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Lecture – 48 Surfactant Extraction: Part - II

Hello everyone. Again, welcome to the latest lecture session. So we have been discussing the aspects relevant to what is it now the surfactant extraction I guess right and we looked at some of the theory and let us take that through and solve a particular problem in this regard right but again a quick recap of what we have been up to right.

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So we typically add surfactants let us say right and how do they help us as in one let us say if you have colloids of NAPL right and now by addition of surfactant you are going to help stabilize them let us say or you know help bring them together either particles or colloids of NAPL, addition of this surfactant will help stabilize them. This is the NAPL and here are your surfactants and surfactants what is that here?

Here you have a hydrophilic head and hydrophobic tail right, so obviously NAPL which is more hydrophobic right and you are going to have the tail thus you know having affinity towards this NAPL and that is what you observe here and then let us say it will also help mobilize the NAPL flow or facilitate NAPL flow as in we looked at the case when we have two soil particles and you have a blob of NAPL. And you want to squeeze this through this particular pore space let us say right but you know this will have high interfacial energy let us say right or high considerable you know so that is relatively difficult to squeeze this through. So addition of this particular surfactant let us say will help in what do we say forming a surface right. Again, without this formation of surface you are going to have to require lot of energy to squeeze this through right.

So again to you know get through that let us say or you know go around that you are going to add the relevant surfactant which will help in formation of the surface and thus you know help in mobilizing the NAPL let us say right. So that is one aspect and the third aspect which we looked at right what was that about, that is the case where it is not the physical characteristics per se right.

But that let say after I add enough of the relevant surfactant so initially all the surfactant that I add will be in the dissolved phase right. So this is the dissolved phase and obviously you see after certain threshold you know the concentration of the dissolved phase is constant. So what happens to the surfactant that we add after you reach this particular threshold which we are referring to as the critical micelle concentration.

Obviously, we are going to have formation of the micelles let us say right and what is the key aspect here that once all the interfaces are occupied, you are going to have the surfactants form micelles and you know they orient themselves in this manner right and these particular micelles act again as what do we say reservoirs for you know adsorbing let us say the relevant NAPL let us say or the relevant hydrophobic contaminant right. So what happens out here?

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We have let us say total mass M at time=0, initially is based on mass and the aqueous phase are dissolved in the water or mass adsorbed onto the soil+mass in the NAPL form right. So after addition of let us say maybe enough surfactant what is going to happen or you know if there is addition of surfactant what is going to happen, so I am going to have mass of the contaminant in the surfactant right.

And because the total is constant what is going to happen, the mass of the contaminant in the soil is going to be transferred to mass in the surfactant and also mass of the NAPL let us say is going to be you know NAPL is going to dissolve and the contaminant is going to change the phase and let us say it is going to adsorbed into the micelle right. So again keep in mind that the total mass is constant.

But that you are just changing the contaminant from one phase to the other as in from soil and the NAPL into the micelle right. So that is what you observe here. So if you add enough surfactant what is going to happen, you are going to see to it that you know your relevant NAPL might completely dissolve depending on how much you add right and also you are going to see that let us say most of the relevant contaminant from your soil is going to be desorbed let us say right.

So that is something to keep in mind and in that context, we are going to have the retardation factor. Without the surfactant what will the retardation factor will be? It will be M time=0 or total mass/mass in the aqueous phase but with the surfactant the retardation factor will

be=mass or total mass/mass in the aqueous phase and mass in the micelle phase right. So as you see R dash is decreasing now right.

And why is this relevant now let us say, as we looked at in previous cases or multiple examples let us say we see that either the absorbed rate constants let us say are more importantly the rate at which you will be able to pump out your particular what do we say solution let us say which here includes both the surfactant and the water right will be affected by the retardation factor or the amount that is let us say adsorbed onto the soil or present as NAPL.

So here by decreasing the R dash or you know by increasing the concentration of the compound in the surfactant what are you doing, you are going to make it easier for you to pump the relevant case out. So what will it look like let us say, so let us say I can have this is my subsurface and this is my pump out let us say right and let us say this is my water level. So along with the surfactant and the water and the contaminant will be pumped out right.

