraction right.

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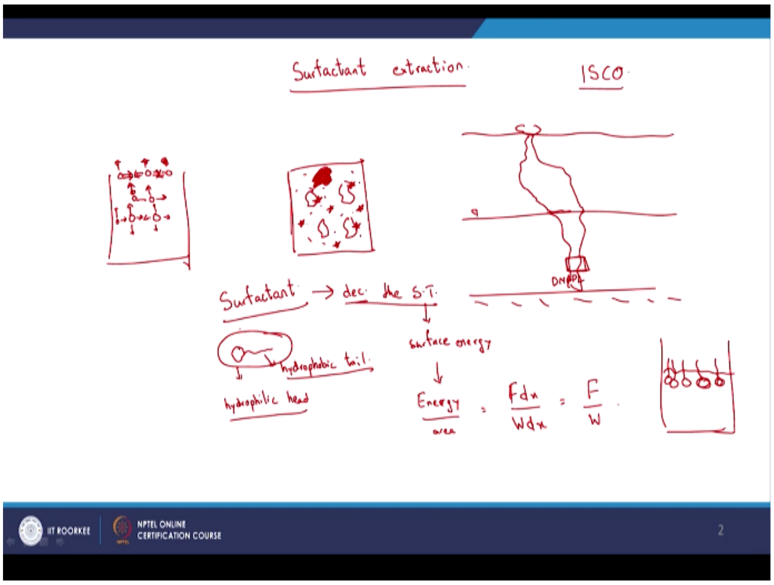

So surfactant or surfactant based extraction let us say right. So until now we have looked at in situ chemical oxidation let us say or you know the relevant and the relevant case history let us see and we did briefly discussed surfactant extraction but let us just have a quick recap of what we have been up to now right. So let us just look at the condition that you would typically face out there.

Let us say if a chlorinated solvent has you know what do we say permeated through or contaminated the relevant subsurface let us say right. So what can you have if you know this is the subsurface and this is my groundwater level, well it would not be like this, there will be some slope or gradient but let us go with that now. So let us say you know there was some spill here and the DNAPL came out here let us say.

And if it is DNAPL it will go through to this semi impermeable layer at the bottom right. So let us say this DNAPL reached here let us say. So if I take this particular sample let us say right if I take this particular sample or if I am for purpose of understanding if I represent that here what am I going to have? I am going to have the soil particles right and obviously the water right.

So if we look at this particular sample and I take that out let us say and try to visualize that. What will I have? I will have soil, obviously the groundwater and what else. I will also have let us say groundwater I will represent by just a few dots let us see. Also, I will have NAPL let us see. You know please excuse my poor drawing skills. Let us just have this blob as this assume that this is the NAPL okay right.

And you will also have some of the NAPL dissolved in the water right and you will also have the NAPL adsorbed onto the soil now right. You will also have some of the NAPL adsorbed on the soil so these are the 3 what do we say phases that we have. What are they? So as in the NAPL dissolved in the water, NAPL adsorbed onto soil and NAPL staying as NAPL itself right. So in the context of pump and treat, I believe we looked at you know pumping this out right.

So pumping out water relatively easy depending upon the site conditions again obviously right but let us say pumping out particular contaminants that adsorbed onto soil as we saw I think the factor of what do we say the time required let us say to pump out the relevant contaminant let us say increased by I think a factor of 10 obviously depending upon the amount of contaminant that is adsorbed onto your soil right.

And then we looked at another case let us say when we have NAPL even very minor fraction I think right I think 0.1% volume let us say or so on or 1% volume. We saw that it takes 100s to maybe I think if you 1000 years to pump that out right. So pumping out the relevant water and trying to remove the NAPL are such when we have desorption and such or assuming desorption right that as we saw was not a feasible option.

So what can we do now right? So we can you know introduce a phase let us say that you know dissolves this NAPL and also let us say tries to dissolve the relevant contaminant into this particular phase let us say right. So the phase that we are going to look at and the one that we are going to introduce is the surfactant let us say right. So what is its role now? So let us say in this particular role what am I going to do?

