Environmental Geotechnics
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Lecture – 38
Sorption & Desorption characteristics of geomaterials-2

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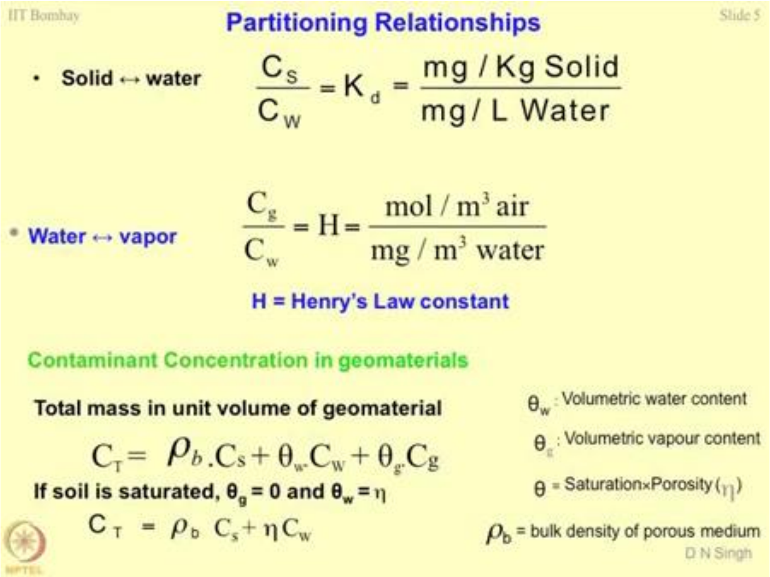

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Slide 5

Partitioning Relationships

- Solid ↔ water $$\frac{C_S}{C_W} = K_d = \frac{\text{mg / Kg Solid}}{\text{mg / L Water}}$$
- Water ↔ vapor $$\frac{C_g}{C_w} = H = \frac{\text{mol / m}^3\text{ air}}{\text{mg / m}^3\text{ water}}$$

H = Henry's Law constant

Contaminant Concentration in geomaterials

Total mass in unit volume of geomaterial

$$C_T = \rho_b.C_s + \theta_w.C_W + \theta_g.C_g$$

If soil is saturated, $\theta_g = 0$ and $\theta_w = \eta$

$$C_T = \rho_b\ C_s + \eta C_w$$

θ_w : Volumetric water content

θ_g : Volumetric vapour content

θ = Saturation×Porosity (η)

ρ_b = bulk density of porous medium

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So, in general how would you quantify these partitioning relationships suppose we are talking about solid water interface saturated soil, now this is how you will define k_d parameter. What is C_s?

Concentration.

Concentration of contaminants which are getting soft on to the solid phase and C_W.

In this solution form.

In this solution in the solution formed. So, if you take the average of these two this is nothing, but k_d it is always defined as milligrams of contaminants per kg solid of the soil mass or the porous media. What are the units of C_W this is the milligrams of contaminants per liter of water or the solution, why are we use the word water here because contaminant is dissolved in the water phase, so to create a certain molarity. So, you take 5 grams of a salt and dissolve it in 1 liter of water. So, for C_W we always use the word milligrams of the contaminants per liter of the water clear.

The second phase is water vapour. So, see what is the significance of solid water interface, the contaminant is getting distributed in solid phase and water phase. Now, look at the situation here the contaminant is getting distributed in vapour phase and water phase. So, third phase is included in to this, so the complete matrix would be solid, water and water vapour interface meaning thereby if I extend this model further K_d if I know what is the amount of gas what amount of concentrations which are getting adhere on to the gaseous phase divided by the concentration of contaminant in the solution phase, this becomes your henrys constant. Now, Henry's constant is nothing, but the constant which is normally used in gas law.

So, for the most of the time when contaminant migrates in the soil mass or out of the soil mass most probably the porous media will remain saturated; however, when you are talking about contaminant migration in unstructured soil mass, then this type of vapor water interaction will come into the picture; is this ok?

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It is a gaseous phase of the contaminant which is getting adhered onto the solid surface. So, that is how you are saying that the certain amount like camphor, what will happen if you have camphor? So, camphor may not get dissolved in water, but the moment it sublimates it goes and gets adhered on to the surface of the solids. So, the gaseous phase of the material which is getting adhered on the solid surface, see partitioning is taking place always from the solid form or from the liquid form or a solution form. So, this is how you will be defining these numbers with respect to liquid phase what fraction has got adhered on the solids, what fraction is got adhered on to the gases.