So this is the subsurface, this is the groundwater level let us say so I am going to pump it out right. So again what are the key aspects here? Let us just understand that, as in one case is that as in I am not adding any additional reagents though right, I am not adding any additional reagents or such right but obviously for this particular system to work as in this particular case of being able to pump the relevant surfactant and the soil out obviously the soil needs to be relatively permeable right.

It needs to be relatively permeable yes that is something to keep in mind; otherwise obviously you are going to have issues with pumping the relevant solution out right. So another aspect is after you have pumped out let us say all the relevant contaminant and most of the surfactant, you are going to still have the residual surfactant in it right. So it is like maybe I guess it is a very generic example.

Let us say you are trying to wash the grease of your shirt let us say and you apply lot of detergent or Surf let us say right and what is going to happen, you are going to obviously have what do we say if you add very high levels of the detergent, you are going to observe that the residual detergent what do we say Surf will be what do we say affecting the cloth quality or such let us say right.

So similarly let us say if you add a lot of surfactant obviously even after you pump out most of the surfactant you will have some or residual surfactant, so that some aspect to keep in mind as in does that introduce any other complications or typically let us say any other toxicity or such effects right that is something to keep in mind right. As in residual surfactant and your ability to even remove that particular residual surfactant needs to be kept in mind right. So these are the aspects obviously we will look at.

So typically when we are pumping it out let us say let us just look at the simple mass balance. What is it going to be like if it is just pumping it out let us say, as we know it is going to be equal to dc/dt right. If I take the advection term on to the right hand side, it is going to be -u dc/dx right but this needs to be affected by the retardation factor right. So now instead of R I have R dash right.

So as you can see now let us say right R dash let us say is smaller than R and you see that the efficiency with which let us say you can pump your relevant contaminant out obviously increases right. So that is something to keep in mind. So one aspect is this let us say. So again how do you typically wash the soil let us say, either in situ right or ex situ as in you pump the not pump excavate the soil, take it out to a particular location.



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And you know relatively wash it there let us say, so you can get it done ex situ and typically quite a few operations look at ex situ too I mean ex situ cases and why is that? Because of what do we say either ease of use let us say and ease of application or because of site

characteristics that would prevent in situ what we say applications of surfactant and pumping the surfactant out right.

So in this case ex situ as in I am removing all the soil, taking it somewhere else and then trying to treat it. So in this case what is the best way to be able to you know maximize or increase the efficiency of your particular operation right. The key is that you have contaminated soil let us say at concentration C0 let us say right and you have surfactant let us say right.

So what is the best way to go about it, it is just that you mix everything as in all the soil, all the surfactant and then remove the surfactant or how best to go about it. As you can see let us say here we are concerned about desorbing the contaminant right from the soil into the surfactant right. So let us say if I can say something like this and if this is my soil particle and this is my contaminant let us say and then I introduce let us say is surfactant let us say all this volume is my surfactant.

So after equilibrium is reached what will happen let us say, let us say this is the initial case when most of it was on these adsorbed on soil right and let us say after equilibrium has been reached let us say or have most of it in the surfactant now right but as you can see this is the case or this is what I have here right.

So what does it depend upon again, there is going to be an equilibrium between the contaminant adsorbed on soil and the contaminant concentration in the micelle or mainly surfactant pardon me right. So there is obviously when will you maximize your efficiency right? So when the gradient or you know when the concentration difference between that in the surfactant and your soil is greater right.

So to achieve that what do we typically look at, rather than mixing everything let us say in one go right and then again having slightly contaminated soil for which again you need to add fresh surfactant or such what do we do, we look at an approach called the counter current let us say, counter current flow right. As in if this is my relevant system right, I introduced the dirty soil here or the contaminated soil let us say, dirty soil here.

And this goes out this way right and here I end up with the clean soil right but here obviously I need to have surfactant and how do I introduce that, if I introduce the clean surfactant here right what is going to be the case, obviously what do we say you are going to have desorption here but the issue is here that as it passes through let us say your slightly contaminated soil will be in contact with the surfactant that already has the relevant contaminant in it.

But to achieve pretty good clean soil let us say what would you do? You would see to it that your cleanest soil let us say would come in contact with relatively clean surfactant let us say right. So even if there is let us say the minor concentration of contaminant adsorbed onto the relevant soil right that will be desorbed because the surfactant is relatively clean. So as it passes through and this is why we call that counter current right.