I am going to introduce a lot of surfactant right you know and then this particular surfactant after you know relevant equilibrium let us say I am going to pump that surfactant out. Surfactant relatively easy to pump out again because of what do we say its ability to form a surface let us say or you know its ability to let us say you know form at the interfaces. Again, we will look at those aspects please.

So surfactant I guess right you know what is its primary role, typically it ends up or reacts in such a way that it ends up decreasing the surface tension let us say right, increasing the surface tension right. So this says obviously property of the surface energy let us say right which is more or less let us say energy per area right and that I think as we looked at right this is the energy force times distance here let us say and here the area let us say right.

So we end up with force per unit length right so surface tension more or less right. Again, what does this surfactant do? Typically, anyway typical action of surfactant is that they decrease this surface tension right. Again, people might have seen or certainly heard of surface tension I am sure or seen or visualize the examples at surface tension typically let us say when you have let us say what do we say in a jar of water let us say maybe.

And undisturbed water let us say and you have what do we say slight bubble and even if you can float what do we say relatively minute pieces of particles on that again why is that because there is surface tension on the you know surface obviously of these you know these surfaces let us say or the water molecules. As in maybe if I can represent it in a layman’s terms, if this is the water molecules let us say right and this is how the force of attraction let us say if I can call that right or going to be let us say right.

But this surface let us say right do not have any force of attraction, this direction right so what do they have? You know there is increased force of attraction at the surface area right. So out here let us say they have forces of attraction in such ways between different water molecules let us say right.

Again, this is the case with respect to water anyway, a generic case again you know we are deviating from it so I would not go further but again the key is that at surface you have you know what you say fluids typically have surface tension alright and these particular surfactants that we add are going to decrease the surface tension now right and how is it possible let us say right.

So when we say surfactant what does it have? It has a head and a tail let us say right and again you know surfactants right again you can think of what you use every day. Let us say you know either soap to wash your hands let us say or you know the detergent that you use to wash your clothes, you know some examples of surfactants but obviously the function is that typically you have a hydrophilic head and a hydrophobic tail right.

So its key aspect is that this particular surfactant has a head and tail right. The head which is hydrophilic or you know wants to or has an affinity to what do we say water and hydrophobic which obviously wants to stay away from water let us say. So let us say how does this act now, let us say if there is water out there and how does it oriented (()) (08:04). This is water let us say on a container you know.

So it is going to, they are going to be oriented like this now right and in such a manner let us say they end up you know decreasing the forces of attraction between the water molecules let us say or in this case let us say the fluid at the surface right. So thereby they decrease the surface tension now right. So again in such a manner they end up decreasing the surface tension now and this is how they orient. Why is that? Obviously as you just mentioned the head is hydrophilic right.

It has an affinity towards water; the tail is hydrophobic now right, so it does not have an affinity for water or rather wants to stay away from water now right. So this is the key aspect for you know almost all surfactants right and again let us look at the aspects that are involved here let us say.

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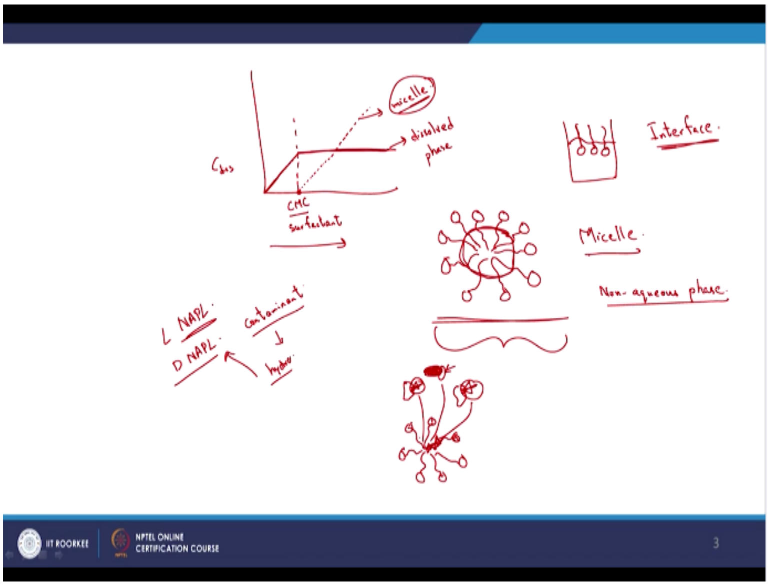

