Environmental Geomechanics

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Lecture No. 40
Contaminant transport through porous media-II

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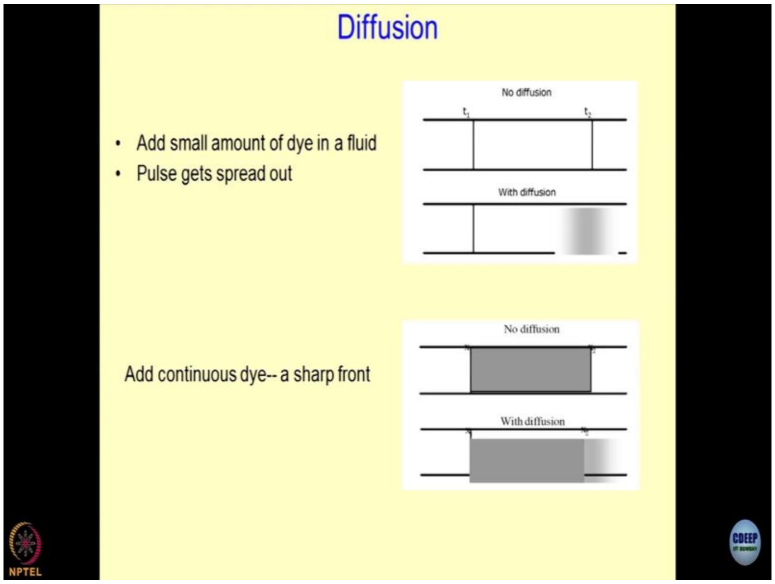

Diffusion

- Add small amount of dye in a fluid
- Pulse gets spread out

Add continuous dye-- a sharp front

This is the best way to study what is diffusive contaminant transport. So, if you add a small amount of dye in a fluid dye could be any colour and what happens after some time this dye diffused in the water when we were kids we were asked to put a small amount of potassium permanganate in a water column. The moment you put a small drop of potassium permanganate, you come after some time, and you find the holes water in the glass have become pinkish, reddish.

So this is a diffusive process, so diffusion is molecular diffusion. You are not shaking it, you are not stirring it, just putting a drop of potassium permanganate, and because of the molecular activity, the entire system is becoming uniformly coloured or contaminated. So, this is a case if I take a solution where the plug remains intact, or like, but there could be a situation where after a certain time, the concentration might drop.

So what I am showing over here is, if you look at this band of the colour, this shows the concentration. So, starting from the initial value, this front is decreasing as far as its width is concerned, and that is because of the diffusion process. So, a better way to understand this would be in this case; there is no diffusion taking place. However, if you really want to show the diffusion, what is going to happen, the intensity of the diffusive contaminant has decreased, and it has spread over in the direction of the flow.

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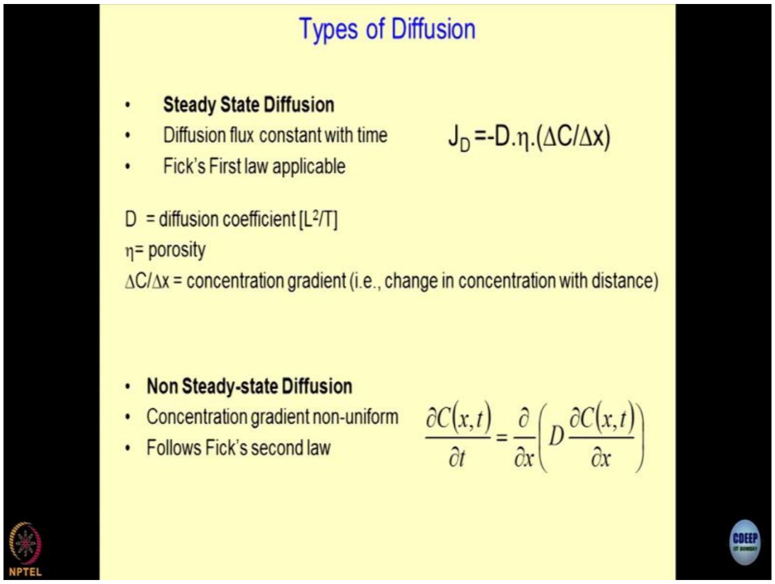

