

Environmental Geotechnics
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Lecture – 37
Sorption & Desorption characteristics of geomaterials – 1

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**SORPTION & DESORPTION CHARACTERISTICS
of Geomaterials**

Excellent philosophy to simulate geomaterial-contaminant interaction

Sorption and Desorption are opposite interaction mechanisms

**Strategies for Remediation of Contaminated Soils/Geomaterials
(Site cleanup/Site remediation)**

- > Soil washing
- > Soil flushing
- > Vitrification
- > Solidification
- > Immobilization

**Important to determine Sorption and Desorption
Characteristics of Geomaterial and Immobilizing Agents**

D N Singh

Sorption and desorption characteristics of geomaterials are becoming very important nowadays. In my opinion, this is an excellent philosophy to simulate geomaterial-contaminant interaction. I normally talk about the philosophy here because it is nothing but the engineering philosophy, where indirectly we are trying to prove our point by studying some phenomena quantifying it mathematically and then showing that these mathematical numbers represent a sort of a contaminant geomaterial interaction. So, sorption and desorption are opposite interaction mechanisms.

In the previous lecture, I had discussed about what is sorption, what is desorption. Sorption is something where contaminant gets adhered on to the surface of a soil particle. And the reverse mechanism by which the contaminant comes out of the surface gets deluged is nothing but desorption mechanism. Now, it so happens that most of the strategies of remediation for contaminated lands if you go through, you will find that there are few methodologies which are included in this. And these methodology

strategies are sometimes also classified as site cleaning program or site remediation program.

The situation is like this that you have a land which is contaminated heavily. And then as an engineer you want to utilize this land for different purpose and that is there you have to devise a strategy for cleaning up the contaminated land or reclaiming the contaminated land or remediating the contaminated lands or sometimes, we call it as site remediation, site cleanup program.

So, in this series, the first activity is soil washing. If soil happens to be heavily contaminated, and you can afford supply of good water fresh water, you can clean the entire land by washing it very easy to say, difficult to execute on sites. You cannot really afford so much of water because water is becoming a commodity. And again, the issue is whatever secondary contaminants are being produced by washing the soil, how we are going to treat them. Here you should agree and you should understand one situation each liter of water is going to create each liter of containments. So, this is a very big issue. However, when contamination is not a very high degree or level soil washing can be thought about.

The second situation is soil flushing; where, you flush out the contaminants on the soil by different techniques. And let me tell you here that each one of these techniques is very, very involved, very elaborate, but I am not going to cover these techniques in this lecture. The idea is just to need the thread by telling you that when you talk about these strategies, the parameters or the mechanisms like sorption desorption become very important. So, this is how I am trying to link today's lecture by giving an example of these methodologies or strategies.

Vitrification of the waste is another situation where you come across these types of mechanisms. Solidification, this is what is adopted most of the time by in most of the projects, most commonly, solidification. You solidify the waste and then buried somewhere now again the question is what are the parameters which are going to define the efficiency of a strategy which is being adopted for cleanup program, all right. So, solidification of the waste itself requires some quantification of the parameters on the mechanisms. And there again you can use sorption and desorption as good controlling parameters to decide upon the efficiency of solidification activity.

And of course, the immobilization, if you want to immobilize the waste which again is a very much sort of a technique or a strategy of cleaning up the contaminated sites. What is meant by immobilization the immobilization is a situation where you fix the contaminates in the matrix of the soil. So, that under any circumstances there will not be any leaching the same mobilization all right.

So, again how good the bonding between the soil and the contaminant is ensured can be quantified by using sorption and desorption mechanisms, so that is were actually you will notice that all these strategies or the techniques as a methodologies of site remediation will require mechanisms like sorption desorption to be understood and to be quantified further. And then using these parameters you can do modelling. So, in the later on, half of the lecture what I will do is I will show you how the parameter which have been estimated can be utilized for mathematical modelling of a given scenario of a real-life situation.

So, all these situations and the strategies lead to the importance of determination of sorption and desorption characteristics of geomaterials and immobilizing agents. Can you name some immobilizing agents which are normally used for immobilizing the contaminated soils? Cement is a good immobilizer. So, you add cement to the soil mass, what happened the entire base gets trapped into the matrix and do not leach out, but then I am sure that you will agree that cement treatment is a very expensive treatment. So, everybody cannot afford it on all the sites. So, this is where you required lot of other admixtures or alternate cementing materials like fly ash or lime fly ash mix or slurries or some chemicals.