So as I keep adding surfactant to the solution let us say right what is going to happen now? So I keep adding to surfactant to the solution, some of it will be dissolved let us say right. So let us say if this is the concentration of surfactant that dissolves. As I keep adding it, the concentration of the surfactant that has dissolved keeps on increasing but after a certain threshold though you know it is constant now right.

The one that has dissolved, one accumulates at the interfaces now right, so that is something to keep in mind will come back to that. So as I keep increasing or keep adding more concentration of surfactant let us say right. If I keep adding the greater the concentration of surfactant, after a certain time the concentration of the surfactants that is dissolved let us say is you know constant, it does not increase.

So what happens to all the surfactants that I am adding now, so that turns into a phase called the micelle phase. So this is the dissolve phase right and this particular phase is the micelle let us say right and again when is this formed, only after a critical micelle concentration is formed that is why this is called CMC. Again, let us just try to understand this figure. So initially when I keep adding the surfactant right as it go in this particular direction adding the surfactant, the dissolved concentration of the surfactant keeps increasing now.

But once we reach this critical micelle concentration right what happens now? Obviously, the dissolved concentration stays the same right. That is the maximum, think of it as solubility let us say right. So it stays the same right but now you start forming these particular particles if I may say called micelles let us say right. So obviously if you want to form micelles, do we need to add enough surfactants such that the critical micelle concentration has been you know achieved let us say or reached right.

So again before we go into further discussion of micelles and why they are important let us try to understand what happens now. So I keep adding what do we say surfactant let us say and where does it first go to let us say, the dissolved one let us say, it goes at the interfaces as we discussed let us say, you know it tries to you know it will first occupy the interfaces right.

So once you know for particular that site let us say, all the interfaces are occupied by the relevant what do we say surfactant right or there is no more interface to be occupied by the surfactant let us say right and then you are going to have formation of these micelles let us say and what is the typical shape of this micelles. So it is something like you know you have the hydrophobic tails inward and hydrophilic heads outward.

So this is the typical concentration of a micelle let us say right. So typically first we will have the interfaces that are occupied right, interface that is self-explanatory and once all the interfaces are occupied let us say and then you have the you also reach the critical micelle concentration then you start observing formation of these micelles let us say right. So what is the key aspect in this particular micelle and why is that relatively important now right.

So one aspect obviously is when you what do we say have these surfactants let us say you know occupying interfaces, again decrease in surface tension let us say right and depending upon the kind of contaminant or such pumping out is relatively easier, that is one aspect or even let us say to stabilize colloids that is going to be easier so we are going to come back to that later on again.

But what is the relevance of these micelles now right. So if you think of this let us say or if you look at this pardon me, you are going to see that all this particular what do we say part of the relevant micelle is hydrophobic let us say right. So this itself acts as a non-aqueous phase right. So keep that in mind as in earlier we came across the term NAPL, non-aqueous phase liquid either LNAPL or DNAPL right.

But typically we have applied them to the relevant contaminants here right and what was the property of these contaminants that you know made us call them as non-aqueous phase liquid, typically they are hydrophobic right. So these contaminants were those contaminants that were hydrophobic right and such we typically call them as non-aqueous phase liquids right. So in same case here again you have a non-aqueous phase within the micelle and what is that now?

That is because of the orientation of these particular surfactants let us say and again here you see that all the hydrophobic tails let us say are you know bunch together if I may call that or you know explain that in that manner and you have the hydrophilic what do we say heads oriented outwards. So now you have a non-aqueous phase so what is the relative importance here? The key is that now that you have a non-aqueous phase right.