We end up with the relatively dirty surfactant here right. Typically, we see that this so the dirty soil comes in, clean soil goes out and in the counter current we add the clean surfactant which then comes in contact with the relatively cleaner soil and while it goes out it is relatively dirty but again it comes in contact with the relatively more dirty soil right. So this is what we typically look at the semi continuous counter flow right.

But what is the aspect here or what is the issue that we face here right. It is that let us say right soil is not easy to you know is not malleable enough let us say right or if I am looking for the better term you know the ease with which you can handle soil or you know put up in such a system is going to be difficult let us say right, it is not easy right. So how do I achieve this counter current flow?

So I make that semi-continuous let us say, semi-continuous counter current flow right. So how do I have that let us say, so I have a series of containers let us say. So I have my soil here let us say dirty soil and so on and so forth right. So what is going to happen let us say; now you know the contaminant let us say is in this direction let us say or you can keep the contaminant in the same container right.

And you will have the surfactant flowing through in this way and this is what is done typically though right. So the surfactant right and this soil comes out. So what do we typically do now? We have a series of bins right, either you change the soil from one bin to the other or just keep the bins moving but what is the aspect here that the cleanest surfactant, here we

introduce the cleaner or cleanest surfactant comes in contact with the relatively cleaner soil now let us say right.

So again here you are going to have relatively more removal of the relevant what do we say contaminant from the soil rather than if you had relatively dirty surfactant in contact with the relevant soil right so that is what you have here, you want to increase the what do we say extent to which you are going to be able to decontaminate the soil. So that is why you have the clean surfactant coming in and that will come in contact with the relatively cleaner soil.

So this particular cleaner batch of soil will be removed right and will be replaced by the next in line relatively dirtier let us say batch of soil and again that is going to come in contact with the fresh batch of the clean surfactant. So what happens to this surfactant though as it keeps passing from one bin of what do we say contaminated soil to the other right and here you are going to have the relatively dirty or contaminated surfactant right.

And this you are going to dispose out there right, so obviously you know you are going to have fresh batch of contaminated soil coming in and what do we say simultaneously let us say a batch of clean soil or decontaminated soil leaving right. At the same case, you will have what do we say the surfactant coming in and the dirty surfactant being removed right. So that is how we typically go about it right.

So now let us move on to maybe looking at a particular minor example let us say. Before we move on to let us say looking at a particular case study or such right. So I believe I have an example here, let us look at that.

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So let us try to understand the system here, so here we have a source zone and looks like that is 200 meter long okay 50 meter wide and 10 meters deep yes and it has bulk density the soil bulk density is given right and the fraction of organic matter is also given Foc and why is this important now again because as we know let us say it is the when we say soil adsorbs the contaminant it is actually the organic content in the relevant soil right.

So that is something to keep in mind right so Foc is relevant here right and porosity of 0.4, this we obviously assumed that it is occupied by water, so it is contaminated with what do we say trichloro or maybe is tetrachloro. I will take it as tetrachloroethene let us say TCE here with an average aqueous concentration of 15 milligram per liter. So it is the average aqueous concentration is 15 milligram per liter of this chlorinated solvent which is a toxic compound TCE, this is in the water now right.

And pure NAPL is present in 1% of this pore space as in yes the fraction of the pore space occupied by the NAPL is 1%. Again, we are saying that the NAPL is pure right. So when I say NAPL is pure so what does that mean, X NAPL the mass fraction of that particular mole fraction pardon me of the NAPL is=1 let us say right. So these are the aspects we have until now and it is to be extracted with the surfactant that has CMC.

What is CMC? It is obviously the critical micelle concentration and we obviously need to add enough surfactant you know such that we are you know we cross this limit of CMC to be able to form the micelles let us say, has a CMC of 200 milligram per liter right. So as in S total is=S dissolved let us say+S in the micelle phase right. Again, for this particular dissolved phase for this micelles to be formed, obviously you need to first raise the CMC here right, CMC let us say is around 200 milligram per liter let us say right.

And the empirical relationship between the partitioning what do we say the two describe the partitioning to micelles formed by this surfactant let us say is given here. As in as we understood earlier, the mass fraction of the contaminant in the micelle is going to be depend upon the mass fraction of the contaminant in the water.