Types of Diffusion

- **Steady State Diffusion**
- Diffusion flux constant with time
- Fick's First law applicable

$J_D = -D.\eta.(\Delta C/\Delta x)$

D = diffusion coefficient $[L^2/T]$
η= porosity
$\Delta C/\Delta x$ = concentration gradient (i.e., change in concentration with distance)

- **Non Steady-state Diffusion**
- Concentration gradient non-uniform
- Follows Fick's second law

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C(x,t)}{\partial x}\right)$$

Now, there are different types of diffuse contaminant transport processes, and we talk about steady-state diffusion, and this is the diffusion flux constant with time. And this is where the Fick's first law is applicable; I am sure you must have studied Fick's law. Do you find this equation somewhere in geomechanics? So, J_D is the diffusive flux, if you remember - corresponds that the concentration of the chemicals is going to decrease with respect to x.

So, you use the sign of minus, eta is the porosity of the porous media, and $\Delta C/\Delta x$ is the concentration gradient. Do you find it somewhere in geomechanics have you used it somewhere if I replace C by the pore water pressure you what is does the $\Delta u/\Delta x$ pore pressure gradient not with respect to time with respect to the length of the sample, where would this be used this concept $\Delta C/\Delta x$ equal to some quotient multiplied by $\Delta^2 U/\Delta x^2$.

Yes. Truly speaking consolidation phenomena is nothing but a diffusive transport of water through the porous media. So, this equation is quite known well known. So, this D is nothing but L^2/T what are the dimensions of C_v coefficient of consolidation that is also L^2/T clear. So, when you talk about the non-steady state diffusion, so, we use this law, this is what is very well known to you.

So, ðC/ðt= ð/ðx multiplied by diffusion coefficient $\Delta C/\Delta x$. So, this becomes a rate of change of concentration with time, and this is the rate of change of concentration with distance. So, when diffusion is occurring, it is a process which is going to happen over a length of the sample and over a period of time, it is a couple of the phenomenon. Is this is correct?

So, there you did a lot of tests to get the value of C_v in the consolidation process. Now again, the question is how you would obtain D value. So, you will have to perform some tests where D can be applied very easily. So, you have to measure the concentrations over a period of time in the sample and along its linear dimensions also.

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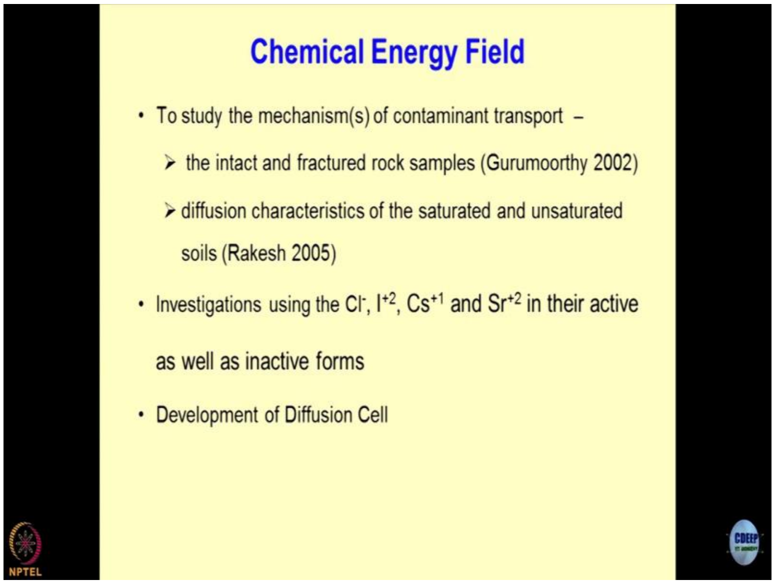

Chemical Energy Field

- To study the mechanism(s) of contaminant transport –
  - the intact and fractured rock samples (Gurumoorthy 2002)
  - diffusion characteristics of the saturated and unsaturated soils (Rakesh 2005)
- Investigations using the Cl^-, I^{+2}, Cs^{+1} and Sr^{+2} in their active as well as inactive forms
- Development of Diffusion Cell

Now coming to the chemical energy field, we have been doing a lot of things in this context and have I did a 3, 4 Ph D thesis, you should go through the Ph D thesis of Dr Gurumoorthy, Dr Rakesh, who are the scientists from atomic energy and they were interested in finding out the contaminant transport through intact and fractured rock mass, particularly of radioisotopes. And

Dr Rakesh was more interested in finding out the contaminant transport through saturated and unsaturated soil mass the reason is simple.