Or let us think of it this way now, how is or what is the driving force for this particular contaminant let us say to be adsorbed on the soil. Is that you have organic fraction in the soil that is again you know acts as let us say reservoir for these hydrophobic compounds. Similarly, here you have a non-aqueous phase so this can now let us say act as a reservoir for the hydrophobic contaminants right.

So now you can have desorption of the relevant contaminant from the soil or dissolution of the NAPL into this particular micelle. So let us just try to visualize that, so let us say earlier you had the soil and the compound adsorbed onto that and also NAPL blob let us say right and now what happens is that as I introduce my micelle let us say or the surfactant after CMC let us say has been achieved, so what happens to these particular contaminants let us say?

They would now let us say what do we say change phase from let us say being adsorbed onto soil into the micelle phase let us say and similarly some of this particular blob let us say will dissolve or when I say dissolve, dissolve into this particular what you say non-aqueous phase inside the micelle right. So that is the key aspect and once you let us say you add enough surfactant to dissolve either the entire NAPL or dissolve most of the contaminant on the soil you can then pump the surfactant out.

It is relatively easy to obviously pump the surfactant out right. So that is something to keep in mind right so let us look at you know some of the aspects let us say practical aspects how this particular mechanisms if I may say so, how addition of surfactant let say helps us let us say now remediation goals.

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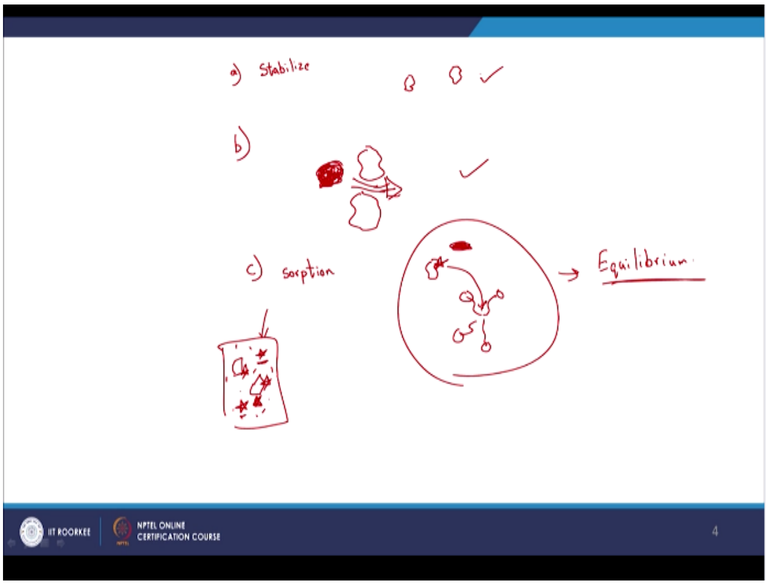

So one aspect is that it helps stabilize colloids let us say right. So let us say you had different colloids let us say you know suspended let us say either blobs let us say or colloids let us say, addition of these particular surfactants let us say now helps bring together these colloids let us say and helps them stabilize let us say. So that is one particular way right and the second aspect is that let us say when you want to or when you have soil let us say and you have a blob of NAPL let us say right.

And you want to squeeze this blob of NAPL through this particular pore space let us say. As in you are trying to pump it out let us say right so here let us say you know because of what do we say you know you want to pump it out let us say because of the energy required let us say soil in this case is relatively more polar if I may call that relative to the NAPL right. So you are going to have issues with pumping this or squeezing if I may call that squeezing this particular blob of NAPL through this particular pore let us say right or pore space pardon me.

So what and how will this particular NAPL not NAPL the surfactant aid now? It will aid in such a manner that by helping in forming a surface right for which the energy is obviously required right. So by helping in forming a surface let us say right it will make it easier for the relative I mean this particular blob to be squeeze it through right. So when pumping it out that it helps in that manner.