So, putting these two together is a three-phase system alright. We can do lot of other things when we use these parameters like contaminant, concentration in geomaterials can be obtained. Now, this is what again defines the fate of contaminants in the geomaterial.

Now, if you talk about the total mass in unit volume of the geomaterial this is how it can be computed, you have density of the porous system multiplied by C_s plus theta w theta w is the volumetric moisture content of the soil mass multiplied by C_w the concentration of contaminants in liquid phase plus theta g gaseous phase multiplied by C_g. Now there is the boundary condition that, if soil is saturated what is going to happen your theta g is equal to 0, where theta g is the volumetric gas content or the vapour content.

$$C_T = \rho_b . C_S + \theta . C_W + \theta_g . C_g$$

Now, have you ever studied what is the value of theta the volumetric moisture content? Volumetric moisture content is defined as saturation multiplied by porosity, the bulk porosity. See this is in fashion these days we do not talk about gravimetric moisture anymore we talk about volumetric moisture. So, saturation multiplied by porosity will give you theta value; so, if saturation is 1 fully saturated soil theta is nothing, but equal to porosity what is the need of defining theta value? Because porosity can be measured very easily and more precisely by using all your TDR, FDR techniques, but gravimetric analysis is always very empirical and not much reliable. Another problem is you have already disturbed the matrix of the soil by bringing the soil sample into the laboratory so it is not the in-situ condition of the moisture.

So, that is a reason everybody is trying to use theta values these days; that means, volumetric water content as theta w volumetric vapour content or gaseous phase content as θ_g, where θ is saturation and porosity multiplication of the 2. So, then this equation will reduce to C_T equal to density bulk density of the system multiplied by C_S plus porosity multiplied by C_W.

$$C_T = \rho_b . C_S + \eta . C_W$$

Now, tell me one thing what is application of this equation? If you want to find out what is the concentration of contaminants present in the porous media you can simply substitute these values the density and the porosity and you should know what is the C_S and C_W phase? And hence you know the C_T value. Now this is the practical situation with which you normally deal with in most of the professional activities. So, this is what is known as concentration determination in porous system or the fate of contaminants, now if C_T tends to 0 what is the implication of this?

No contaminants.

No contaminants. What is the meaning of that? Either no contaminant gets trapped into the porous media or there is no sorption process going on in the porous media. So, again there are two things which you should not forget to apply; clear, what it indicates? Either the contaminants are inactive or the porous media is inactive or the time given to the system is so less than nothing gets written on to this and so on. There are there can be so many combinations and permutations of this type of a phenomenon, but in normal situation what would you prefer as an administrator not let say as an engineer or a scientist C_T should be 0 or C_T should not be 0?

Why I say administrator, suppose you are the chairman of municipal corporation what do you expect everywhere? Completely clean land C_T is always 0 clear of course, its hypothetical situation. Or C_T should be a very high number; that means, the soil mass is never going to release any contaminants in the geoenvironment. Now, if you are somewhere in between the life is precarious, now these are the boundary condition which you have to put in your modelling; mathematical modeling. Is the concept of modelling clear to you now? And most of the times C_T concentrations are defined by pollution control boards.

So, they come up with their norms that in a certain country at a certain location, whether it is a thermal power plant or a rubber manufacturing unit electroplating unit, the permissible concentration of a contaminant should be less than this. So, this becomes third boundary condition. So, you have many constraints for which you have to solve this linear equation. And here you can use the concept of optimization mathematical programming, linear programming operational research and so on o r and o e and what not and this becomes a good PhD thesis for people who are trying to and their doctorate is this any doubts questions? So, all of you are now experts in modelling contaminant transport in soil mass, this question is that in these equation C_T, time is not come into the picture.

Truly speaking, time is inbuilt. Now I will show you how time gets automatically reflected in this equation, because C_s and C_w both of them are functions of time. So, we always talk about equilibration time beyond which even if the interaction is prolong nothing much different is going to happen. So, in all these relationships the most important parameter is to establish equilibration time, all right. So, when you conduct any test one of the most important parameters would be what is the time of interaction and what happens beyond equilibration period; is this ok?