This work is related to the deep disposal of atomic waste, where if you remember I think we have discussed this earlier we dispose of the atomic waste of intermediate and high concentrations in geological repositories in rocks, which are unfragmented non weathered, however when you are talking about the low-level waste, this could be disposed in the trenches, and the depth of disposal will be hardly 10 to 15 meter of the trenches of the vaults. Vaults are the ones which are specially maintained system by RCC lining and in which the atomic waste is deposited.

So, these are the two situations which we are studied that is the rocks and the soils. Soils are saturated, unsaturated and rocks are intact and fractured. I would say this is the first time somebody had studied radionuclide migration through fractured and intact rock mass in 2002 as early as that and Dr Rakesh studied this in saturated, unsaturated soils way back in 2005 So, we studied fluoride, iodide, caesium and strontium and that active as well as inactive forms.

So, active form when I write for these anions and cations, these are radioisotopes, particularly of caesium and strontium. And so, we have completed the studies on all four possibilities. That is intact rock, fractured rock, saturated soils, saturated, unsaturated and saturated soils, reactive contaminants and non-reactive contaminants. And this is where the question was how will you obtained the diffusion coefficient. So we developed diffusion cells.

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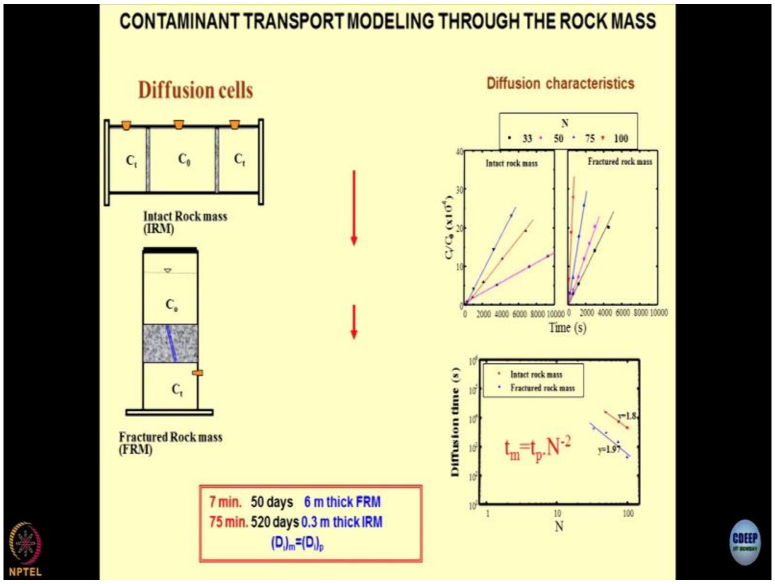
CONTAMINANT TRANSPORT MODELING THROUGH THE ROCK MASS

Diffusion cells

Diffusion characteristics

7 min. 50 days 6 m thick FRM
75 min. 520 days 0.3 m thick IRM
$(D_i)_m=(D_i)_p$

So these are the simple diffusion cells which we created, they would not cost you even a thousand rupees. So, what I have done is I have taken a small glass tube and partitioned it in 3 compartments by using the rock samples. So, this system I have utilized for finding out the diffusion coefficient through the intact rock mass. So those of you who play carrom board who have the strikers. So, what you have to do is you have to collect the rock samples from the field and make thin samples out of it 1 mm 2 mm 5 mm 10 mm thick samples.

And those samples have been fixed in the diffusion cells clearly. So, these are the compartments which get created. I can create a groove on the top of this through which the samples can be taken over a period of time. This is what is known as sampling the central portion is filled out with the contaminant in the liquid form, and then we keep the system as it is for several days. So, as and when diffusion occurs from the central portion to the left and right portion, the Ct can be obtained by sampling through the port we call this as a sampling port and to avoid evaporation of the solution we keep it close most of the time.