So, even calcium hydroxide when you do lime treatment of the soil, this is sort of a immobilization you can use some PVC granules or some minerals which will immobilize the waste coming out of the matrix. So, what you have to do or what should be the attribute of these minerals, these minerals should have very high cation exchange capacity, so that the sorption process gets enhanced. So, it is a sort of a molecular trapping of the waste form which will not move out of the soil matrix.

So, you have creating a bonding between the soil particles and the wastes by using minerals which are highly active. So, this is nothing but an immobilizing material would be. Any questions?

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Yes, a good question what is the difference between solidification and immobilization the order of treatment which is given to the soil mass is quite low when you talk about immobilization. A mechanical treatment may result in a good immobilization of the waste. A good example is compaction. So, you decrease the hydraulic conductivity and then you can say that by compacting the soil mass I have immobilize the movement of the waste. But when you talk about solidification it has to be at elevated temperatures with the help of a specialize chemicals under specialized conditions.

So, there was a time when our country used to dispose a nuclear waste by solidifying it in a cement brick or a concrete brick and then disposing it somewhere. Now, of course, there is a ban on this type of activities. Is it ok? Most of the time these studies or these types of activities are taken up by the environmental engineers, but now geotechnical engineers are also finding a good scope of you know getting involved in this type of activities.

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Importance of Sorption and Desorption Characteristics

- **Fate and Transport of Reactive Contaminant(s)**
- **Efficiency of Environmental Cleanup Strategies**
- **Selection of Suitable Geological Formations and Backfill Materials**
- **Design of Barrier Layers of Waste Containment System**
- **Accumulation of Heavy Metals and Pesticides in Subsoil**

Challenge

Precise Determination of these Characteristics (k_d & $k_{d,l}$) in a short duration

k_d : the coefficient describing sorption process
 $k_{d,l}$: the coefficient describing desorption process
(subscript l corresponds to leaching process)

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Let us talk about the importance of sorption and desorption characteristics or the mechanisms. When you are studying fate and transport of reactive contaminants, I have shown in the previous lectures that even if you talk about the one-dimensional advection diffusion equation, there k_d terms and other parameters like retardation coefficients appear. That means, you cannot ignore sorption desorption phenomena when

contaminant migrates in a porous system. So, the most important application of these type of studies would be in contaminant transport modelling, that means, what happens to the contaminant after certain time at a certain distance, and if it is a particular reactive contaminant, because nonreactive contaminant passive contaminants will not react with a soil mass and hence there is no point in talking about sorption desorption characteristics of passive contaminants.

The second situation is efficiency of environmental cleanup strategies this I had discuss in the previous slide. You have so many methodology strategies now which strategy should be adopted for a given situation, whether I should go for immobilization of the waste, whether I should go for solidification of the waste, vitrification of the waste, vitrification by the way is a costliest. And most intricate strategy of waste immobilization where you have to have very high temperatures above 4000 degree centigrade by using some laser torch or plasma torch.

So, in other words if you just want to establish the efficiency of the strategies and there is a question in the mind that which strategy is most applicable for a given situation. So, this again where sorption desorption parameters can help you. Of course, this type of work not has been done has not been done by the people yet, but what I pursue in a near future is that there should be a sort of a guiding or guidelines available where you can use sorption desorption parameters in isolating a mechanism which is going to be a most suitable for environmental cleanup projects, it is a is a big research area.

Then comes selection of suitable geological formations and backfill materials. If you remember in the first or second lecture, I have been talking about selection of geological formations in which formation a certain type of waste should be disposed, is it not, high level waste, intermediate level waste or low-level waste. So, depending upon the type of the waste, so those are the attributes of the waste. Now, when you are selecting the attributes of the porous system, again you have to talk about sorption desorption phenomena or the characteristics to select the most ideal repository. So, repositories are place where the waste is being dumped.

