Lecture No. 44
Sorption-desorption characteristics-III

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Partitioning relationships partitioning could happen from solid to the water phase, alright. Saturated soils pores are filled up with water; C_s is the concentration of the solids concentration retained on the solids. C_w is the concentration of the contaminant, which remains in the water. So, this is the K_d parameter. So, imagine if I have one gram of clay and if I dip it in a solution of some molarity some concentration of cations, how many cations have got sorbed on the clay particle can be obtained by deducting the C_w from the initial concentration by using ICP or atomic absorption spectrophotometry is this okay.

So, C_s is the sorbate which is sorbed on the solids and C_w is a sorbate which is remaining in the solution at equilibrium. The second one which is quite intricate and difficult to simulate in the laboratory condition would be water vapour and nature does it very beautiful it is not easy to create an interface between water and vapour in the laboratory circumstances, you must have

heard Henry's law. Right. So, what is C_g? Here we use C_s/C_w. This C_s/C_w, but the guys who are working in the field of climate science, aerosols, air quality analysis for them, I hope you realize the water vapour interaction is going to be extremely important.

So C_g is the concentration of the gas which is getting sorbed on the solids divided by the concentration of the sorbate, which is remaining in the liquid phase. So, we have solid water, or we have water vapour two types of interaction then you can compute the total mass per unit volume of the geomaterial by using these relationships. So, θ_w is the volumetric moisture content, θ_g is the volumetric vapour content, theta is the volumetric moisture content, which is equal to saturation into porosity, this is the gas component. This is the fluid phase component, and this gets converted into when you are talking about no gaseous phase, this gets converted into the concentration of the solids concentration on the solids and concentration which remains in the water solution. This is how the partitioning is defined. Do not write down these equations, you just understand. If you get a chance to work in this area, you will learn it automatically so far so good.

I hope you realize the intricacies associated with the environmental geomechanics; henceforth we are still attempting it. A good example of this would be gas hydrates, where we have a 3 phase system, and we will lower down the pressure or increase the temperature, and the decoupling takes place in the material.

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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)

Well, so, to start with, determination of sorption and desorption of geomaterials, normally batch tests are done, or column tests are done. Batch tests are you take some material, few grams of soil or geomaterial or in a powdered form why you have made powder so that all the particles contribute to the process and then put them in a solution which is not a beaker or a container. What is happening is that you are allowing 100% interaction between each and every particles with the solution.

So, this is the best possible form of studying contaminant geomaterial interaction or the immobilizing agents. Unfortunately, this type of situation is not going to occur in the field, why because the soil mass is in a compact form. So, all the surface of the grains is not really contributing to the interaction because when you compact it what happens, a substantial amount of the surface of each grain gets hidden by next grain. So, it does not come in contact with the contaminant directly. So, that means if you are doing the batch test, you are going to get something which is extremely lowered value of the k_d parameter.

So, what people do is they do batch-test sorry column tests. So, you make the columns and let contaminants pass through them, and then see how much has been sorbed by the soil column or the geomaterial column. Now, this is going to be realistic because in nature also you have soil beds. But unfortunately it is a very time-consuming process. Why? Because the permeation through the compacted soils and the geomaterials is time-consuming and extremely expensive.

So this is going to give you a very lower value of the k_d, but yes, these are the two tests which you can do.

Whatever parameters we get from batch tests and the column test, somewhere in between, we have to select the right parameter for doing our mathematical model. So, these are the 2 bounds of the k_d parameters which you get by conducting laboratory experiments. This is where you can do centrifuge modelling also. And I will show you some of the results which our group has published were centrifuge was used to obtaining the k_d parameters from the column test, we can also do these tests in the field, we can do field modelling tests, there is another method which is known as distribution coefficient.

Which can be obtained because of the presence of organic content in the soils. So, the soil which has higher organic contents would have higher distribution coefficient. So, there is an empirical relationship which has been given by $k_{OC} = k_d \times 100/OC$. So, k_{OC} the organic carbon normalized adsorption coefficient, and OC is a percentage of organic carbon which is present in the sample. Do not write these things. These things are available in the codes, and you can use them in case you are working on these topics.

