Environmental Geomechanics

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Lecture No. 42
Sorption-desorption characteristics-I

Since several lectures I have been discussing about the geometrical characterization and in particular, the chemical characterization. We have discussed lot of things under the realm of chemical characterization. And in particular in the previous lecture, we were discussing about the contaminant transport through porous media.

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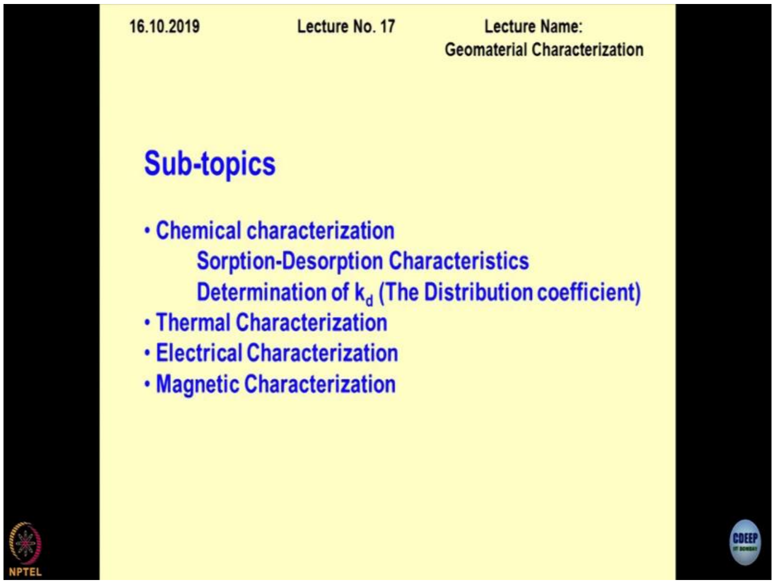

16.10.2019 Lecture No. 17 Lecture Name: Geomaterial Characterization

Sub-topics

- Chemical characterization
    - Sorption-Desorption Characteristics
    - Determination of k_d (The Distribution coefficient)
- Thermal Characterization
- Electrical Characterization
- Magnetic Characterization

And this is where I had coined this concept of sorption desorption mechanisms or the characteristics we had discussed the one-dimensional advection-diffusion equation. And I had also informed you that this is the best way to quantify the geomaterial contaminant interaction. So, today's discussion would be revolving around the mechanisms of sorption desorption, and how would you determine the K_d parameter? Because if you remember in the previous lecture when we were discussing the one-dimensional ADE, there I had pinpointed that, unless the K_d parameter.

You cannot get the retardation coefficient R, and you cannot solve the equation, which would give you the concentration of contaminant with respect to distance and time. So, this is where the K_d becomes very important. In other words, K_d is also important to quantify the amount of sorption or the reverse process, which is desorption is going to occur. Incidentally, K_d is known as the distribution coefficient. And having done this, I will go back to thermal characterization, electrical characterization and magnetic characterization. So, to begin with.

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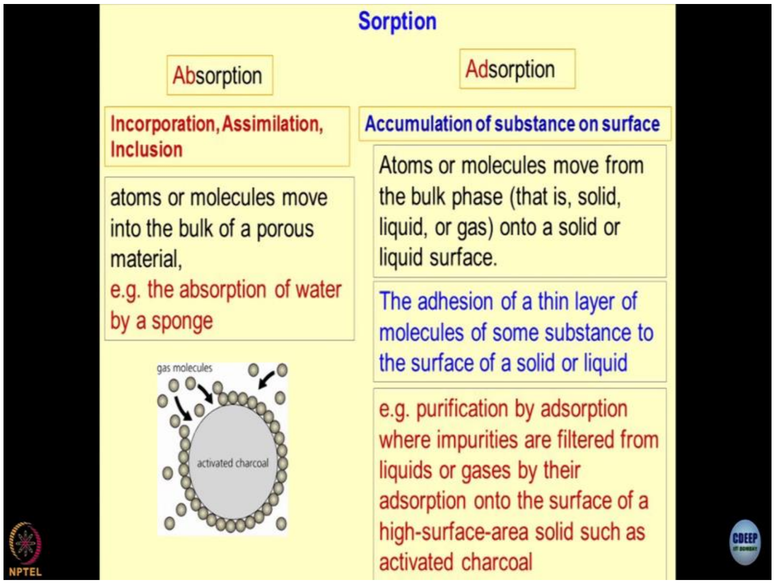