So, selection of suitable geological formations and backfill materials, I have talked about this situation in one of my previous lectures that backfill materials are very specialized minerals. So, how do you select out of given five, six minerals, the mineral which is

most suitable for a given situation. Again, we can conduct quickly sorption desorption tests and we can establish in that which mineral is going to be the most ideal one. Design of barrier layers for waste containment system. Again, the same situation a system which is less permeable, more tolerant to the thermal flux, more tolerant to the chemical flux, stability should be there, it should not be biodegradable and so on.

So, if you remember, I just told you that sorption desorption characteristics include in total everything whatever comes in the real life, so that is why it becomes very important to study or to characterize the porous system for its sorption and desorption properties or characteristics. Accumulation of heavy metals and pesticides in subsoils. What type of heavy metals are getting accumulated because of even too much of urea or too much of fertilizer or the manure which is being given to the plants or the pesticides. So, what is happening to the subsoil? So, you can do some experiments where the contaminant becomes a manure.

And then you can see how much of the manure and the heavy metals out of it are getting adsorbed onto the soil mass. And at the same time if I reverse the process what is the probability that these ions or heavy metals will move out of the soil matrix, and hence the leaching may start. So, these are the situations where all these parameters become highly important to be analyzed or to be determined.

So, what is the challenge the challenge is precise determination of these characteristics, and this is where I have used the term k_d or k_{dl} . Now, k_d is the coefficient when sorption is taking place, we call it as distribution coefficient. K_{dl} , subscript l corresponds to leaching. So, leaching is equivalent to desorption. So, when you are talking about sorption process it is k_d ; when you are talking about desorption process then it is k_{dl} the leaching part in the short duration.

Now, writing this line is very easy, but truly speaking conducting these tests coming up with the methodologies, using them in the most proper manner is a very big challenge. And this is where I have been telling you that the Government of India has a very specialized focus on the subject, where one of the big a department of the atomic energy is working in all sorts of you know heavy metals and the minerals which are being excavated and what is the response with soil and the rock mass depending upon the geographical locations.

So, k_d is the coefficient describing sorption process. And k_{d1} is the coefficient describing desorption process; subscript 1 corresponds to leaching process or the desorption process. Any doubts questions or suggestions? Is quite coherent you have kind of able to follow? All right?

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The coefficient k_d

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Also known as the partition or distribution coefficient

Is a measure of sorption of contaminants to soils/rocks/admixtures (geomaterials).

Defined as the ratio of the quantity of the sorbate sorbed per unit mass of solids (C_s) to the amount of the sorbate remaining in solution (C_w), at equilibrium.

The reverse is true for desorption (leaching) process

K_d measurement, some issues

- Experimental conditions
- Measurement methodology
- Contaminant chemical characteristics
- Sorbents (particle size, geochemistry)
- Type (active/passive) and concentration of the sorbate

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Let us now define the coefficient k_d . So, this is also known as the partitioning coefficient or distribution coefficient. So, the name partitioning phase some fraction of the contaminant is getting partition. Now, this is where the philosophy starts. When partitioning is taking place, it will occur in a certain phase of the soil. So, even if you talk about three phase system, the partitioning could be in water, partitioning could be in gaseous phase or partitioning could be in solid phase. So, the moment you talk about let us say four-degree model or four phase model of the soil mass, again the partitioning will be in all the four phases. So, suppose ice is also present in the soil mass.

So, you have solid phase of water, you have liquid phase of water, you have vapor phase of water, and you have solids of the soil. Now, you think of a situation how contaminant is going to affect each of these phases of the soil mass. So, certain fraction of the contaminant is going to get adhere to the soil mass which is the adherence to the solid phase, certain fraction is going to get adhered into the liquid phase which is nothing but the solvent or soil solution. Another phase may get associated with the vapors which are

present in the soil mass either air or contaminants or whatever. So, this is how the partitioning is taking place, clear.

So, this becomes a very intricate situation when contaminant passes through the soil mass, you have to superimpose the influence of contaminant onto the porous media by keeping in mind that what type of partitioning is occurring is this part clear. So, we call it as a partitioning coefficient or distribution coefficient, of course, is not so difficult. It is very easy to model these things and let's discuss and see how this can be done. So, in the simplest possible words k_d is a measure of sorption of contaminants to soils rocks admixtures in general geomaterials.

