Environmental Geotechnics
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Lecture – 39
Sorption & Desorption characteristics of geomaterials – 3

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Factors Influencing Sorption and Desorption Characteristics

- *Specific-surface Area*
- *Pozzolanic Activity* (Lime Reactivity)
- CEC Value
- Liquid to Solid Ratio
- pH of the Soil Solution
- Buffer Capacity of the Sorbent
- Temperature
- Grain Size
- Presence of other Ions
- Ionic Strength
- Organic Content & Fe- Mn Oxides
- Carbonate Content

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So, the first thing is the specific surface area of the geomaterial. Pozzolanic activity that is the lime reactivity talks about the percentage of free lime which is present in the soil mass, cation exchange capacity for the value liquid to solid ratio L/S, pH of the soil solution. Now, what is your feeling if pH varies both sides of the you know normal value or neutral value, what should happen to kd? It will remain same or it should change or it should change because both sides of the pH equal to 7 at the pH less than 7 or pH more than 7 the tendency of the system would be different.

More aggressive the environment more acidic the environment the chances are that k_d will be less because the system itself is unstable under more acidity, buffer capacity of the solvent temperature, grain size, presence of other ions. Now, this is what actually gives rise to the competitive sorption which I was talking about, dimension of the ion and its valency ok. So, when you say presence of other ions there is a sort of a competition going on between different cations that which one should get adhered for which is going to get a chance to get adhere on to be clay or the solids.

Their ionic strength, valency, organic contains particularly iron manganese oxide; if your more and then outside the cation exchange capacities are going to be less; is it not. And hence the distribution coefficients are going to be less, the carbonate content carbonate contains if it is more in the soil mass the soil mass becomes passive and hence these parameters will get affected accordingly.

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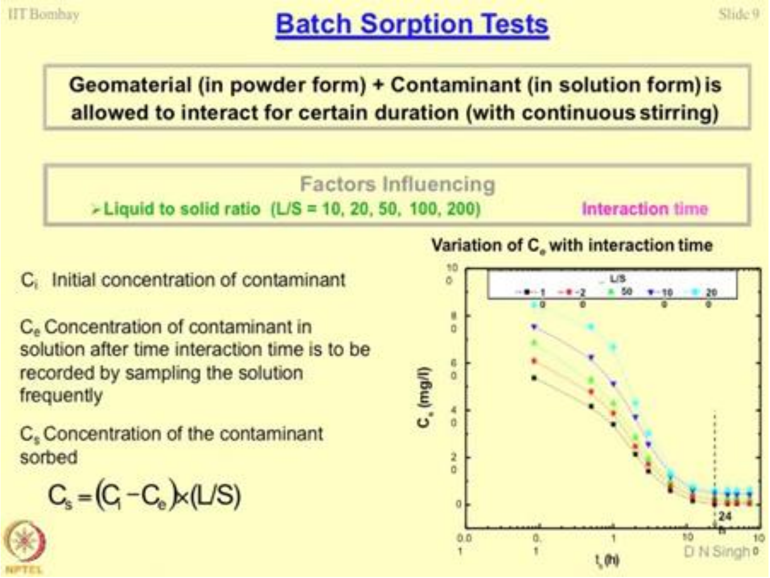

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Batch Sorption Tests

Geomaterial (in powder form) + Contaminant (in solution form) is allowed to interact for certain duration (with continuous stirring)

Factors Influencing

- Liquid to solid ratio (L/S = 10, 20, 50, 100, 200)

Interaction time

C_i Initial concentration of contaminant

C_e Concentration of contaminant in solution after time interaction time is to be recorded by sampling the solution frequently

C_s Concentration of the contaminant sorbed

$$C_s = (C_i - C_e) \times (L/S)$$

Variation of C_e with interaction time

Let us talk about now batch sorption test, take the geomaterial in the powder form and add contaminant in the solution form, this interaction is allowed for a certain duration with continuous stirring. And the fact was which are important or which influence this interaction would be liquid to solid ratio and interaction time. Now, if C_i is the initial concentration of the contaminant in the liquid phase C_e is the concentration of the contaminant in the solution after time interaction time is to be recorded.