Sorption

Absorption

Incorporation, Assimilation, Inclusion

atoms or molecules move into the bulk of a porous material,
e.g. the absorption of water by a sponge

Adsorption

Accumulation of substance on surface

Atoms or molecules move from the bulk phase (that is, solid, liquid, or gas) onto a solid or liquid surface.

The adhesion of a thin layer of molecules of some substance to the surface of a solid or liquid

e.g. purification by adsorption where impurities are filtered from liquids or gases by their adsorption onto the surface of a high-surface-area solid such as activated charcoal

The first question in mind is that what is sorption. Sorption is a mechanism which constitutes of two components that is absorption and adsorption. So, as the name suggests absorption is something which is assimilation, inclusion or incorporation of something in a matrix while the adsorption processes are surficial. This is the accumulation of substance on the surface, and when we say our surface, this has to be a sort of a substrate like a clay particle. So, imagine that on the clay particle, the cation is getting pumped.

So, this is a sort of adsorption phenomena. However, coming back to the absorption, the molecules are the atoms they have a tendency in bulk to occupy the space or the pores. So, like absorption of water by the porous media, particularly like sponges or stones which are having very high porosity. So, this is the absorption process. The adoption is something that the atoms and molecules moved from the phase that is a solid-liquid of gases, and they get deposited onto the solid or liquid surface. So, this becomes the adsorption process.

So, as the name suggests, the adsorption is going to be something which is related to adherence or like we have used this term in conventional job mechanics also in the form of the hygroscopic moisture content. Where the thin layer of water gets adhered on to the particles and that thin layer could also contain the contaminants, and when this process happens, we say the addition of a thin layer of molecules of some substance which is surrounding the surface of the solids or the liquids.

So, this becomes adsorption. I hope you can realize from this comparison that until now, in classical geomechanics, we have been using the concepts of absorption. The simple answers to this type of discussions will be if you are to find out the porosity of a porous media. So, suppose if I give you a rock sample and if I ask you what the porosity is. So, the normal procedure is you sold the water sold the sample in the water for 3 to 4 days take it out, find out the way difference of the wet to dry and then compute the moisture content and which gives you a sort of indication of what the porous structure would be very gross way of finding out the philosophy of the system.

Because, with the discussion which we had until now, in this class, you must have realized that water molecules might not be penetrating through the very very fine pores which are present in the porous media. And hence, this method is an empirical method it does not give you the complete porosity, particularly the porosity which is going to contribute to most of the mechanisms which control the contaminant transport in the geomaterial.

So, another way of looking at this would suppose there is a particle of activated charcoal which happens to be a substrate and this activated particle. Is attracting the gas molecules are the liquid molecules to get adhered on the surface, and this is what the adsorption phenomena would be, I can use this concept to create filters of different types so if I create a situation where the particles or the substrates are extremely active chemically.

These particles are going to attract that which are present in the sludges. Or the gas molecules and they have a tendency to create a bonding with them, and hence the purification process can be done. So, by definition, this type of situation can be defined as the purification by absorption, wherein impurities are filtered from the liquids or the gases by their adsorption onto the surface of a high surface area solid, which is a substrate such as activated charcoal.

I am sure you must have realized that what we have done is from the liquid, gaseous phases, we have separated out some molecules or atoms, which are adhering on the substrate. So, we have created a sort of partitioning, we have created a partition between the system from the liquid phase it has got separated to a phase where these molecules or atoms come and sit on a solid surface. And that is the reason we call this as a partitioning phenomenon or distribution phenomenon.