This is the mass fraction, what is this? Mass of contaminant per mass of micelle let us say or mass of surfactant in the micelle phase that is Y right and this is mass of contaminant per mass of water let us say right and that is the relationship depend upon the micelle water partitioning coefficient. I guess it is self-explanatory. Again, we looked at Octanol water partitioning coefficient.

So again rather than measuring micelle water partitioning coefficient we come up we have this empirical relationship that gives us an idea about how Kmw is dependent upon Kow and that is what we are going to use here right to be able to come up with this Kmw right. It is difficult to obviously measure that directly. So here we have 3 aspects to look at and let us look at what they are right.

So we have that we need to calculate the minimum total surfactant concentration that we need to completely dissolve the NAPL right. So we are going to have two you know come up with this concentration which will what do we say lead to that all this NAPL 1% NAPL let us say is completely going to dissolve let us say. If the extractant solution were added to soil at a volumetric ratio of 5 as in volume of surfactant solution to total volume of soil.

So again obviously the aspect is that we add a lot of surfactant right, as we keep adding and looking at it, so we are looking at the total what do we say equilibrium case let us say right or the holistic equilibrium case. So key aspect is that if the extractant solution were added to the soil at a ratio of 5 which is the case with respect to surfactant solution to total volume of soil so that is one aspect we look at how to solve this and what would be the equilibrium concentration in the aqueous phase.

And the total concentration aqueous phase+micelle phase of the extracting solution if the same surfactant concentration calculated from this particular case were at volumetric ratio of 3 instead of 5 right. So as in let us say earlier in case A we are adding or we planned to add what do we say a certain volume of surfactant but in case B let us say we are adding a relatively lesser volume of surfactant let us say and we want to achieve the same results.

And then we are obviously asked to calculate let us say the concentration let us say in the solution which means concentration in both the water and the micelle phase right and then the same case with respect to now as in repeat the calculations of part B at a volumetric ratio of 7 let us say. As in initially we looked at a case when we are adding the volume of surfactant at ratio of 5 compared to the volume of the soil.

Then, we are looking at a case as in what will happen if we have lesser amount of surfactant and also obviously more amount of surfactant right. So let us look at case A first and then take it through from there right.





So let us look at case A. What do we have here now? We have what is the approach here? Total mass we can calculate right based on the mass of the relevant contaminant in the dissolved phase+mass of the contaminant adsorbed on soil+mass of the contaminant in this particular NAPL let us say right. So this is how will calculate the initial or total mass let us say and this total mass obviously is going to be constant or the same even after you add the surfactant right.

As in that you are going to have the change in the relevant concentrations and so on but here we do not have enough data or some data is you know not available. So we need to be able to make some assumption. As in let us say, we know that you know this is nothing but epsilon VC0 right+V rho b*q so this will be 1-S, so this is V*or S epsilon V*X NAPL. This is 1 so I will skip that and density of NAPL let us say right.

So here is density of NAPL given well it is not given right this NAPL is TCE so this density of TCE can be found out from the relevant literature that we can find out right. So we do have density of what do we say the relevant soil though right. So we do have density of soil, we have C0, I think we have partitioning coefficient here somewhere yes and if not we can get that particular case too.

Even if we do not have partitioning coefficient we can get that right for this particular TCE we can get that from relevant literature too right. Again, from that I can calculate q, I have C0 and so on but what happens to this system, once I add surfactant though right. You are going to see a decrease in C, decrease in C0 and you know we are going to look at complete dissolution of this NAPL let us say right.

But here as in we do not know what the concentration is going to be in the water after let us say dissolution of this NAPL or addition of surfactant right. So to be able to get around that you know we are going to make a conservative estimate. The conservative estimate is that you know we are going to estimate that even after addition of surfactant that this concentration C dash will almost be=C0 but this is not a great assumption.

But this is a conservative what do we say estimate or assumption that we are making here right, so that is fine for now right, so what is the approach here. We are going to assume that this C0 is going to stay the same even after addition of surfactant but as you know that is not going to be the case right but after addition of surfactant how is this going to transform into? It is going to be the total mass will be equal to the one in the dissolved phase+one in the soil+the one in the surfactant right.