After certain time interaction time is to be recorded by sampling the solution frequently and the C_S is the concentration of the contaminant which is soft. Now this is the equation which gives you C_S. Now, if you know C_S this will be nothing, but initial concentration minus C_e. So, what is C_e the containment in the solution? So, this divided by C_e will give you inverse of k_d, clear; because C_S is the conservation of the solids divided by C_e is nothing, but C_W.

$C_S = (C_i - C_e). L/S$

So, this way you will be getting if you plot C_e with respect to time for different L/S what you will notice is that after certain time the concentration which is remaining in the solution remains practically constant; now this is the equilibration time or this is the interaction time. So, the question which you had asked you have to establish for each contaminant porous system what is the equilibration time, beyond which the concentration the solution is not going to change. Once you have got this time you can go ahead with your tests.

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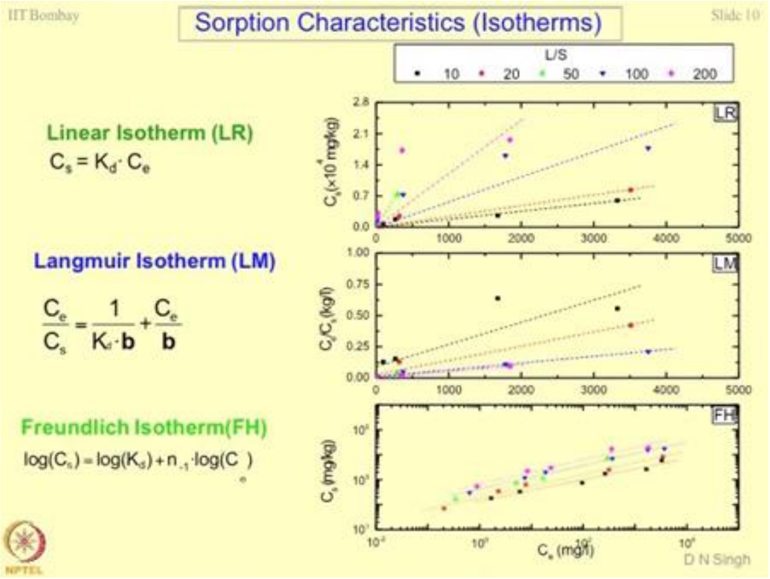
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Sorption Characteristics (Isotherms)

Linear Isotherm (LR)

$C_s = K_d \cdot C_e$

Langmuir Isotherm (LM)

$$\frac{C_e}{C_s} = \frac{1}{K_d \cdot b} + \frac{C_e}{b}$$

Freundlich Isotherm(FH)

$\log(C_s) = \log(K_d) + n_{-1} \cdot \log(C_e)$

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Now, comes the concept of isotherms. So, the first isotherms; isotherm word is a misnomer here please understand. Isothermal is normally used for the equal temperatures, but it has nothing to do when we talk about the concentration profiles. So, linear isotherm is given as LR.

where $C_S = k_d . C_e$, C_S is the concentration on the solids C_e is the concentration of cations or contaminants in the solution phase. This is the one way of defining it another way of defining is a Langmuir isotherm LM.

So, this is how this equation is given $C_e/C_S = (1/k_d.b) + (C_e/b)$; b is a unknown. So, if you are using Langmuir isotherm by doing lot of experiments you have to establish for a given contaminant porous media the values of b so that you can use this b values and you can use this equation to get k_d parameter. The third one is known as Freundlich isotherm

FH, where log of C_S equal to log (k_d) plus some coefficient n inverse of that multiplied by log (C_e).

Now, in this form you have to plot the results, on y axis you have C_e C_S on x axis you have C_e. So, if you plot using linear isotherm you will be getting this type of relationship, if you use Langmuir isotherm you will be getting these types of relationship between C by C_S and C_e.

So, the slope of this line will give you one upon k_d, slope of this lines will give you k_d here n parameter can be obtained. So, the intercept on the y axis will give you log (k_d) and hence you can obtain k_d value. So, these are different techniques of plotting the results which you get from the batch experiments. Now, the question is which isotherm I should select? What you will be noticing here is for the same experiment for the same test results the trends are different and what you notice is that FH that is the Freundlich gives the best possible fit clear. And there could be a situation where LR gives you a better fit or LM gives you a better fit.