So, imagine there is some concentration of contaminants in the liquid or gaseous form. And when I bring this system very close to an activated surface, which could be clay, naturally activated or chemically activated. So, what is going to happen these atoms or molecules, they will get parked on the surface of the system which is a substrate, and hence the partitioning has occurred this is the concept of sorption phenomena.

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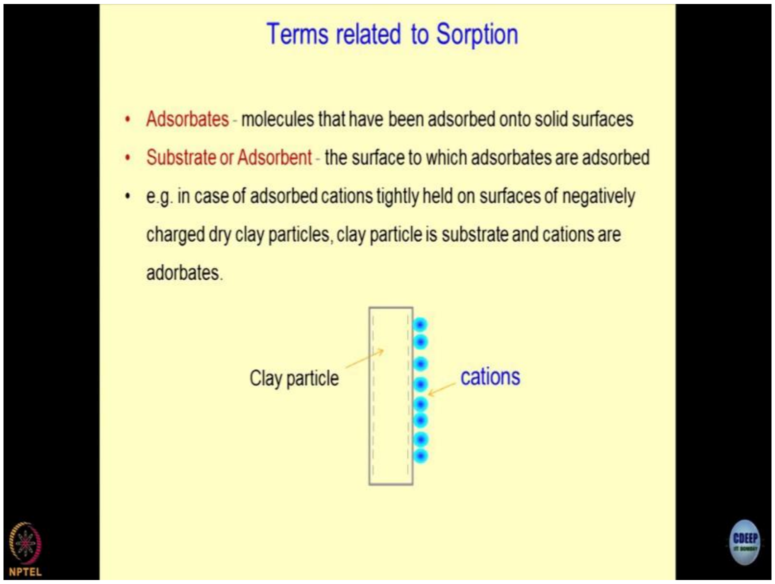

Terms related to Sorption

- Adsorbates - molecules that have been adsorbed onto solid surfaces
- Substrate or Adsorbent - the surface to which adsorbates are adsorbed
- e.g. in case of adsorbed cations tightly held on surfaces of negatively charged dry clay particles, clay particle is substrate and cations are adorbates.

Now the terms which we use in sorption for defining this sorption mechanism are adsorbates and the second one is adsorbent, so, the substrate is also known as the adsorbent substrate is a clay particles charcoal particle, any surface which is participating in adsorption phenomena, adsorbates are the ones which get sorbed onto the surface. Mostly molecules or the atoms. Cations let us say so; they will get piled on the substrates or adsorbents. So, in case of the adsorbed cations, they get tightly held on the surface of the negatively charged dry clay particles, clay particles are the substrates, and the cations are adsorbates.

I think I have discussed and you must be able to realize what it is. So in a very Layman's Language, the sorption phenomena can be simulated like designing a parking lot. So, imagine in the parking lot what happens most of the vehicles come in they get parked. So, many times they use the term that molecules get parked on a parking lot. So, this parking lot is nothing but the substrate a clay particle. And the vehicles which are coming and parked are the molecules or the cations.

Now, I think you can visualize the whole scenario that several trucks and small cars and the big cars competing together to get a place in the parking lot. Something of them of the same sort is happening in case of suction phenomena also. So, sorption would depend basically on the size of the cations as well. And the valency of the cations as well and the chances are depending upon their valency they might get preference, but a bulky cation might have to wait because of its size.

So, when we were talking about the cation exchange capacity of the geomaterials, one of you had asked this question that what is the significance of washing several times and allowing the material to interact with sodium acetate and calcium chloride solution. So, I think now you can realize what we have done in the process of determining the cation exchange capacity is we had allowed sorption and desorption to occur.

So, all the sodium ions which are present in the geomaterial under natural circumstances will get displaced by the cations like calcium, which have higher preference. So, this is the sorption process. Then in the next step what we have done is we have washed this with the water. So, we are done a desorption process, ultimately what we have done is by repeating the cycle we have tried to quantify how many times can still remain parked on the surface of the adsorbent.