Now, when you are dealing with a fractured rock mass, this fracture was done under the laboratory situation, there are sampling sample splitters which have been designed and done. So, you keep a rock sample or a rock core, and then by using a splitter, you can create cleavage or a fracture in the sample. And then, just like as if I am doing a falling head test, I will fit this rock core in a standing tube fill-up the upstream side with the contaminant solution, so this becomes

C0 fill up the bottom portion with pure water and let the contaminant migrate through this. And I can keep a port over here through which I can sample out over a period of time.

So this becomes Ct the way it is. Now I think I am going to answer your question about what you are asking, the setup is ready, and then I can record these results. So what you will observe here is these are known as diffusion characteristics. To save our time, we kept both the diffusion cells in the centrifuge, and we did studies at elevated g value, though we let on realize that the g is not going to influence the diffusion of the copy because this is molecular diffusion.

So, this was the paper which was read by several reviewers, and this is history now anyway, so what you get is you get a C_t/C_0, with respect to time. And normally, these tests were done for months together 3 to 4 or 5 months. Because for getting one sample each point on this curve through a rock mass let us say granite, where the permeability would be 10^{-21} m/s would take you several days or months.

So, this is the game of patience like you have to do this test and be very patient, what centrifugation did is it accelerated the seepage which is taking place through the rock samples advective flow. So, once you have got these diffusive characteristics, we normally consider the initial portion takes the slope of this, and we have shown that this is how the diffusion gets modelled with respect to n, n is the centrifugation effort which you are putting in, and then you can solve these equations you can use $\Delta C/\Delta t = D\times \Delta C.\ \text{Ծ}^2 C/ \delta x^2$ to solve this.

And what we have shown is that the diffusion coefficient in the model is same as the diffusion coefficient in the prototype, which has to be true by using this modelling what we could do is for fragmented or the fractured rock mass and the intact rock mass we have done in 7 minutes we have simulated 50 days of the response of 6 m thick fragment rock mass. In 75 minutes of centrifugation, it is about more than one and a half year of simulation for a 0.3 m thick intact rock mass.

So, these techniques are utilized for the first time, I would say, and we could get some results which were used by people who are into the mathematical modelling. They have used these coefficients and the parameter which you have suggested, and they have gone for the environmental impact analysis. Now, it all looks very simple, but I am sure when this was done, we had no clues. We started from scratch.

And we were lucky to be successful in whatever we touched. I hope you can realize anything which comes to your mind. You got the answer to your question, how the slope is computed how the sorption and other things are done. So the question is like this diffusion will always occur or not because if it is a molecule phenomenon like then, you will always behaving like, there is no concept of conservative or non-conservative in this like if it is a molecule phenomenon, then you always will be having some sort of diffusion. So, go to the concepts.

Diffusion is caused because of the concentration gradient. So as long as ΔC is not 0, the diffusive contaminant will occur. Clear. It is fine. That is what your question is. Anything else?. Yes. **"Professor - student conversation starts"** And this diffusion like it is not related to how do I say it like the chemical sits on the molecule particle-like what happens when we say molecular diffusion the molecular diffusion is occurring through the liquid phase water clear. **"Professor - student conversation ends."**

I gave you an example that if you put the drop of potassium permanganate in this standing water still water even then the entire water becomes pinkish, reddish, and that is because of the molecular diffusion. In the geomaterial, like I was trying to think about what it happens, pores are important we will come to that. So, the liquid phase which is present in the pores of the geomaterials. The molecular diffusion is that going to occur through that.

Imagine all the ports are filled with water, and then there is a concentration gradient. So, what is going to happen all this concentration will migrate through the pore solutions and then it will get equilibrated once is $C_1 = C_2$. As long as $C_1 > C_2$ this whole thing will keep on migrating. Geomaterial has nothing to do with this thing that is what I am asking. Geomaterials are only going to have the pores but still. Pores cannot be in the air. I think I have given you the best possible technical answer.

So, the pores which are saturated in the geomaterials are allowing they are acting like the pipes which are connected with the point number 1 to point number 2, and the entire system is fully saturated. So, the pores are completely filled up with water is it not? There could be a partial saturation also which we are going to talk about is this okay. So, the pores are within the porous media, but yes you can create a diffusive contaminant transport in this room also. Do you have any answer to how you would create this?