So we know that this we can calculate from this particular set of variables and we are going to then substitute out here and calculate the relevant variable here, what is the minimum total

surfactant concentration right, so that is something that we are going to calculate. So let us see let us have the relevant approach here.

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So mass of TCE in the contaminated source as we know as I mentioned earlier this is the one in the dissolved phase right and this is the one in adsorbed on to the soil and this is the one in the relevant NAPL let us say right. So this is what we have right now or the initial case and the total volume, this is the total volume and we are calculating that total volume as 1*10 power 5 meter cube right.

This is from 200*50*10 that is given in the question. So we have that particular case let us say right. So let us move on.

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So we have the mass fraction or not mass fraction pardon me the pore fraction let us say that is occupied by NAPL that was at 1% right so that is why this s is=0.01 and porosity we also have that at 0.4, So Kp is=foc*Koc and again foc was given, foc is nothing but the fraction of the organic content I guess right and Koc again this is from a literature value let us say for this particular case of TCE right.

So again what is this, this is the partitioning coefficient which is going to be dependent upon the amount of organic content in the soil and also the partitioning coefficient between organic carbon and the relevant what do we say water for that particular contaminant let us say right. So that is what we have here and this I guess was 0.5% that is what we have here and looks like the partitioning coefficient is something like 0.63 mL of the TCE let us say, is it of TCE?

Yes I guess, so because the units are going to be in such a case right per gram let us say right. So that is something to keep in mind, the units are something to keep in mind here and you will be able to understand the units let us say once you look at these the units of this particular Koc here let us say right. So we have the partitioning coefficient here.

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So from that what can I calculate, again I have the density of NAPL given and this mole fraction of NAPL again pure NAPL right. Mole fraction is nothing but what do we say moles of that particular NAPL let us say or that particular contaminant let us say by the total number of moles right but as we know let us say it is pure what do we say NAPL so you do not have anything else other than that particular contaminant let us say right.

So this is going to be equal to 1 and that is what we see here and moving on let us say so this mass is nothing but 1-s*porosity times volume times concentration of the relevant contaminant in the water right. So this is nothing but the volume of the contaminant that is dissolved in the relevant water here right. So let us look at the other case. So here we have V right and I think this is the bulk density and this is your V rho b and q is it?

I guess right so it is V rho b times q right that is what we showed, supposed to have s and this is nothing but the contaminant concentration in the relevant soil so this is what we have out here.



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And this may be needs to be multiplied by 15 maybe I am missing that particular value as in we know that the mass in the relevant soil is going to be equal to V rho b*q right and that is going to be equal to nothing but volume times rho b*Kp*C right. So we have these 3 variables here right so this has to be multiplied by that 15 gram per or you know this particular concentration of the relevant contaminant in the relevant soil let us say right.

That is what we have here okay so this is nothing but the concentration of contaminant in the NAPL so let us look at what we have, this is s times porosity times volume and density of NAPL, mole fraction of NAPL right and that is what we have. This is just changing in the units, so this is the mass in the soil in the water, mass in the soil and mass in the NAPL right. **(Refer Slide Time: 29:17)**



So let us just look at those values here. As you see, we have 5.95*10 power 5 order of 10 power 5 let us say. This is order of 10 power 6 and this is order of 10 power 8 let us say and total we end up with these many grams will come back to that but the reason I write it out in this way is that let us say compared to the amount if I look at the fraction what is it now? 1:10: let us say 1000 right.

So if one part of the contaminant is dissolved in the relevant what do we say water you have 10 parts adsorbed onto the soil and 1000 parts present as the NAPL. Again, NAPL was only present as 1% of that particular pore space right. So you should understand the relevant what do we say criticality of having or you know complexity of having NAPL present in your particular what do we say contaminated site let us say right.

So I end up with almost let us say 5.88*10 power 5 kg now right so you can understand the mass of the contaminant that we are talking about in just this 200*50*10 space of the relevant contaminated soil right. So I guess I am you know out of time so will continue this in the next class. Again, what is the approach here; we now have this particular mass of contaminant, will just equate that to the case when let us say we have no NAPL but just the surfactant right. So I guess with that I will end the session for today and thank you.