So, that is the quantification which you have already done. So, this is the basic model, if you take the clay particle which is negatively charged, the cations will come and get parked on the surface, and this is a sort of a sorption process. So, I just need a surface this might happen in the air also aerosol formation. So, during winters mornings and nights what you have observed, the particulate matter which is present in the environment.

Because of the temperature attracts dust particles and these dust particles get logged over there, and they cannot precipitate because of their very low density. So, this could happen in the gaseous with also this sorption phenomenon.

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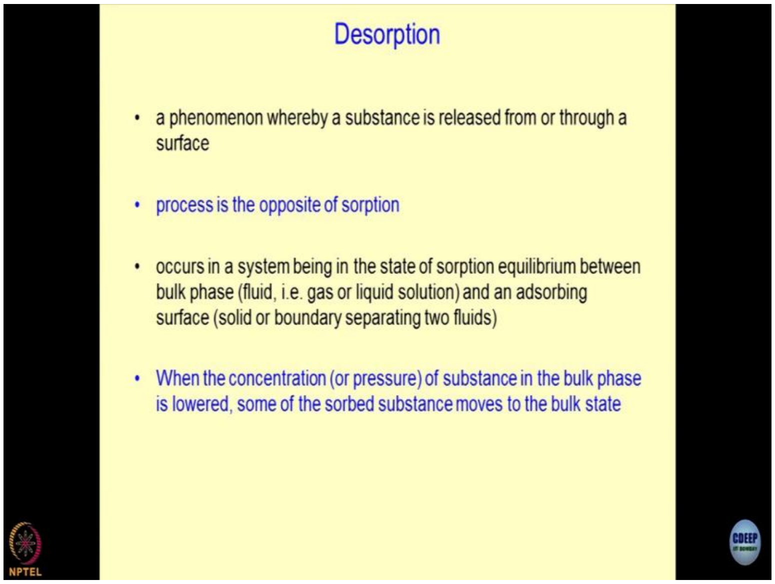

Desorption

- a phenomenon whereby a substance is released from or through a surface
- process is the opposite of sorption
- occurs in a system being in the state of sorption equilibrium between bulk phase (fluid, i.e. gas or liquid solution) and an adsorbing surface (solid or boundary separating two fluids)
- When the concentration (or pressure) of substance in the bulk phase is lowered, some of the sorbed substance moves to the bulk state

So, desorption is a reverse process. So, until now, what we talked about is the sorption process, what is desorption, desorption is the phenomena where the substance is released from or through a surface. Washing, cleaning up process is a reverse process of the sorption phenomena. So, this is opposite to the sorption process. And this type of mechanism is going to occur once the sorption has got equilibrated after eating sufficient food, what is our tendency. We repel food? Is it not? So, after getting saturated, satiated the tendency is that you say no no, I would not take anything. It is a sort of an eversion; it is a sort of repulsion.

So that means the desorption process will always start after the sorption has occurred and it has achieved its equilibrium position. So, equilibration is between the fluid phase that is the gaseous phase or the liquid phase and an adsorbing surface. So this adsorbing surface could be the boundary of the two fluids, or this could be the solids like clay particles. So, I am sure now you realize that these mechanisms would control the quantification of contaminant geomaterial interaction, if I asked you a question, whether a geomaterial is going to interact with a contaminant or not.

The best way to answer this question would be you allow the interaction to occur and see, how much concentration of contaminants has got parked onto the surface if it is insignificant. The analysis of the answer would be either your geomaterial is passive, or the contaminants are also passive. But if it happens to be substantial, then obviously, the indications would be that contaminants are also active, and the surface is also very active.

So, these are the two extremes. You can always create another two extremes by saying that the contaminants are less active surfaces, more active surfaces less active and contaminants are more active. So, when the concentration or the pressure of the substance in the bulk phase is lowered some of the sorbed substance make a move out of the system, and they may get again dissolved into the bulk phase, this is what is known as depressurization technique.

So, if you lower down the pressure, what will happen, there could be a process by which the bonding between the surface and the molecules gets reduced and hence, molecules are free to move into the phase through which they came onto the surface. These are some basic concepts which I thought I would give you before we start discussing further you can apply suction. So, you can suck out the contaminants, and that is the technique which is normally used in the field also to decontaminate the soils.