Gases are let us say you bring a small bottle of scent, perfume open it at that end, and what happens slowly you can smell it over there. So, this is the diffusive transport off chemicals in a fluid which is air. This is also molecular by the way because this molecular diffusion is taking place in the air, but we are talking about molecular diffusion through the water. So, sometimes we also call this as the free molecular diffusion in water.

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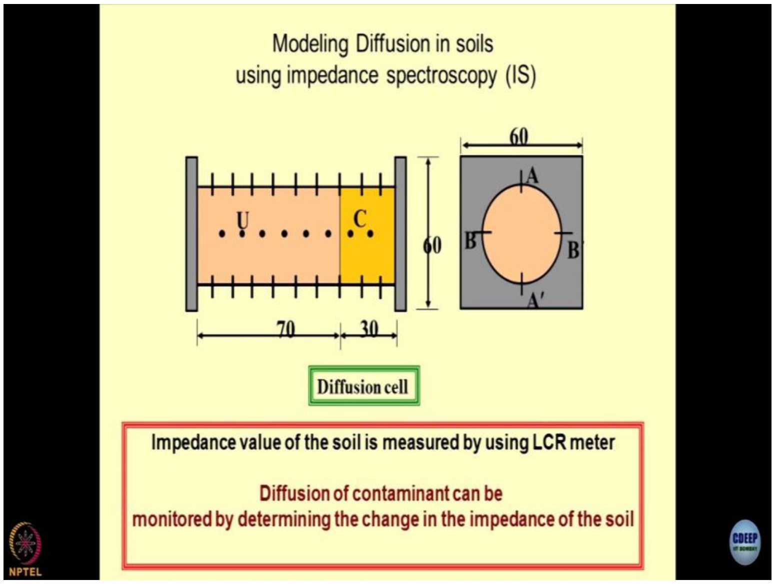

Modeling Diffusion in soils
using impedance spectroscopy (IS)

Diffusion cell

Impedance value of the soil is measured by using LCR meter

Diffusion of contaminant can be
monitored by determining the change in the impedance of the soil

This is something which was created by my student Dr Sreedeep for his Ph D thesis. We were trying to study how diffusion occurs in soils, and this is where we have clubbed the effect of migration of concentration and electric field. So, in today's discussion, if you remember, I started with four modules of advection-diffusion, thermal heat flux and electrical flow. So, this is a beautiful example of how the migration of contaminants can be studied by using impedance spectroscopy. So, impedance spectroscopy is the electromagnetic field.

Which you are using for detecting the moment of contaminant front in soils. So, again we took a tube, and this tube 1/3rd of this tube was filled up with soil which was mixed with some contaminant. So, this becomes a so, this is the tube which has been taken glass tube, or it could be a perplex tube in which 1/3rd of the portion has been filled up with the soil which is spiked with contaminants. And then rest 2/3rd is the uncontaminated soils. So, you just keep the system over a period of time on a horizontal platform and then what you will observe is that the contamination species from C will migrate into U.

And I wanted to see how this pattern of contaminant migration would be. Unfortunately, you cannot take XRA, x-ray or XRD not XRD, x-ray you cannot do of these type of systems. So, a better way is to utilize the electromagnetic field in the form of electrical properties. So, what we have done we have embedded different electrodes, and this is how the electrodes have been embedded into the sample AA prime forms one pair BB prime forms another pair.

So, across the diameter of the sample, we measure the electrical properties, and we are showing how diffusion migrates. So, the objective is to see how much contaminant migrates from right to left and for that impedance spectroscopy has been done. So, this cell itself became a very interesting tool which was created by Dr Sreedeep and by using this type of systems we could study the diffusion coefficient of the saturated and unsaturated soils for different contaminants if you are interested in knowing how this was done, please read the papers written by him.