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These are the codes and the information which is available already. I hope you can realize as far as the Indian context is concerned, we do not have any guidelines. So, these are mostly ASTM

standards, and the OCED standards do what OCED is? Organization for Economic Cooperation and Development. These type of treaties and the guidelines are useful when you are exporting and importing any material from any country that becomes a mandatory thing.

 If you send a courier through any of courier agencies, they will take a declaration from you that this material is not toxic. There will be some 20-page gazette associated with this document which you have to sign, and you have to declare that the material which you are sending as a consignment does not fall in the category of toxic material, export and import. So, these are the standards and international norms which have to be followed.

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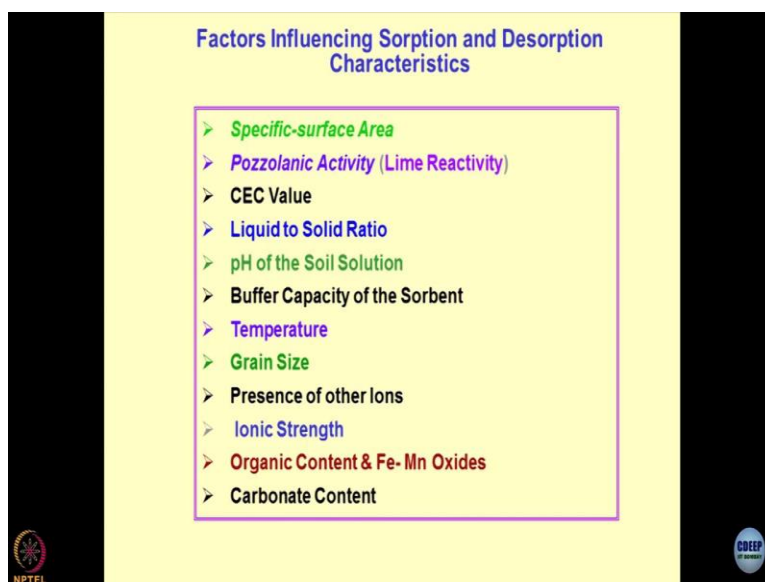
The list of the parameters which influence the sorption and desorption mechanisms is big whatever comes to your mind can be written here, but primarily surface area contributes a lot because surface area contributes to the cation exchange capacity also, the pozzolanic activity of material, liquid to the solid ratio? What is liquid to solid ratio if I take one litre of water and if I add into some salt of known weight, I can create a solution of certain molarity. This is your 10+2 science. So, this becomes my contaminant in this contaminant, if I add one gram of soil.

So, one gram of soil I am adding to 1000cc of or ml of water. So, this becomes liquid to solid ratio of 1000. So, what I have done indirectly, I have simulated a situation which is similar to the pore solution. So all the studies I will be doing by using this liquid, solid ratio, where the soil is

one gram and the solution is 1000ml, so, the more realistic value would be 20,25 10 that means 20 times solution.

One gram of soil, pH of the solution, the buffer capacity of the sorbent, temperature, grain size presence of other ions, ionic strength, organic content, iron, magnesium oxides and the carbonate content the list is very big, I have just given you some parameters which would be influencing the k_d parameter directly. Just to remind you why k_d parameter is required because you wanted to solve one-dimensional ADE. Do you remember?. So, unless you get k_d parameter, you cannot get C_t as a function of x y z and t.