So, what I should be first I will add some water into the soil so that the cations will leach out into the pore solution and then I may suck out the pore solution, and in the process of sucking out the pore solution, it might so happen that this pore solution will also accelerate the desorption process of the cations or the molecules. So, you are inducing, a pressure gradient which might be resulting in the desorption process is the mechanism.

"Professor - student conversation starts" Sir, in sorption process how can you make sure that only the contaminants are getting adsorbed to the substrate useful minerals from the geomaterial can also. No, repeat your question, please. How can we make sure that only the contaminants from the geomaterials are getting adsorbed to the surface? Adsorbed or desorbed. So, this is the process of sorption because only cations will get sorbed on a surface because of the clay particles are negative charge and contains has positively charged. **"Professor - student conversation ends."**

So, what is going to happen only the positive will come and sit on the negatively charged particles. If the surface happens to be neutral, then this is not going to happen. So, you may extend this logic to the situation that sands will not sorb anything. So, when you are designing the filters which are made up of sands, there sorption desorption mechanism will not work because sands are neutral particles fine.

But most of the time, what you see is what do you see is that these filter beds are granular media are realizing where the engineering would be. So, if I take these sand particles and if I activate them by using some bioactivity now, what I have done I have done the coating on the surface of the sand particles in the form of a microbial coating, and these microbes are themselves negatively charged. So, practically there is no difference between the clay surface and the sand surface as far as the charge carrying capacity is concerned.

Now, this is the technology which you have done, you have converted a material which was inert into an electromagnetically charged particle by putting a layer of bacteria got it. Now, this is for acting as an environmental filter. You are talking about whether we can create barriers by using this concept or not, yes, it is a barrier system. So, when we talked about permeable reactive barriers, so, these are the good examples, your permeable reactive barrier has to sorb everything. At the same time, it allows permeation through it also.

So, that means absorption is going on, as well as adoption is also going on. Imagine you close your eyes and imagine that unless the fluid enters into the pores adsorption is not going to occur. So, for adoption to occur, the first thing is absorption just a minute. So that means the fluid phase has to enter the porous media. Imagine all the pores are filled up with the fluids when there is sufficient time now what is going to happen? Now, there are exchange phenomena which are going to get actuated between the fluids which are present in the pores and the solid matrix.

So, absorption has to happen first, followed by adsorption. Once everything gets saturated, if you take out this system and put it in freshwater, what is going to happen, concentration gradients are going to develop and higher concentration which is present in the system porous media would move out and this becomes a desorption process. So, when you design PRBs, you have to talk about desorption sorption mechanisms. Yes, please.

How good they are in like the activated clay particle how good they are in like arresting the heavy metals. These all heavy metals know. Cations are heavy metals like yes. So, when you design environmental filters basically wanted to get rid of heavy metals, which are cations. Strontium, chromium, mercury, nickel, cadmium whatever these are mostly like we assume that in landfill leachate these are the. Yes, correct.

So, there are a lot of studies that people have done, where they have utilized different type of contaminants synthetic as well as naturally occurring lot of studies have been done where the synthetic groundwater has been created. And particularly these type of studies are done in the atomic industry, where you try to simulate the groundwater with different species of cations. And then you try to see the competitive sorption taking place, and what is the net result of sorption phenomena, these studies are quite prevalent. Fine. I will try to explain it more and more as we move on anything else.