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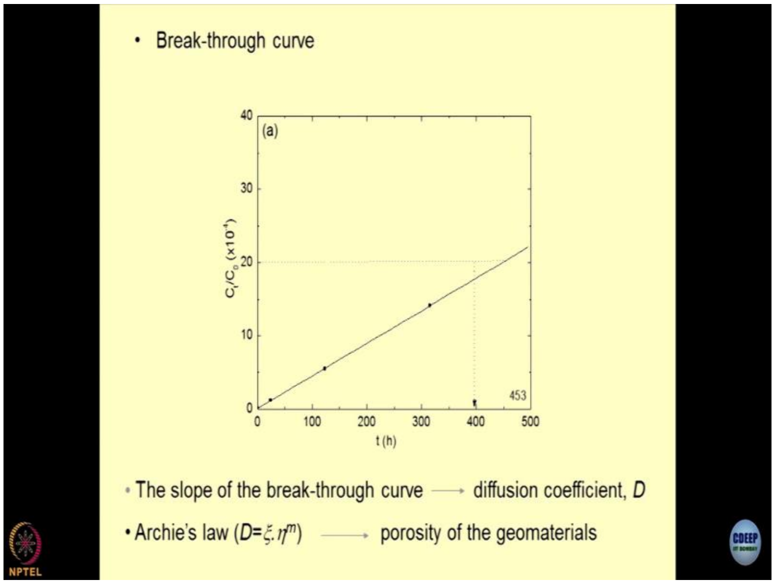

- Break-through curve

- The slope of the break-through curve → diffusion coefficient, *D*
- Archie's law ($D=\xi.\eta^m$) → porosity of the geomaterials

This is another interpretation of the break-through curve. So, if you have C_t/C_0 versus time, we take the slope of this curve, and this is what is defined as the diffusion coefficient. And there is a law which is defined as Archie's law; this is $D= \xi\times\eta^m$. So if you see the papers which have been published by my student, Dr Paresh shah we have tried to come out with a classification scheme for soils where we test our several soils, and we have obtained a diffusion coefficient for a different type of contaminants passing through the soils.

Can you tell me where could this equation be utilized if I know the values of the two parameters eta and small n so, if I say D is known, and if these coefficients are known, I can apply this equation for obtaining the porosity of the geomaterial? So, I am sure you must realize that obtaining porosity is a very difficult task that to the precise conventional way of taking the sample and putting it in water and taking out and weighing it is not going to give you the real porosity of the system. Why? Because the porous might be smaller than the water molecule.

So, under no circumstances is water molecule is going to enter into the pores of the geomaterial. And hence, we have to change these techniques of determination of porosity. So, one of the ways to determine the porosity in the most precise manner would do good diffusion test and if the diffusion coefficient of the contaminant and the porous media because diffusion coefficient is a constant for a given system of contaminant and the porous media. It is an interaction between porous media and the contaminants then I can obtain the porosity.

So, people who are working in the atomic industry and those who are interested in the disposal of the waste in the best possible manner, so that the waste does not contaminate the near field and the far-field. Do you remember we have talked about all this at the beginning of the course? Far fields would be in few kilometres with time ranging from letting us say 10s of years 200s of years. However, if I want to see what is happening immediately, within a few hours within a few days, a few meters away from the disposal site, this becomes a near field.

So, those who are working in these type of studies, they want to not take any risk, and they want the best possible characterization of the geomaterials. So, this is an interesting way of looking at the things that if I am doing a contaminant transport test, diffusive contaminant transport test, I can obtain the porosity also.

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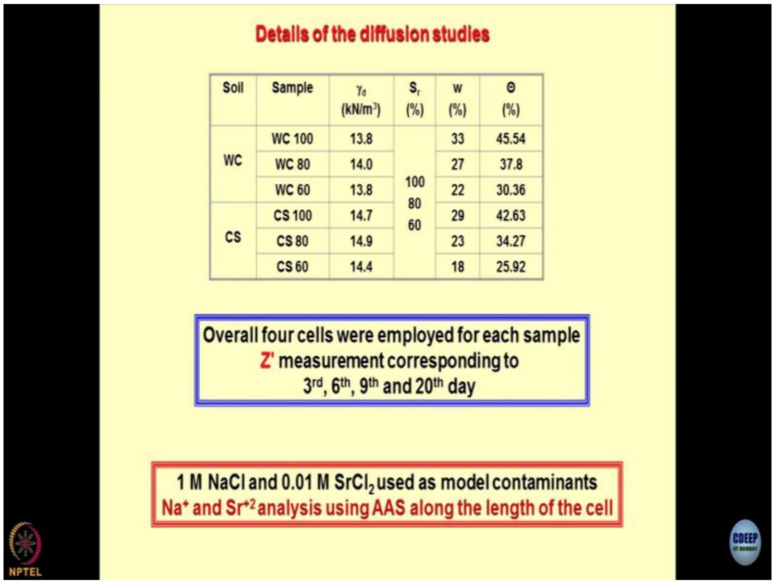