And thus we just discussed the form of or when we talked about sorption right. As in earlier let us say compounds that were adsorbed either onto the soil or were in phase of NAPL now let us say will now be sorbed into the micelle let us say. They will now be sorbed or adsorbed if adsorbed might not be the great term but sorbed into the NAPL now right. So 3 cases as in stabilize the colloids, helping what do we say to squeeze through the relevant NAPL let us say and also in sorption let us say right.

So 3 cases, obviously these are more physical characteristics but here obviously we need to look at the aspects relevant to equilibrium now right with respect to equilibrium. Why is that? Again, similar to the case when we had just water and the soil, there is going to be a case as in when we had let us just have a quick relook now. As in if I have just soil and water let us say all around and then I introduced some contaminant what is going to happen?

After I let the system reach equilibrium depending upon the type of compound let us say some of the contaminant will be dissolved in the water, some will be adsorbed onto the soil let us say right. The fraction will depend upon the its hydrophobicity let us say or the Octanol water partitioning coefficient right. So again now there is going to be an equilibrium between two phases, what are they? Soil and the relevant water here.

If there was NAPL let us say that is the third phase, so there would be equilibrium between all the 3 phases between the water phase I mean the one dissolved in the water phase or the aqueous phase, soil phase then the NAPL phase but now we are adding the fourth particular phase which is the surfactant right. So there is going to be an equilibrium between all these 4 phases and that is something that we are going to look at let us say right. So obviously we are going to look at the case of equilibrium.

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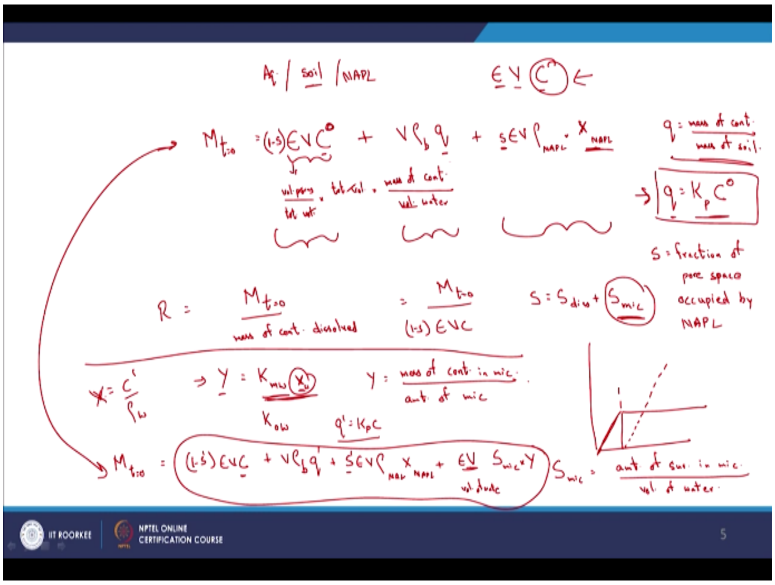

Aq / soil / NAPL

$\epsilon V \boxed{C^0} \leftarrow$

$M_{t=0} = \underbrace{(1-S)\epsilon V C^0}_{\frac{\text{vol. pores}}{\text{tot. vol.}} \times \text{tot. vol.} \times \frac{\text{mass of cont.}}{\text{vol. water}}} + V \rho_b q + S \epsilon V \rho_{NAPL} \cdot X_{NAPL}$

$q = \frac{\text{mass of cont.}}{\text{mass of soil}}$

$\rightarrow \boxed{q = K_p C^0}$

S = fraction of pore space occupied by NAPL

$R = \frac{M_{t=0}}{\text{mass of cont. dissolved}} = \frac{M_{t=0}}{(1-S)\epsilon V C}$

$S = S_{diss} + \boxed{S_{mic}}$

$X = \frac{C'}{\rho_w}$

$\rightarrow Y = K_{mw} \boxed{X_w}$

K_{ow}

$Y = \frac{\text{mass of cont. in mic.}}{\text{amt. of mic}}$

$q' = K_p C$

$M_{t=0} = \boxed{(1-S)\epsilon V C + V \rho_b q' + S \epsilon V \rho_{NAPL} X_{NAPL} + \epsilon V S_{mic} Y}$