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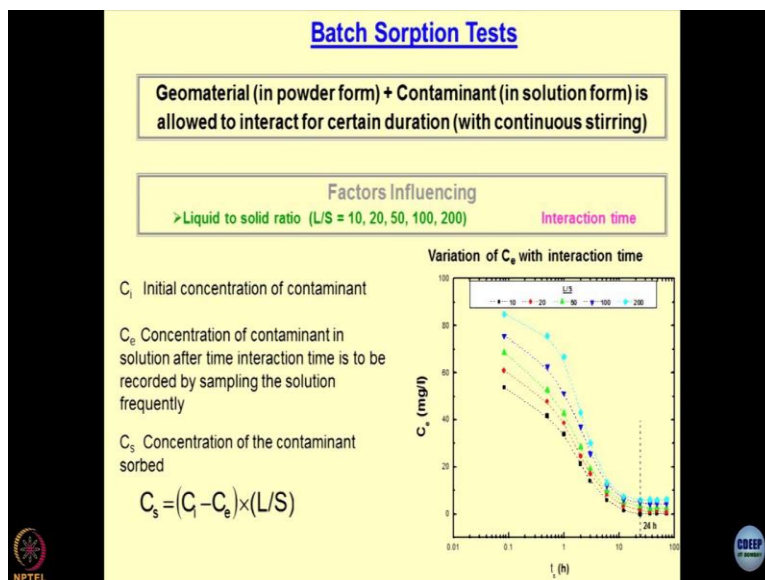
So, the batch tests are you take a certain amount of soil or the geomaterial in the powder form, put it in the solution, stir it over a period of time, heat it also if you want and then create different liquid, solid ratios and then keep on sampling out from the solution and see what concentration of chemicals is getting sorbed on to the solid phase. So, this is what I was discussing. The CS is the concentration of contaminant in the sorbed form, which can be obtained by subtracting whatever is the concentration in the solution after equilibration. From the initial concentration multiplied by L/S.

So this is how we do this test. These tests are extremely intensive to conduct each point you might be getting after a few days. So there was my student, Dr. Pankaj Pathak. She did her PhD

on this. And I think she is one of the pioneers in this subject. She has published 3 international journal papers in ASCE and 2 patents. That is really remarkable. And the patents are in the form of the guidelines which have been created, how to perform these tests?. You may not be aware that there are no guidelines which are available to select the concentration of the chemicals and the amount of soils.

And we realized from the completely negative results, that if you do the census of results properly, you can get an extremely interesting idea which can be published in the form of a paper and a patent. So, never ignore the results that you get, which appear to be incorrect, because there is a story behind that also, if you have time and if you sit down and apply your mind you will realize there is something interesting which has happened and which was going totally unnoticed. So, at different L by S of the solutions when I take certain soil and when I allow interaction to occur, what you are observing here is Ce is the concentration of the contaminant the solution.

So, the concentration of contaminant the solution decreases over a period of time, why, because this concentration is getting solved onto the solid phase and hence this option is going on. So, after a certain time, what you observe is that concentration becomes almost constant; this is what is known as equilibration time. So, for every contaminant and geomaterial, the incubation time is going to be different. So, the moment you change the parameters here, the equilibration time changes, tests are so sensitive.

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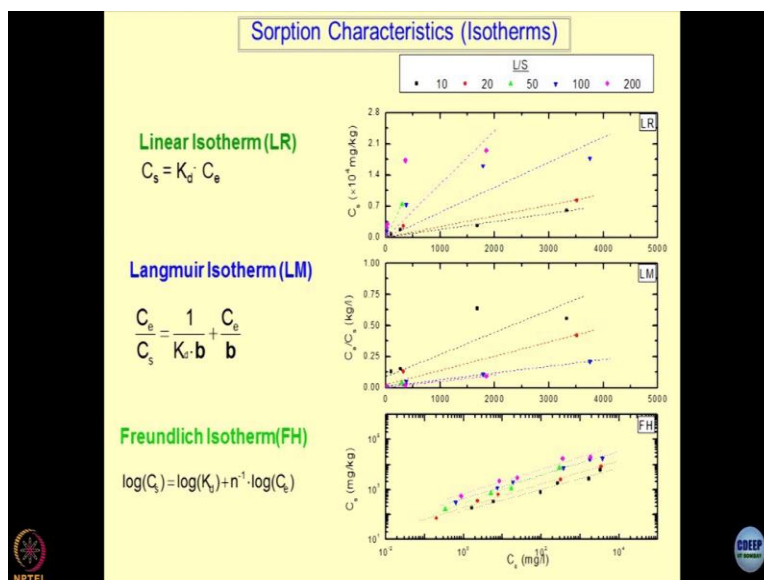
Now how to analyze these results. How to get the sorption characteristics. So, sorption characteristics are obtained by using these three mathematical models. And these three mathematical models are known as isotherms. The term therm, which is associated with this model is a misnomer. It has nothing to do with the temperature because these are the plots of concentrations, but, because the concentration is very much susceptible to the temperature, all these parameters have obtained at a constant temperature and hence, all these graphs which are being shown correspond to a specific temperature.