So, you have to plot all the three types of isotherms and justify that why you are selecting a certain type of isotherm. Once you have selected this you can get the value of k_d directly, is this part clear. And of course, these two isotherms are named after the researchers who have proposed them.

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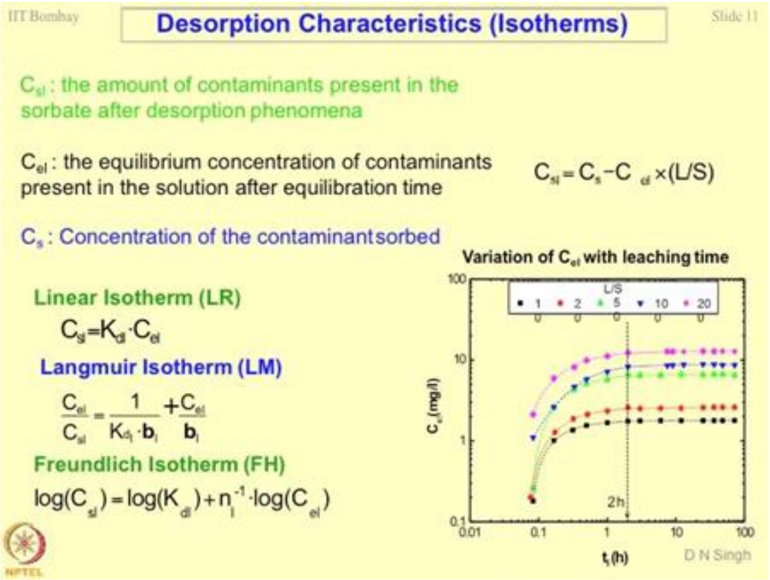

Desorption Characteristics (Isotherms)

C_{sl} : the amount of contaminants present in the sorbate after desorption phenomena

C_{el} : the equilibrium concentration of contaminants present in the solution after equilibration time

$$C_{sl} = C_s - C_{el} \times (L/S)$$

C_s : Concentration of the contaminant sorbed

Linear Isotherm (LR)

$$C_{sl} = K_{dl} \cdot C_{el}$$

Langmuir Isotherm (LM)

$$\frac{C_{el}}{C_{sl}} = \frac{1}{K_{dl} \cdot \mathbf{b}_l} + \frac{C_{el}}{\mathbf{b}_l}$$

Freundlich Isotherm (FH)

$$\log(C_{sl}) = \log(K_{dl}) + n_l^{-1} \cdot \log(C_{el})$$

Variation of C_{el} with leaching time

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These option process will be a inverse phenomena. So, here if you use the words like C_{Sl} what is C_{sl} the amount of contaminants which is present in the sorbate after desorption phenomenon and C_{el} is the equilibrium concentration of contaminants present in the solution after equilibration time and C_S is the concentration of the contaminants which is getting sorb. So, using this expression you can get C_{sl} and then again you can use the same equations, only thing is the parameters will get changed by L. So, this is the leaching or the desorption phenomena C_{sl} is leaching C_{el} is a leaching and so on.

And then what you have to do is you have to establish the equilibration time for leaching; that means, for different L/S if you plot what is the value of C_{el} with respect to time. Now, C_{el} is nothing, but the equilibration concentration of contaminants in the solution, it is very easy you can dip your electrodes take the solution measure the concentration of contaminant and then again you have to find out after which time practically there is no change in the C_{el} value. That means, even if the leaching is taking place nothing leaches out much into the solution phase and hence this is the most critical value. So, this again becomes your equilibration time.

So, once you have got this equilibration time the leaching should be done only for that period and by using these isotherms again you can get the parameters associated with leaching which is k_d. So, you know sorption coefficient, you know desorption coefficient; is this part ok? It must be giving a feel of how these parameters are obtained nothing more than that. You know need not to worry too much do not try to remember these equations and all only thing is we should understand that given parameters how you can obtain what is desirable and how it is obtained.