$S_{mic} = \frac{\text{amt. of sur. in mic.}}{\text{vol. of water}}$

So let us look at the case when we have only let us say what is it now the aqueous or the dissolved phase adsorbed onto the soil and NAPL present let us say right. So this is something we have looked at but let us just try to understand the total mass at time=0 right or initial total mass let us say. What is that equal to? So obviously it is let us say if porosity of the relevant system, total volume and concentration of the compound in the water let us say.

These are the 3 terms we have typically used, so I have epsilon V*C right. So this obviously gives me the mass of the relevant contaminant dissolved in the water. Again, we did look at this but let us look at again, this is pore volume right, volume of pores by total volume, volume of pores which is when I say volume of pores occupancy this is occupied by water right, volume of pores/total volume*total volume*concentration is mass of contaminant per volume of water, volume of water means nothing but volume of pores in this context right.

So all these relevant terms cancel out and I am left with mass of the contaminant that dissolved in water. So that is what we have here epsilon VC+what else we are looking at soil, similarly I believe we looked at this volume, the bulk density of the soil times the mass of the I mean concentration of the contaminant adsorbed onto the soil right.

So that is q, q is the concentration of the contaminant adsorbed on soil as in mass of contaminant adsorbed onto soil per mass of soil let us say right. So that is what we have. As we know, it is going to be in equilibrium with the concentration of the relevant what we say compound that dissolved in water right. I think we were looking at a linear relationship or considering a linear relationship we have q=Kp*C that is something we looked at.

And if we have NAPL too right, obviously it is going to be within the relevant or you know be present within the pore space right so let us say the fraction of the pore space occupied by the relevant NAPL is S=the fraction of pore space occupied/NAPL right and then the volume will be epsilon V right and then we have the density of NAPL right times the you know mole fraction let us say of the relevant contaminant that you are looking at let us say in the NAPL right.

So typically if it is a pure NAPL that we are talking about which is the contaminant, this is going to be this as x is going to be=1 right. So since here we are considering the fraction of the pore space is occupied by the relevant NAPL, we also need to derive that particular case here or take that into account right. So again what do we have here, this is the mass of the contaminant dissolved in the water.

This is the mass of the contaminant adsorbed on soil, this is the mass of the contaminant what do we say in the NAPL phase right. So in this context we look at retardation factor which affects let us say your ability to pump stuff out or such right and what is that, that is nothing but M total/mass of contaminant that is dissolved let us say right. So that is nothing but equal to M total/epsilon or 1-epsilon VC0 right depending on how we are terming that.

So this is what we have, so let us look at the scenario or the changed scenario when we add the micelle let us say right. So when we are adding the micelle, obviously there are you know a few factors that we need to keep in mind as in what are they so as we know first it is going to be in the dissolved phase right and only then will you have formation of the micelle right. So the total surfactant let us say will be=surfactant in the dissolved phase+surfactant in the micelle phase right.

So that is something to keep in mind and only the micelle phase can adsorb the relevant contaminant right. So we are typically now going to look at this particular case and what is this? This is nothing but S micelle is nothing but amount of surfactant in micelle per volume of water let us say okay, so that is what we have here and that is the S micelle here right.

Again, this is the amount of surfactant in the micelle phase for per volume of water let us say. So now let us try to you know understand this particular or how this particular scenario is going to change when we add the surfactant right. So when I add the surfactant let us say some of the mass of the contaminant will be in the micelle right and that I am going to represent as Y which is the mass fraction is=K micelle water partitioning coefficient.

So this is similar to let us say your K Octanol water partitioning coefficient as in what does Octanol water partitioning coefficient gives an idea about as in if I have Octanol and water and I introduce a contaminant and then I will get a fraction of the concentration or the ratio of the concentration of the compound in Octanol to concentration of the compound in water let us say. So this will give me an idea about how hydrophobic it is or such.