So, what normally is done is you plot C_s vs C_e just to remind you C_s, is the concentration which is sorbed on the solid phase and C_e the concentration which is still available in the solution phase. So, when you plot these 2 against each other, these are the models which are used linear isotherm, Langmuir isotherm, Freundlich isotherm, you just understand how the interpretation is made, what you will observe is out of the three which are very common, you can also come out with your own isotherm. So, that would become x y z isotherm in this matter is still the subject is under the developmental stage. So, if you propose a kinetic process, it goes in your credit.

So, once you draw the straight lines are fitting to fit the best fit to the data which you are getting, what you will observe is that some of the isotherms do not follow experimental conditions, there are some which will follow better. So, like in this case what we have presented here the Freundlich isotherm is giving very good results as compared to the linear isotherm. Alright?. So,

this is how you ever train the experimental data. The slope of these lines is nothing but k_d parameter. So, here you can observe C_s/C_e is k_d.

So, once you have plotted these graphs, the trends take the slopes, this is k_d parameter. So, Most of the cases, the slope of the line is the k_d parameter. I hope now the methodology is known to you. You can perform these tests, and you can use them. The best example of k_d parameter would be in the pharmaceutical industry, how I hope that the carrier of the medicines are the tablets that you are taking is a clay mineral, and that clay mineral is dosed with different types of medicines.

So, the moment you swallow it, you want to accelerate the desorption process or sorption process, so, depends upon the doctor. Imagine if your colon is full of bacteria. What I would like to do, I would like to insert something which goes inside and attracts everything and then comes out to excreta. At the same time if I want to impregnate your body with some chemicals which are required as nutrients.

So what I will do, I will take this matrix of the clay minerals, charge them with that particular species of the bacteria, medicine, whatever. And the best way to inject this would be through your oesophagus; you eat it, it goes in your stomach becomes a part of the blood tomorrow. So, sorption and desorption in the best possible way can be practised in this manner. Think about it. I hope you are getting all the applications of how to use this. You must have realized what we will do is after achieving the equilibration in the sorption, you take out those samples which are fully contaminated, put them in freshwater.

And as the time increases, what happens the contaminants which were sorbed there will ooze out into the fluid phase and keep measuring them every time. So, after a certain time, what you will observe the concentration of the contaminants in the solution phase is going to increase and becomes constant. So, this is a desorption characteristic and is what is known as desorption equilibration time.

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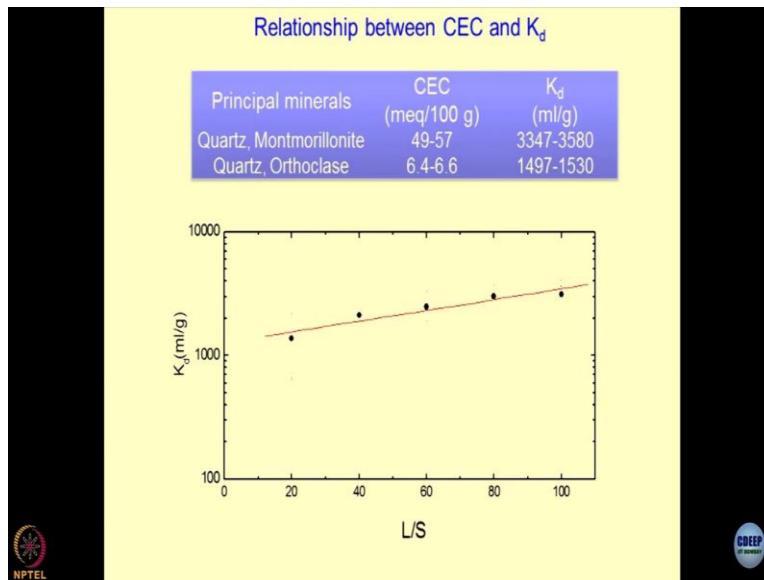
Rest methodology is same you can find out the k_d parameter for sorption desorption by using the same isotherms, and you can designate the geomaterial to contaminate interaction, many people are trying to quantify this contaminant geomaterial interaction the form of CEC, and I hope you understand that CEC is linked with the surface area. So, why the surface area becomes very important because it gives an indication of CEC. And CEC gives an indication of k_d so they are all interrelated. So, we were trying to work on this model.