So, now let me ask you a question, if you do not want to add any admixture to the soil for immobilizing base, clear, what is the best possible attribute which you can study or which you can use the mineral itself? And need not to add anything extra to the soil mass if the mineralogy is like that. If minerals are highly active, we are not going to allow any contaminants to come out just by compacting them up to a certain compaction effort, I can reduce permeation of the waste and even the diffusion of waste also. So, that means, both advective diffusive contaminant transport can be checked just by using or selecting right minerals. And what is the attribute of the minerals? Their sorption capacity should be maximum that is it.

Now, when you are using some geomaterials, the question is with geomaterial should be used as a good admixture in the soil mass. So, if we have a fly ash for which cation exchange capacity is very high is a good admixture, and need not too spend much money in selecting an immobilizer which is going to be put in these strategies of clean a project. So, there fly ash becomes a good immobilizing agent.

So, here you will notice that all your parameter like surface area and you have studied the surface area, specific surface area is related to cation exchange capacity. So, a material for which CEC is very high surface area is also going to be very high, its activity is also going to be very high should be use for as an immobilizing material clear. So, that is what sometimes people say that k_d is a black box. It has fingerprints of each and every phenomenon which is going to take place when porous media is going to interact with contaminants or vice versa all right.

Now, this is defined as the ratio of the quantity of the sorbate sorbed per unit mass of the solids to the amount of the sorbate remaining in the solution fingerprints of each and every phenomenon which is going to take place when porous media is going to interact with contaminants or vice versa all right. Now, this is defined as the ratio of the quantity of the sorbate, sorbed per unit mass of the solids to the amount of the sorbate remaining in the solution at the stage of equilibrium.

So, if I use two notations like C_s and C_w , now C_s corresponds to the contaminants which are adhering onto the surface of the solids, and C_w is the contaminants which remain in the solution phase. So, I am sure now you must have visualized that how partitioning has occurred. So, in a two-phase system where the soil mass of the porous system happens to be completely saturated, the partitioning is happening in two ways one is on to the solid surface another one is in the liquid or the solid form.

So, if you take the ratio of the solid's concentration of contaminants on the solids divided by concentration of contaminants in the liquid phase that is nothing but k_d , is this ok. So, what is your opinion k_d should always be more than 1 or less than 1? If it is less than 1, you have to change your strategy; you cannot use it as a good immobilizer. So, you always require a k_d which is much, much more than unity. So, higher the k_d value is going to be a very good immobilizing material or it is going to be a very active mineral. Why, because the tendency of the system is to take more and more cations from the solution phase, so that nothing goes into the environment. See that is what I said this is whole philosophy.

Did you miss the first slide of the today's lecture? Yeah that is the reason, because it is nothing but the perception difference. So, is this clear now? Now, the reverse phenomena is true for desorption. So, the material which we were going to select where k_d s are very small is going to be a good dissolving material. In nature have you heard ever that in the eastern part of the country, you have mostly arsenic come it out coming out of the soils, then have you heard of this, what is the reason? Sorbing capacity is more or desorbing capacity was more

Desorbing.

Desorbing capacity soil is more. So, the moment it comes in contacted with ground water, what happens these minerals automatically come out in the solution phase. So,

they leak the solid phase, they get unplug from the solid phase and they migrate into the liquid phase. Now, this is what is nothing but desorption or leaching process. So, using these parameters you can define or quantify leaching also. However, there are few issues when you are measuring k_d parameter. And these issues are k_d is most sensitive to experimental conditions. Why, what are the experimental conditions normally we talk about temperature, pressure, humidity ok, measurement methodology.

So, nowadays people have realized that they should be a unique methodology to determine and to define k_d parameter; otherwise in every lab they used to follow different method and they used to come up with a different number. And they are use to be lot of chaos. So, in order to streamline all these, the measurement methodology is also going to be streamlined.

Contaminant chemical characteristics of course, it depends upon the sorbents. What are sorbents? Sorbents are the ones who are going to sorb cations porous media. Is this clear? So, the particle size is very important, the geochemistry is very important. Geochemistry will include everything cation exchange capacity of course, the k_d parameters, sorption parameter and so on.

And of course, the type of the contaminants or the sorbate the one which is getting sorbed on to the solid surface, so the type active passive and concentration of the sorbate. Unfortunately, you cannot do away with geochemistry. In today's world is becoming a very important tool for all engineering professions, corrosion of piles, corrosion of foundations.