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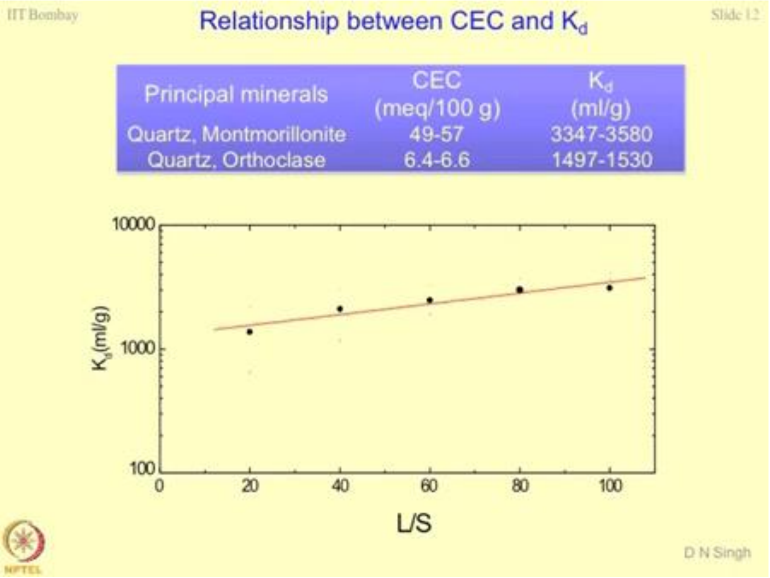

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Relationship between CEC and K_d

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Principal minerals	CEC (meq/100 g)	K_d (ml/g)
Quartz, Montmorillonite	49-57	3347-3580
Quartz, Orthoclase	6.4-6.6	1497-1530

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Now, just to give an idea about the CEC and k_d inter relationship I have included some minerals for a soil we have quartz and montmorillonite both are present, it is a typical marine clay and what you will notice is that the CEC varies from 49 to 57 and the k_d is 3000 to 3600 about. However, if you have quartz and orthoclase like your white clay, kaolin where the cation exchange capacity will be very small and then k_d will also be very small. So, what is your conclusive remark by looking at these values? Even if the mineralogy is not favourable clear the surface area itself is contributing towards k_d up to a certain extent, you got this point.

So, even if you are working on a passive soil where the minerals are not very active the fineness itself is good enough to give you more parking lots for cations to get plum simply. On the top of this would be the mineralogy, where the tendency of the soil is to catch more and more cations on to it and then you can correlate CEC and k_d directly more CEC more $k_{d.}$ So, a day should come where just based on k_d you should be able to characterize the soil mass and its activity and reactivity towards the environment, that would be the ultimate in our subject clear.

So, if you if you think of a situation like any type of a soil, any type of contaminant and you have a matrix of k_d values. So, looking at the k_d values itself you can say that this seems to be a combination between clay and this type of a contaminant and that can be you know very much useful to the professionals. Now, another interesting thing is if you plot k_d as a function of L/S what is Sneha was asking L/S is nothing, but a sort of moisture content. So, this could be in the geometric moisture content form liquid to solid form or even the volumetric moisture content form so they all similar.

L/S is nothing but w and w is equivalent to theta, clear. So, if I plot this what you will notices if L/S is more mobility is there and hence k_d will be more.

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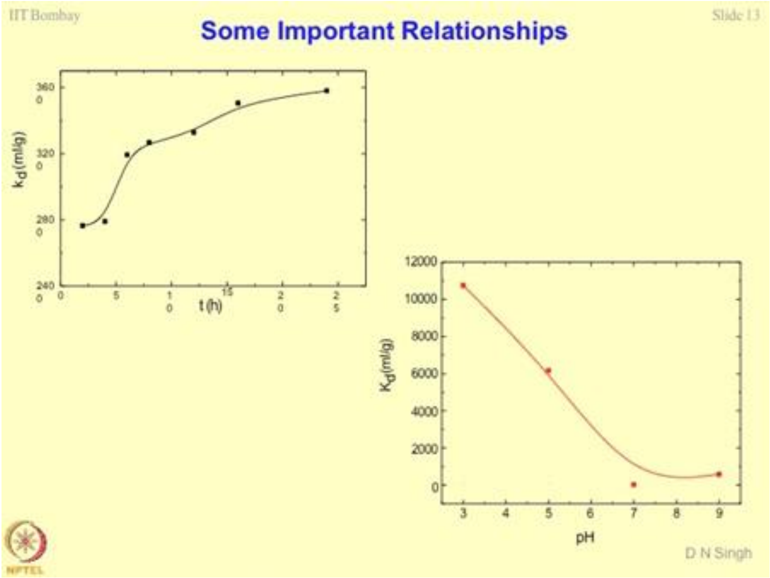