So, That we can get rid of the conventional soil classification system. Conventional soil classification systems cannot be used for environmental geomechanics applications, because nowhere you talk about the geomaterials interacting with contaminants. I hope you will agree with this agreement. But we have created so many case studies to make you convince that you cannot isolate the geomaterials from the environment. Geoenvironment, which is either man-made or natural. So, this is becoming a very interesting debate in the international fraternity.

Can we eliminate all these conventional tests and come out with simple parameters which would define how geomaterial interacts with geoenvironment. So once you have done this, this is going to be ultimate bramhastra. That is what people are trying to do. So, we have shown here k_d is dependent upon L/S, a different type of minerals are related to k_d to CEC. We have shown how k_d changes with time? How k_d changes with pH. So, these are the subjects which have to be

studied further. This is the thesis of my PhD student Dr. Naidu is a faculty member now that IIT Chennai.

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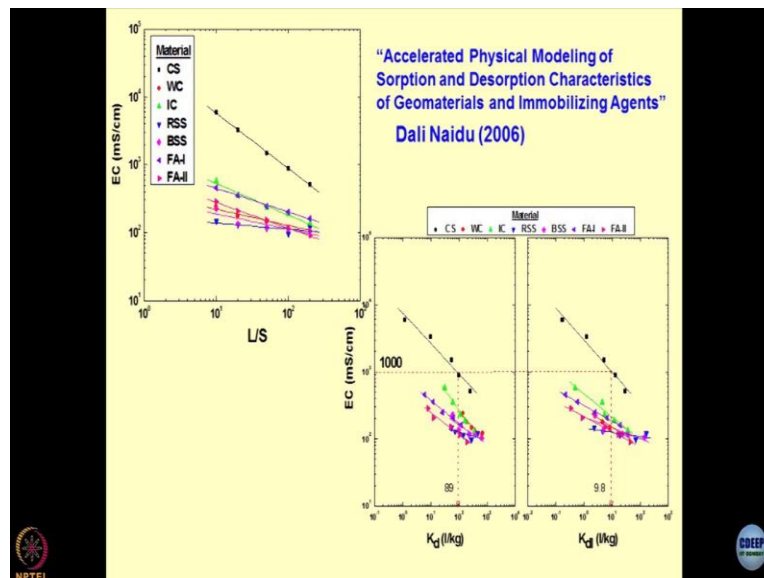
He did remarkable work, and he was the first one to crack this problem of electrical conductivity of a geomaterial-contaminant system directly giving the k_d parameter. So, imagine if I create some probes or sensors. So, sensors will give me directly the EC value and that EC value can I from that EC value? Can I obtain the k_d in sorption and k_d desorption? If this can be done, this would be an interesting thing.

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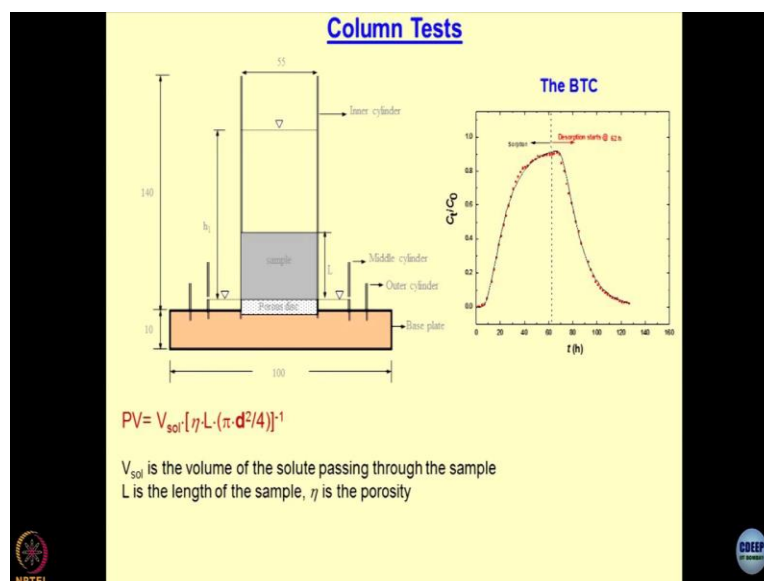
Now comes the column tests having talked about the batch test, we create a column here, something similar to the falling head permeameter test which you normally do, this is a sample which is sitting on porous stone, and the whole system has been mounted on a base plate, where we have two more concentric cylinders, what we do is we fill up the inner cylinder up to a certain point with the contaminants they percolate through the sample.