Details of the diffusion studies

Soil	Sample	γ_d (kN/m^3)	S_r (%)	w (%)	Θ (%)
WC	WC 100	13.8	100 80 60	33	45.54
	WC 80	14.0		27	37.8
	WC 60	13.8		22	30.36
CS	CS 100	14.7		29	42.63
	CS 80	14.9		23	34.27
	CS 60	14.4		18	25.92

Overall four cells were employed for each sample
Z' measurement corresponding to
3rd, 6th, 9th and 20th day

1 M NaCl and 0.01 M $SrCl_2$ used as model contaminants
Na^+ and Sr^{+2} analysis using AAS along the length of the cell

So, we did several tests by taking the soils of different types with different saturations. 100, 80, 60 corresponds to saturation levels, the moisture content and the volumetric moisture content and different densities. These are two different types of soils. And what we have measured is that we have measured the impedance. So, I will show you quickly how this impedance can be of some help in establishing the migration of diffusive contaminant front.

So, we have created one molar sodium chloride solution and point not one molar strontium chloride solution. Because these contaminants are normally present in most of the sludges which are coming out of the industrial sludge. And then you can analyze the sodium concentration and strengthen concentration by using ICP or atomic absorption. So, this is a classical way of doing this.

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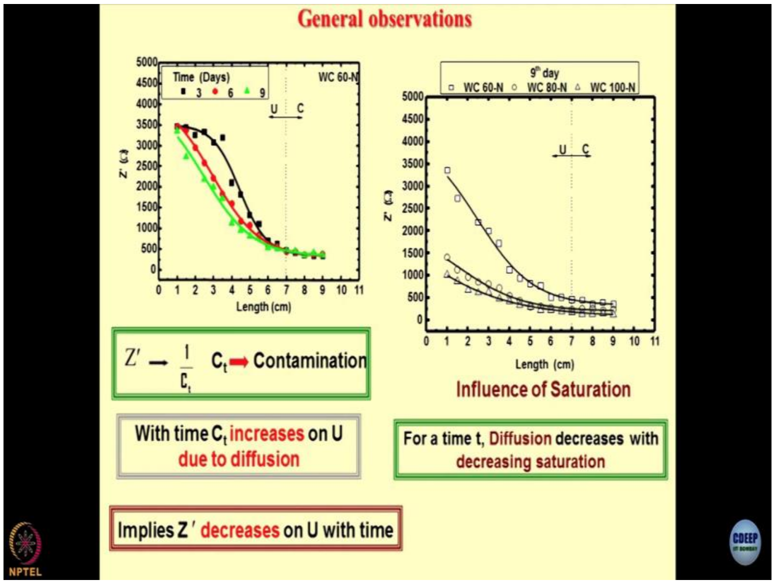
General observations

$Z' \rightarrow \frac{1}{C_t}$ $C_t \rightarrow$ Contamination

With time C_t increases on U due to diffusion

Implies Z′ decreases on U with time

Influence of Saturation

For a time t, Diffusion decreases with decreasing saturation

Now, what you are observing over here is if you plot impedance with respect to the length of the sample, do you remember that setup here I have shown you uncontaminated soil up to one third and sorry uncontaminated soil up to two thirds and contaminated soil up to 1/3rd of the sample two compartments. So, this is the contaminated soil, and this is the uncontaminated soil. And when you leave this over a period of time, what you will observe is the contaminants migrate into uncontaminated soil region.

And because of migration of the contaminants, the impedance, what happens to the impedance. Impedance should increase, or impedance should decrease impedance decreases, why because the soil becomes more conducting. So, this concert we have utilized that impedance is inversely proportional to the concentration of chemicals, and by doing some simulation and modelling, we have obtained the diffusion coefficient of the soils. So, this is how the influence of saturation has been plotted, when you have them at a given time for different states of the material, how the diffusive contaminant transport will occur.