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Some Important Relationships

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Some other important relationship are if you plot k_d with respect to time, now this is nothing, but the interaction time. So, more the interaction time more k_d clear similarly k_d versus pH. Now, this is what I had asked you sometime back, that what is your intuitive feeling that if pH changes look at this just about 7 it touches the minimum. So, in the acidic ranges k_d happens to be wearing too much for a given type of a porous media soil system; however, this curve cannot be generalized so easily.

So, this is one of the trends which somebody might have got for his or her experiments and on the you know basic side that is when pH is more than 7 the influence on k_d is not much.

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Exactly that is what I have been telling you because this is the acidic environment where the system itself is very unstable. So, what is going to happen in the long term is not very known and mind you all these experiments have been done for less than 24 hours. So, within 24 hours degradation of the porous media is ruled out, but the biggest challenge is the parameters which you are getting in the laboratory how you are going to delegate them to the field situations. And one of the challenges would be how to talk about the pH changes on the k_d parameter.

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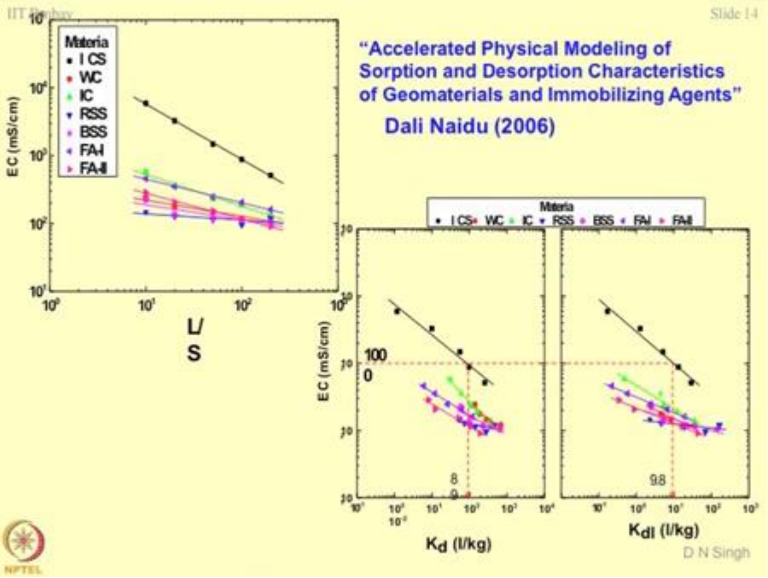

"Accelerated Physical Modeling of Sorption and Desorption Characteristics of Geomaterials and Immobilizing Agents"

Dali Naidu (2006)

Well there was another philosophy that which was proposed by doctor Naidu in 2006; what he try to do is he tried to link electrical conductivity with L/S. So, I am sure you will agree with this that if liquid to solid ratio is more what will happen to the electrical conductivity, it will decrease; when the concentration of ions is less in on this axis when you move from x to y the concentration of ions is becoming less and hence conducted is decreasing.

So, we wanted to develop a nomogram without doing. So, much of work just by measuring electrical conductivity which is very easy to measure you just have to have a electrode and selective electrode which measures the electrical conductivity.

And from there I should be getting what is the value of sorption and desorption parameters. So, we trained our methodology for different types of geomaterials, fly ashes clays rocks, clays, marine clays, kaolin and so on. And then we came up with the proposal that if you measure EC which can be measured very easily, you can directly know the k_d and you can also know the k_{dl}. So, both sorption and desorption parameters can be obtained just by measuring electrical conductivity, but this was premise incomplete, but I have shared with you the philosophy.