So similarly I have the K micelle water partitioning coefficient and that times let us say X let us say this is again mass fraction of the compound in the relevant water let us say. Keep in mind that this X is different from the other X variables that we have used earlier. So maybe let us use this. So Y is the mass fraction right, so that is nothing but Y=mass of contaminant in the micelle/mass of micelle or amount of micelle here right.

So that is something to keep in mind. Again, what do we see here it is an equilibrium between the contaminant in the water which I am representing by X here right and also the contaminant in the micelle again it is an equilibrium between 4 phases now, surfactant and NAPL, soil and water right. So again all of these are tied up by what do we say their different relationships obviously with the concentration in the aqueous phase?

And this is one such relationship, so now let us try to write this down right. Now I am going to let us say initially I had C0 let us say, q is again=Kp C0 right in the initial case anyway right, C0 is the initial concentration let us say of the relevant contaminant in the what do we say in the water but let us say one thing to understand or you know keep in mind is that if there is NAPL right which is the pure solution let us say.

Or if I am assuming that it is pure solution let us say of the relevant contaminant or the pure contaminant what is C going to be and if the equilibrium has been reached again the reframe the question. Let us say if you have the pure contaminant as the NAPL and you have that having reached equilibrium with the water and the soil. What will this C be? C is again the contaminant concentration in the water let us say.

It is going to be the solubility right, solubility will give you an idea about the maximum concentration of the relevant compound that this particular solution of water can hold right that would have been the C solubility. Again, that is something to keep in mind right. So again let us come back to this case and write down the new M total. So M total will be=it is going to be the same.

This M total is still the same, the total mass has not changed right but it will now change within this particular what do we say case as in let us say 1-S epsilon VC. It is now going to be something else right. Why is it something else, because I added surfactant and some of the concentration of the contaminant will be taken in by this surfactant let us say right. So the C is not going to be C0 anymore.

And V rho b*q dash let us say and what is q dash that is nothing but equal to Kp*C right this C here. What is q? Again, mass of the contaminant adsorbed onto the soil per mass of contaminant in the relevant pardon me not in what do we say is water; it is mass of contaminant adsorbed onto the soil per mass of the relevant soil right. So again that is going to be depend upon or in equilibrium with the concentration of the contaminant in the water.

That is what we have here and if we still have the relevant NAPL let us say and X here right, so this S might decrease, now this S might decrease, why is that, this S might decrease because as I add surfactant some of the relevant NAPL will dissolve and move into the micelle now right. So obviously I will have S dash here, S dash X NAPL and now let us represent this particular micelle let us say.

So I am going to assume that it is going to be in the same pore volume let us say, so it is epsilon V right and what else do I need to have, this will be the volume of water right, volume of water so it will have to be multiplied by S micelle obviously right and then by Y right. So this is what we have right and again what is Y? Y is nothing but Kmw*X right, X is again the mass fraction of the contaminant in the water.

So how can I represent it in terms of variables that I have here, X will be nothing but C dash/density of water let us say right. So here I have this relationship but let us just try to understand that.

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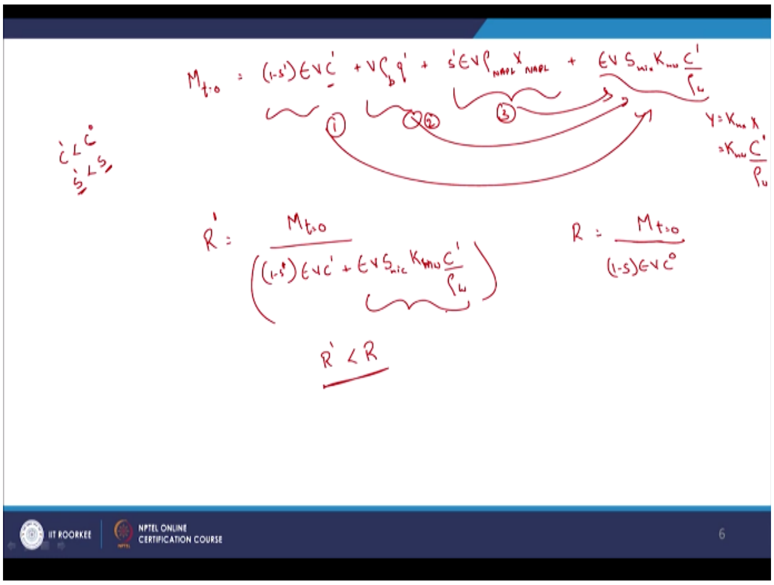