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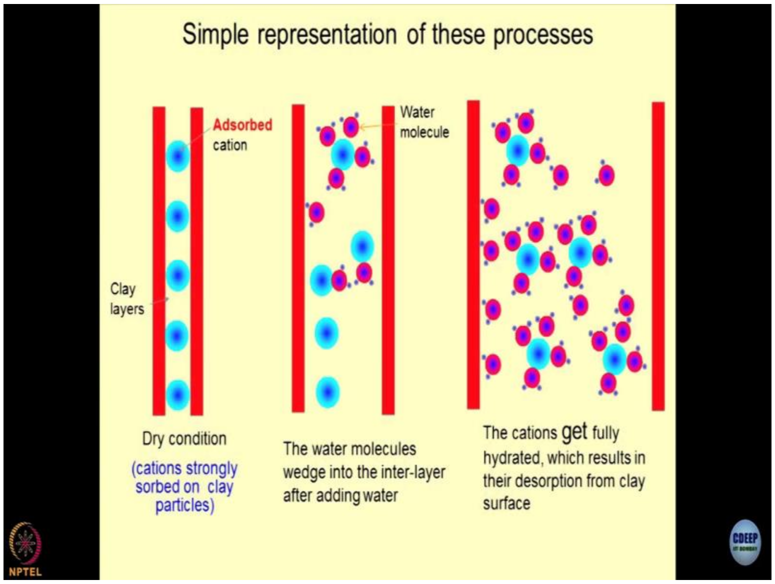

Simple representation of these processes

Dry condition
(cations strongly sorbed on clay particles)

The water molecules wedge into the inter-layer after adding water

The cations get fully hydrated, which results in their desorption from clay surface

So, this is a simple depiction of sorption desorption process. If you consider the clay particles there is an adsorbed cation, which is adhering to the surface of the clay particles in the dry condition, there is no fluid. So, cations are strongly sorbed on clay particles. A good example of this would be most of the time you use talcum powder why have you ever questioned, talcum powder is in the dry form.

So, why do you use it on your skin? Question this. This is a beautiful example and talcum powder is nothing but a sort of a clay particle, very fine particles surface area is very high mineralogical, it is very active. So, what it is going to do?. It is going to soak all your sweat. So basically this is a sorption process which is taking place on talcum powder and of the sweat, sweat is a negatively charged fluid, having a lot of bacteria in it. So, this is the mechanism.

Now add a little bit of water to this. So, the moment you add a little bit of water to this what happens the water molecule goes and sits inside the system where the patterns and the clay platelets are already present. So, the water molecules enter into the interlayers we call them as interlace once the water is added. A stage comes where this system becomes saturated like this. And once the system becomes saturated.

You must be noticing the key layers are getting separated out, why this is diffused double layer concept. So, diffused double layer once it gets saturated completely, the desorption process starts. This is a simple mechanism. So, once the cations get fully hydrated, so, water acts as a source of the mechanism which causes sorption and desorption to occur because fluid phase, particularly gaseous phase sorption is going to be a difficult process to simulate.

Why it is not easy to park gas particles on a substrate, though people are trying to do this carbon sequestration is a good example of this. Coal bed methane is another good example of CBM. So, if you type on the net, you will get a lot of information CO_2 sequestration and coal bed methane, CBM. So, what they are trying to do, they are capturing carbon dioxide from the atmosphere, injecting it into the porous media.

So, they are recharging the reservoirs of hydrocarbons, which we are otherwise consuming and this becomes a sustainable solution fine yes **"Professor - student conversation starts"** water has a strong adherence as compared to the inactive the cations like from the picture it depicts like this, it can come in the way and replace that cations that were earlier adhered. That is possible there is something known as the solubility of the cationic suspensions. Ya, it is possible.

And Sir, one question is like slightly different from this at what really that day we were discussing like double layer is fully formed at very high water content. So, in the simple Atterberg limits, we simply say it is around liquid limit it is formed, but do you have any idea like around what water content this double is fully formed? Or there is like ambiguity in that. See double-layer normally is not ascribed to the moisture content, first of all, the double layer is ascribed to the thickness of the system the cationic layer, which is getting adhered onto the substrate.

So, the double layer is always at associated with the size of the clay particles, after the cations have stabilized on it, they have adhered on this, we do not usually attribute it to the moisture content. Like in compaction theory and everywhere we always talk about this phenomena. So, here we are not talking about these mechanisms double layer and all we do not talk about this. We should have, in fact, a sufficient amount of free water for double layer gets formed. So, that means all these concepts are valid beyond the liquid limit or at the liquid limit. **"Professor - student conversation ends."**