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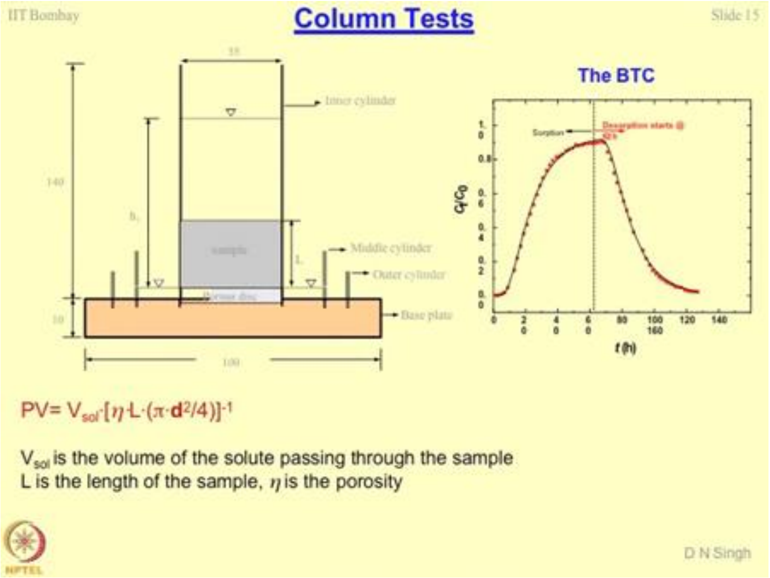

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Column Tests

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$PV = V_{sol} \cdot [\eta \cdot L \cdot (\pi \cdot \mathbf{d}^2/4)]^{-1}$

V_{sol} is the volume of the solute passing through the sample
L is the length of the sample, η is the porosity

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Let me quickly go through the column tests, is this part clear about the batch tests. So, in short you are aligning interaction of the loose form of the material in the powder form with the contaminants and trying to find out the equilibration time beyond which no more sorption will take place on the solids and that is the point where you say the equilibration time and you find out what is the concentrations sorbed on to the solids what is the consultation remaining in the solution, average of the two will give you the k_d parameter.

And when you are doing desorption tests you take the contaminated soil put it in freshwater and see how much in leaching out in a certain time. So, that becomes equilibration time for leaching and within this time you are trying to again defining how much remains on the solid phase, how much comes out in the liquid phase and the ratio of the two will be k_{dl}.

Now, let us talk about the column tests. As I said it will be very difficult to perform column tests in the prototype. So, this is modeling exercise which is normally conducted in a centrifuge, a take a small sample where L is the length of the sample and this sample is packed in a container, the bottom of this setup there is a water table. So, whatever percolates through this comes out and gets accumulated into the system on the standing water table. So, you can dose the system from the top whatever percolates will be getting collected into the outer cylinders.

Now, this is where the concept of pore volume comes into the picture; how many pore volumes of the contaminant you have to pore from the top. So, that something meaningful comes out of the sample. So, this is where you have to define how many pore volumes are present in the soil mass, in any compacted soil mass the biggest question is when it gets completely saturated and when it will start expelling water out from it, clear.

So, this number PV is nothing but the volume of the solution multiplied by porosity of the system and this is nothing, but the volume of the sample. So, inverse of the volume into porosity multiplied by volume of solution is nothing but pore volumes, where L is the length of the sample or the thickness of the sample, D is the diameter of the sample and volume is the v volume is the volume of the solid passing through the sample.

Now, in this situation important thing would be how much time I should allow for the interaction. How do you obtain this is a very big question, I hope you you will realize this? Now, this is a relationship which we will be getting the breakthrough curve if you remember on the y axis this is C_T/C_0 the concentration which is coming out from the downstream side, you collect analyze it in a atomic absorption or ICP get the value of C_T/C_0 is the concentration of the fluid which is being put into. So, that normalized C_T/C_0 value is nothing, but 0 to 1 it will vary.

Now, as time increases what happens C_T/C_0 will start increasing and it will go up to a maximum value, but the moment it becomes close to 0.9 now this is where we started washing it. So, you add fresh water. So, that does desorption process takes place. So, this is the sorption process or the sorption breakthrough curve and this is the desorption breakthrough. You can go for several cycles of sorption desorption to understand what is the resilient modulus of the material as for as sorption desorption is concerned. See you have talked about resilient modulus, for a loading static both as well as the dynamic loading.