What is her question is that is there any limit on saturation? See the most simple situation is when saturation is 100 %, because we have been dealing with saturated state of the material in terms of hydraulic conductivity and what not, but the most problematic situation would be, when your 2 phase system is trying to become 3 phase particularly for unsaturated soils you are the saturation is less than 80 %.

Hello.

All right and has we have been talking about since last so many lectures that most of the locations in the country or anywhere in the world, you will not have soil mass which is fully saturated because the water table keeps on either fluctuating or it is much deeper. So, to answer your question let me put it like this that C_S and C_W or in the words k_d parameter itself is a function of volumetric moisture content is this clear. So, k_d is a function of theta. Now, please tell me one thing if theta is more k_d will be more or less. If you have more water present in the soil mass the distribution will be faster or lesser?

Faster.

Exactly so; that means, higher the degree of saturation your k_d’s will be very high the sorption capacity of the porous media will be extremely high is this answer is this what you are asking. So, the moment theta changes your suction value comes in the picture, the soil becomes unsaturated the contaminant transport starts taking place in unsaturated soil mass all right.

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What about the.

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Good.

Further soil itself is there any.

Very good. So, what happens when you go to many malls in Bombay city, where they say parking full no parking lot available. What you do normally, the same thing happens landing does not take place on Bombay airport because of traffic congestion. So, what do they do? They keep on hovering the same thing happens to the atoms and the moment they get a chance to get stuck to the soil they get stuck. So, you think of a situation where around the particle they will be multi layers of cations clear. So, the most high valence cation should be sitting close to the atom.

Close.

Or excrement?

Close.

No. That again depends upon lot of things that will depend upon the valency, that will depend upon the pH and so many other factors pressure and all. So, is very difficult to generalize anything. So, the easiest way to set is there will be so many parameters which will again guide which cation should come and get parked on to the surface? Suppose a truck cannot get parked in a parking lot, but a motorcycle can be parked very easily; the same thing would not happen in this case also. A small diameter cation will have much more easy access to the soil particle as compared to a bigger diameter cation.

But then valency comes into picture, the place is reserved for somebody to come and park the vehicle. So, lot of things are there is a black box clear, but I think this must have given you some reasonable idea about what are the uncertainty is associated with determination of k_d parameters. So, most of these experiments are done with single cation species, but the real-life situation would be where multiple cations are coming in the sludge or the industrial waste.

And hence you have to model a complex solution for finding out its k_d parameter. So, there are lot of things to be done yet all right; any other question? See the easiest path is what either the contaminants will get adhered on to the solid surface or on to the gaseous surface? Because even if they get interaction with liquid phase they will get dissolved again so, partitioning cannot be from water to water phase; so, it is always with water to solid phase and with water to gaseous phase; is this ok? If no water face is there then what happens you tell me a solid contaminant unless it vaporizes there will not be any distribution.

So, that is what I give you an example of camphor, it will not liquefy it will state away sublimate so; that means, from solid state will directly get converted into the gaseous phase, the entire gaseous phase will get adhered onto the surface of the solids this is what is known as gas sorption. So, when you do your carbon dioxide sequestration and all, this is what is more important.

So, you will be conducting an experiment where you are not interested in soil coming in contact with the liquid phase of the contaminant, all your experiments will be diverted towards how much gas can be retained into the solid phase how much carbon dioxide from the atmosphere can be a squeezed and sequestrated into the solids. Is this ok? So, there your connotation of k_d will be h, but not from the liquid phase, incidentally we have talked about gas sorption for finding out SSA a specific surface area.

So, that is also sort of a k_d parameter which we are getting whether sorb where the gas is getting sorb onto the solid phase and hence giving you the surface area. If you remember all your monolayer thickness of the EGMG ethylene blue, we have talked about is nothing, but the layer of molecules of ethylene blue getting adhered on to the particles and depending upon how much amount is adhering you can find out what is surface area?