Whatever percolate comes, or the leachates come they get accumulated in the middle cylinder, in case they overflow, they will get accumulated in the outer cylinder. So, these are typical column tests which are done; this is where we use the concept of pore volumes. How much volume of the solution should be added, which will ensure that the contaminant is passing through the sample and saturating all the pores?

So, this is a philosophy we created like the number of pore volumes is equal to the volume of the soil divided by the volume of the physical volume of the sample. So, if you see this term, where the porosity has been multiplied, so porosity is the volume of voids, multiplied by the total volume of the soil sample. So truly speaking, this is nothing but the volume of the voids. So the number of pore volumes are volume of the solution, divided by the volume of voids.

So if the volume of voids is unity, I have to add 5 times the pore solution to do these tests, we get a very interesting relationship like this. I hope if you concentrate on y-axis and x-axis, you will realize that this is also sort of a BTC, breakthrough curve where we have Ct by C not increasing with time first, this is the sorption process. And at this point, if I start desorbing washing, I get the tale of the curve where C_t/C_0 decrease very fast with time. We did this test in the centrifuge. We saved our time, and this was the first of this kind of the study which was done by somebody Dr. Naidu, where we established the breakthrough curves in the centrifuge for a soil contaminant system fine and how to get the k_d parameters from there. And what we have done is, we have used this information.

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To solve one-dimensional ADE, this is the form of the ADE do you remember $\partial C/\partial t$ equal to the diffusion coefficient $(\partial^2 C/\partial z^2)$- $V_s\times (\partial C/\partial z)$- $\rho_{dry}\times(k_d/\eta)\times (\partial C/\partial t)$. If I take this time over here, this will become $\partial C/\partial t =(D_i/R)\times (\partial^2 C/\partial z^2)-(V_s/R)\times(\partial C/\partial z)$.

Porosity can be determined by using porosimetry, mercury intrusive porosimeter, MIP. The best possible way. The porosity of the porous media is known if k_d is known radiation coefficient can be obtained. So, by conducting these tests, you can get k_d parameter also. And once you get k_d parameter, you get R parameter also, and now you can solve the ADE. I hope you have understood the whole story.

So, just out of curiosity, what we did is we did centrifuge modelling of sorption desorption process, I think, you are doing a course on centrifuge modelling. So, the big question was, can we model the phenomena in the centrifuge and what happens in the prototypes and we modelled the time T_p corresponds to prototype, T_m corresponds to model and is the centrifugation effort. So, if I say that $T_p= Tm\times N_A{}^y$ this is what is going to give me the complete picture, this is how we were doing this modelling of sorption desorption mechanisms.

And what we observed is that we got for sorption we call them as scaling parameters scaling factors. So, for sorption process, which is a slow process, if you remember, if you see this graph, you will realize that sorption is a slow process contaminant getting assimilated with the surface,

but desorption is very fast. If you see there, the desorption, time factor is point 5. So, these are the interesting things which we did a lot is to be done in this area.

I hope this discussion of today must have given you an idea about where we are where we could contribute to the knowledge and what needs to be done further. The practical utility of this type of work is extreme, and I hope you can realize that if you have to safeguard the environment against its contamination. Many times you have to come back and fall on this equation and predict what the impact of our activities on the geomaterials is?

Which, if you remember, we discussed at the beginning of the course under the realm of EIA, environmental impact analysis. So, because of any industrial activity, the waste is generated. And if I am dumping the waste somewhere, anybody is going to ask me a question, what are the impact of this waste in the near fields and the far fields over a period of time? So, when you answer all these questions, you have to resort to mathematical modelling.

But as I said, it is very easy to resort to the mathematical modelling provided, the coefficients, which are unknown. And in order to get these coefficients, you have to make a long journey; you have to create your own setups, to derive the expressions you have to analyze the whole situation. And those parameters have to be plugged in over here. The suitable boundary conditions to get the answer. So, this is where we are. I hope people like you will contribute further and the subject grows much much much.