Here we can expose the sample to chemical loading in cycles and we would like to see what is the characteristic of porous media contaminant interaction; is this part clear? Now, the tale of this graph over here corresponds to something, what it says is up to this much portion of the graph where C_T/C_0 is almost 0. What is the significance of this? No concentration of contaminant is coming out of a sample; that means, if you check out from here this will give you a time up to which the system has a tendency to sorb only.

So, this is a sorping capacity of the material. Now, after this more and more flux of chemicals come in to the system and what happen, there is a accumulation of concentration and hence C_T/C_0 keeps on increasing very rapidly. And again, you will notice a time comes where further change in C_T becomes almost negligible and this is a point where you say saturation limit of the material; that means, no further interaction is going to take place between contaminant and porous system.

And this is where if you add fresh water somewhere here, what will happen? The desorption will start. So, this is the best way of doing sorption desorption in a column experiment. This work is also by the way incomplete, because of the lack of time we could not do this work completely.

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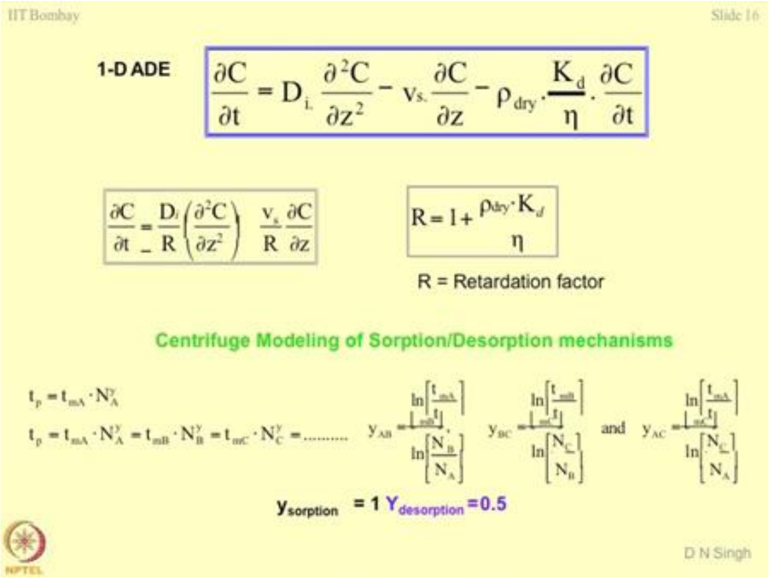

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1-D ADE

$$\boxed{\frac{\partial C}{\partial t} = D_{i.} \frac{\partial^2 C}{\partial z^2} - v_{s.} \frac{\partial C}{\partial z} - \rho_{dry} \cdot \frac{K_d}{\eta} \cdot \frac{\partial C}{\partial t}}$$

$$\boxed{\frac{\partial C}{\partial t} = \frac{D_i}{R}\left(\frac{\partial^2 C}{\partial z^2}\right) - \frac{v_s}{R}\frac{\partial C}{\partial z}}$$

$$\boxed{R = 1 + \frac{\rho_{dry} \cdot K_d}{\eta}}$$

R = Retardation factor

Centrifuge Modeling of Sorption/Desorption mechanisms

$$t_p = t_{mA} \cdot N_A^y$$

$$t_p = t_{mA} \cdot N_A^y = t_{mB} \cdot N_B^y = t_{mC} \cdot N_C^y = \ldots\ldots\ldots \quad y_{AB} = \frac{\ln\left[\frac{t_{mA}}{t_{mB}}\right]}{\ln\left[\frac{N_B}{N_A}\right]}, \quad y_{BC} = \frac{\ln\left[\frac{t_{mB}}{t_{mC}}\right]}{\ln\left[\frac{N_C}{N_B}\right]} \text{ and } y_{AC} = \frac{\ln\left[\frac{t_{mA}}{t_{mC}}\right]}{\ln\left[\frac{N_C}{N_A}\right]}$$

$y_{sorption} = 1$ $Y_{desorption} = 0.5$

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Now, coming back to the modeling part; so, another 5 minutes you just try to understand what I have been discussing, this is the crux of the whole discussion. You have been utilizing this equation to define contaminant transport in x t domain, access the distance or z t domain z is the distance and t is the time. So,

$\Delta C/\Delta t = D_i . (\Delta^2 C/\Delta z^2) - V_S . (\Delta C/\Delta z) - \rho_{dry} . (k_d/\eta) . (\Delta C/\Delta t)$.