$$M_{t=0} = \underbrace{(1-S')\epsilon V \underline{C'}}_{①} + \underbrace{V\rho_b q'}_{②} + \underbrace{S'\epsilon V \rho_{NAPL} X_{NAPL}}_{③} + \underbrace{\epsilon V S_{mic} K_{mw} \frac{C'}{\rho_w}}$$

$$Y = K_{mw} X = K_{mw}\frac{C'}{\rho_w}$$

$C' < C^0$

$\underline{S' < S}$

$$R' = \frac{M_{t=0}}{\left((1-S')\epsilon V C' + \underbrace{\epsilon V S_{mic} K_{mw}\frac{C'}{\rho_w}}\right)} \qquad R = \frac{M_{t=0}}{(1-S)\epsilon V C^0}$$

$$\underline{R' < R}$$

Let me rewrite that here, so the total mass of the contaminant is now equal to 1-S dash I believe epsilon VC right+rho b and V I guess right rho b V rho b q dash. This is the contaminant present in the soil+S dash epsilon V right and what am I writing here, the NAPL case right X NAPL so all these set of variables given an idea about the mass in the NAPL and now the mass in the relevant micelle right epsilon V.

And what else do we have here? So S micelle and Y is nothing but Kmw*X and that is nothing but Kmw*X is concentration of the water/density of water. So that is what I end up having here Kmw right*C dash/density of water. Again, there are different terms or such but it will make better sense maybe once you solve one of those homework problems but let us try to understand why this is important now.

Earlier the C or this particular concentration or C dash if I make call that let us say because I am calling that C dash here was higher let us say right. Why is that? Because you did not have the micelle but now C dash will typically be less than what do we say C here, the earlier C0 here right and also S dash will be less than S, what is this S or S dash? It is the fraction of the pore space occupied by the NAPL.

And why is that decreasing? Because now you have the micelle right and that particular micelle can adsorb your particular contaminant so the contaminant which is in the form of NAPL will dissolve and now you know change phase into the micelle case right. So some of the contaminant that was in these 3 phases earlier now have moved into this particular phase mostly from these two cases let us say 2 and 3 rather than from 1 right.

So that is the aspect to keep in mind so here what is the retardation factor, it is still M total which is the same/the amount n solution let us say but when we say solution it obviously also includes the right it also includes the contaminant present in the NAPL not NAPL pardon me the micelle so epsilon V S micelle Kmw C dash/density of water. This is the new R dash. What was it earlier? It was R was just M total/the mass in solution.

I think in that case it was epsilon VC not 1-S epsilon VC0 right. So what is happening to R? As you see, R is decreasing here right. R is decreasing, so the retardation factor has decreased. Why is that? Obviously because now I have more of my particular contaminant in solution. Again, keep in mind that I am considering that or you know obviously that is the case that logically that the micelle is also part of the solution right.

So that you know now more of the contaminant has moved from being adsorbed or present as NAPL into the relevant solution. So looks like I am pretty much out of time right so I will continue this in the next session but what is the take home message here, by adding the surfactant we are either dissolving the NAPL or let us say desorbing the relevant contaminant from the relevant soil now right.

So the other case is that when we add enough micelle or enough surfactant what is going to happen? All the NAPL is going to dissolve and most of the compound adsorbed onto the relevant soil will what we say desorbed into the relevant micelle right. So that is the relevant aspect but I guess I will continue this in the next session and thank you.