As I say if you really want to understand and learn about these processes, please follow the papers which have been written by Sreedeep and myself and you can come across the trivialities and the difficulties associated in doing this test. Fortunately, all these things are well established now, and you can go through, and you can follow it better. What I wanted to demonstrate is that simple equipment simple techniques can be developed in modern-day. Persuasion of science and technology and you need not depend upon hi-fi gadgets to execute your research ideas.

In contaminated soil, why is it remaining constant concentrations decrease? It is a good question. So, concentration the contaminant could be so high that there is a minor change, and for all practical purposes, I can assume the concentration of contaminated soil to remain constant. Suppose 30,000 ppm and what is diffusing is hardly 1 or 2 ppm. So, it is a sort of a constant loading which I am maintaining on the system. And similarly, in this case, this is a case of constant concentration being exposed to the soil sample so, ΔC is insignificant, and as the reason, the C remains constant. Good observation.

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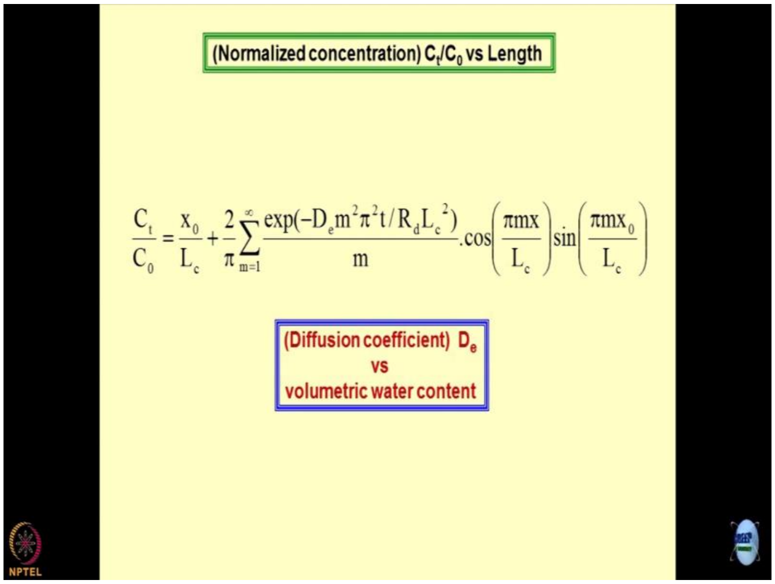

(Normalized concentration) C_t/C_0 vs Length

$$\frac{C_t}{C_0}=\frac{x_0}{L_c}+\frac{2}{\pi}\sum_{m=1}^{\infty}\frac{\exp(-D_e m^2\pi^2 t/R_d L_c^2)}{m}.\cos\left(\frac{\pi m x}{L_c}\right)\sin\left(\frac{\pi m x_0}{L_c}\right)$$

(Diffusion coefficient) D_e
vs
volumetric water content

Then this is the equation diffusion contaminant transport, where if you look at this equation, this is one of the forms of the solutions, which we have discussed earlier second Fick's law C ðt = D into $\Delta^2 C/\Delta x^2$. So, C_t/C_0 is nothing but the normalized concentration L is the length of the sample.

And Rd is what is appearing over here is the retardation coefficient. I think we discussed this sometime back and I did ask you to write down on the on your notebook.

Which I am going to discuss. So, this Rd coefficient indicates that what is the retardation coefficient of the geomaterial which is related to the sorption of the geomaterial. Now, D_e is the diffusion coefficient, not free. This is through the pores we call it an effective diffusion coefficient. What people are trying to do is they are trying to solve this expression the moment I get D_e to term the moment I get Rd term. Rd term is dependent upon the density of the soil mass and is volumetric moisture content.

What it indicates is that C_t/C_0 over a period of time and length is going to be an exponential decay is this okay?. Exponential - d time and L_c. L_c could be the total length of the sample and x is the distance. So, those terms are appearing in cos and sin terms in the form of x and x_0 at different t values. So, if you saw this expression, you can get how C_t/C_0 is changing with respect to x. It is a time series, so, this is all you have got the time factor from the consolidation equation also.