Now, there could be a situation where k_d is principle known as well as principle unknown. If you are doing field experiments, what happens then? It is a principal unknown, but if you are doing batch tests then your k_d is a principle known. So, you can do both type of modelling forward and reverse modelling that is a beauty of this type of exercise. So, if you put these terms together $(\Delta C/\Delta t)_{+1}$ that is 1 + $(\rho_d.k_d/\eta)$= D_i. $(\Delta^2 C/\Delta z^2)$. if R =1 + $(\rho_d.k_d/\eta)$.

Now, this r item which is appearing here is known as retardation coefficient. What is the physical meaning of the word retardation? Stopped, is it not retained? So, R is the retardation factor which is directly proportional to k_d; so more the k_d the tendency of the porous media is to retard the contaminant transport clear. So, in the same time the system is getting more and more retardation, the contaminants are not going to flow out easily and hence k_d will also depict a dynamic phenomenon I think somebody was talking on.

Suchith, just you are asking what the time dependent situation. So, because R is a parameter which includes k_d and k_d is going to be time dependent by virtue of these qualities, you can do time modelling for contaminant transport.

However, if you do the centrifuge modelling where you must be using this law, I am sure, for a given model p is the prototype, m is the model suppose this is sample A. So, you can say that t_p equal to t model of A into N_A to the power y, and if I am testing many models, I can generalize this equation like this and if I take their log form this is what it is going to happened. Now, if you look at the previous graph which I have shown you the BTC, the Breakthrough Curves for sorption desorption; which one is steeper, sorption or desorption?

Desorption.

Desorption. What is the meaning of this? If I find out the y value it will be more for sorption or desorption. So, when your y term is 0.5 is very fast it is less than 1 so; that means, for desorption the scaling law would be tp equal to tm n to the power 0.5 clear. So, this is how you can establish the scaling laws for the entire exercise. So, what is the moral of the story? The moral of the story is all this was done to understand how contaminants and geomaterials are going to interact and this interaction can lead to all this what is possible.

So, at the end of the day if I know D_i, if I know V_s, if I know k_d porosity is known $(\Delta C/\Delta t)$ can be monitored by doing experiments and then I can work out what is del c by del z. That means, rate of change of concentration at a given dep means distance and reverse this problem if $(\Delta C/\Delta z)$ is known I can find out what is the concentration migration at a given point at a given time; two applications.

The third one is if $(\Delta C/\Delta t)$ is known $(\Delta C/\Delta z)$ is known I can get the metal properties also; that means, contaminant transport equation can also be utilized for characterization of porous media. The fourth application would be, if you know the porous media if you know $(\Delta C/\Delta t)$ if you know $(\Delta C/\Delta z)$ you can use this equation for obtaining what type of contaminant transport is taking place advective diffusive.

If v s is sorbed be 0 what is D i? If D_i is 0, what is V_s and so on. So, these are 5 6 combinations which can be worked on by using ADE and the biggest question was how to get the parameters. So, this is what we have discussed in details. So, with this I finish chemical characterization of geomaterials. And then hopefully from next lecture onwards I will be talking about thermal characterization electrical characterization. Now, one question is still remaining in my mind is we have been talking about environmental geomechanics. So, where is the mechanics component coming into all this? That has to be realized.

So, if you concentrate on the very first lecture I have been talking about, that we are not talking about the mechanical forces mechanical stress is directly we are talking about this stresses which have been ignored till now; like thermal flux, electrical flux, chemical flux; combination of these fluxes along with mechanical stresses which are going to act on the system. So, that is where actually you require the concepts of environmental geomechanics to solve a problem in total or details; ok.