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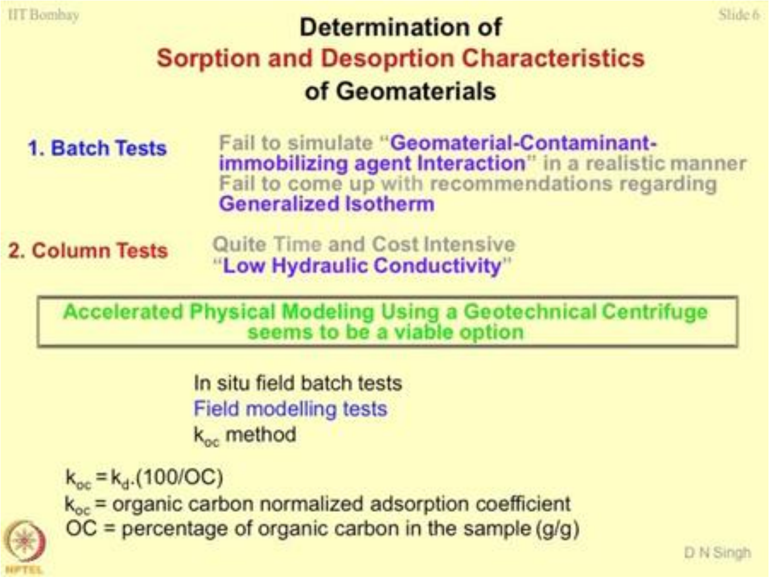

Determination of Sorption and Desoprtion Characteristics of Geomaterials

1. Batch Tests

Fail to simulate "**Geomaterial-Contaminant-immobilizing agent Interaction**" in a realistic manner

Fail to come up with recommendations regarding **Generalized Isotherm**

2. Column Tests

Quite Time and Cost Intensive

"**Low Hydraulic Conductivity**"

Accelerated Physical Modeling Using a Geotechnical Centrifuge seems to be a viable option

In situ field batch tests

Field modelling tests

k_{oc} method

$k_{oc} = k_d.(100/OC)$

k_{oc} = organic carbon normalized adsorption coefficient

OC = percentage of organic carbon in the sample (g/g)

Now, let us discuss the methodology of determination of sorption and desorption characteristics of geomaterials and immobilizing materials admixtures.

First of all, the easiest thing is to perform batch tests or to perform column tests, you might have heard about these tests I am sure, in your environmental engineering course you must have done this. What is batch tests? You take certain amount of the material geo material and mix it with some solution of a contaminant and allow this interaction for a long duration; however, this will fail to simulate geometrical contaminant immobilizing agent interaction in a realistic manner. Why?

In nature this is never going to happen that you take some soil put it in the solution there is always a percolation taking place. So, you this is an acid spell and the rains come what happened this acid as a tendency to migrate into the porous system. So, batch tests will not really give you a clear picture of what is happening in the nature. Water column sorry fail to come up with a recommendation regarding journalize isotherms, I will be talking about what is meant by isotherms. What about column tests? So, you make a column of the soil or admixture and pore certain number of contaminants from the top and let it percolate from the other end.

So, depending upon the sorption capacity of the soil whatever concentration difference is coming in the outflow can be again quantified as a k_d parameter. So, these are typical column tests; column tests are quite near to what happens in the nature, but unfortunately column tests which are done in the laboratory will depend upon the distorted texture of the soil from that which exist in the nature.

So, again they will be giving you very distorted picture of the real-life situation and they are very time-consuming cost intensive. Another thing is supposed if you are simulating a 2-metre-long soil column is it possible to make a 2-metre-long 3 metre long column in the laboratory of a soil mass that to undisturbed, it is not so possible easily. So, you have to live with uncertainties and the problems associated determination of parameters.

But in still we would like to come up with some numbers, so that we can use them in our modeling exercise. Another problem is whenever you are doing column tests the permeability is a very big issue. So, it will take you for 1 metre long column how much time it will take for permeation? If 10^{-11} m/s is a permeability of the clay; how much time it will take you to complete one test? Your M tech will be over definitely by that time.

So, this is where actually people are resorting to centrifuge modeling, this is a good example of how centrifuge modelling can be done Dr. Naidu had done extensively this type of studies for his mass PhD thesis where he has established isotherms utility of some nomograms for selection of a material.

Unfortunately, this paper is not published yet it is in the press accelerated physical modelling using a geotechnical centrifuge is a good solution for finding out sorbing and desorbing characteristics of porous media, I will show you in the later half of the lecture how this can be utilized. So, it seems that the laboratory tests are not going to be very reliable. So, it forces you to conduct this test in the field allow interaction between the soil and contaminant in nature, what do you know what are the difficulties involved clear? Of course, this will give you a real-life situation real life picture, but then very cumbersome process.

Similarly, you can do field modelling test, where you model the contaminant migration into the soil mass, use some pre established numerical models and find out from them the k_d parameter so it becomes a very long exercise. And third one is whenever you are working with highly organic material is what is known as k_{OC} method? So, k_{OC} is nothing, but the organic carbon normalized adsorption coefficient; that means, if you have a soil for which the organic content is very high. Find out the organic content of the material now what is your gut feeling because of organic content the k_d will be more or less.

More.

More. So, what is that you are doing over here?

Normalizing.

Yeah, you are normalizing with respect to 100 percent. So, even if your OC organic content is 100 % k_{OC} will be equal to k_d. So, k_{OC} will always be higher than the k_d parameter because of the organic contents present in the soil mass. So, it is a simple logic which is used to determine the k_{OC} for the organic soils normally this method is not utilized. So, much, but then this is one of the techniques of determining the k_d parameters is this part ok.

So, ultimately people come back to batch tests and the column tests to get some reasonable picture of you know what is happening, it is very difficult to do in situ and the field tests.

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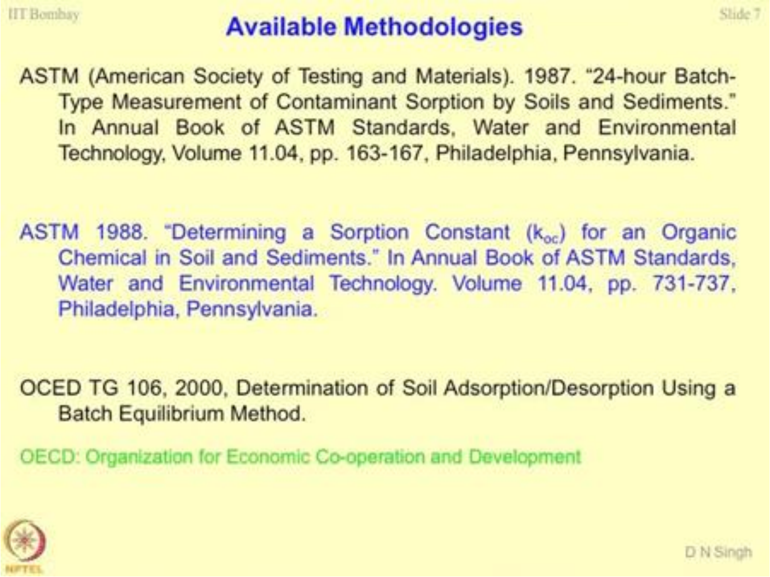

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Available Methodologies

ASTM (American Society of Testing and Materials). 1987. "24-hour Batch-Type Measurement of Contaminant Sorption by Soils and Sediments." In Annual Book of ASTM Standards, Water and Environmental Technology, Volume 11.04, pp. 163-167, Philadelphia, Pennsylvania.

ASTM 1988. "Determining a Sorption Constant (k_{oc}) for an Organic Chemical in Soil and Sediments." In Annual Book of ASTM Standards, Water and Environmental Technology. Volume 11.04, pp. 731-737, Philadelphia, Pennsylvania.

OCED TG 106, 2000, Determination of Soil Adsorption/Desorption Using a Batch Equilibrium Method.

OECD: Organization for Economic Co-operation and Development

NPTEL

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These are the codes which are available in literature, ASTM American Society of Testing Materials has two codes, which are available on 24 hours batch tests for finding out sorption and desorption processes and ASTM 1988 determining this sorption coefficient for an organic chemical soil and sediments. There is another code which is given by OCED there is organization for economic cooperation and development.

One thing you should realize that environmental geotechnology geomechanics is gaining a momentum because of the organizations like this. This is the organization for economic cooperation and development; is it not? As the civilization is progressing is a requirement for developing the course which are going to be helpful and taking major decisions. So, this is how in 2000 they have come up with a guideline determination of soil adsorption, desorption, using a batch equilibrium method.