Environmental Remediation of Contaminated Sites
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Lecture 37
Different Contaminant Reactions during Solidification and Stabilization

Hello, everyone. Welcome back to the relevant session. So we have been discussing solidification and stabilization in the context of remediating contaminated soils or sediments, yes and what is the relevant principle here that we are looking at. We typically do not you know degrade the contaminant or such what are we trying to do. We are trying to see to it that you know the contaminant stage where is it, let us say right.

Or is not transported to greater extent let us see maybe you can think of this as containment, but you are not putting a barrier around it or such, but you know you are billing a relevant or your are transforming relevant solid let us say right and how are we doing that again by solidifying it let us say. So solidifying it as in we are improving the physical strength or physical characteristics of the relevant material right or the structural integrity, if I may say so.

Then stabilization, right. In stabilization what are we looking at, we are trying to make the contaminant immobile right. Again different ways, so depending on the contaminants sometimes we can also try to add mixtures, so that you are going to be able to degrade the contaminant, but generally though we are only look at solidification and stabilization and not degrading the contaminant.

So within this context, we looked at let us say, how you know we add various binders right, we need binders and what are the some of the binder that we typically look at. I think we looked at obviously cement and then flyash right and then there are other cases like blast of furnace slag and so on and so forth, but you know depending upon the type of contaminant, you might go for them or depending upon their availability.

But typically we choose cement or flyash. Again what is the principle here, cement is rich in calcium and silica let us say and once you add water and its hydrated, you have the CSH matrix being formed and that is what more or less I believe give strength to your particular, what you say cement, now once it hardens or is hydrated pardon, right. So CSH matrix is what you are trying to form. So what is the role of flyash here, typically your fly ash is rich in silica.

Depending upon the type of coal, it will either have some or sufficient calcium or no little calcium. So in that context you will either have to add lime for source of calcium or that let us say you also add cement, some flyash and water because you know, as we saw in the relevant reactions let say, as you added or hydrated cement with water, you know calcium hydroxide was being given out and that calcium again can be a source for the CSH matrix when you have flyash present right.

So typically you can to reduce the cause obviously add cement, flyash, and water and again sometimes water, you might need to add that additionally or the water present in the relevant way itself will need to be taken right. So that is something that we have looked at right. Again, we looked at some aspects and few minor what do we say examples where these particular aspects were implemented.

As in we looked at 2 cases when we have either a shallow excavation, not excavation, pardon me, yes, I believe excavation and then actually to solidification and stabilization and then one where we had to the relevant people had to look out solidification for up to a depth of almost 20 feet now right. So we looked at 3 three different examples now right. So in this context with respect to the contaminant what do we say transformation or contaminant reactions right.

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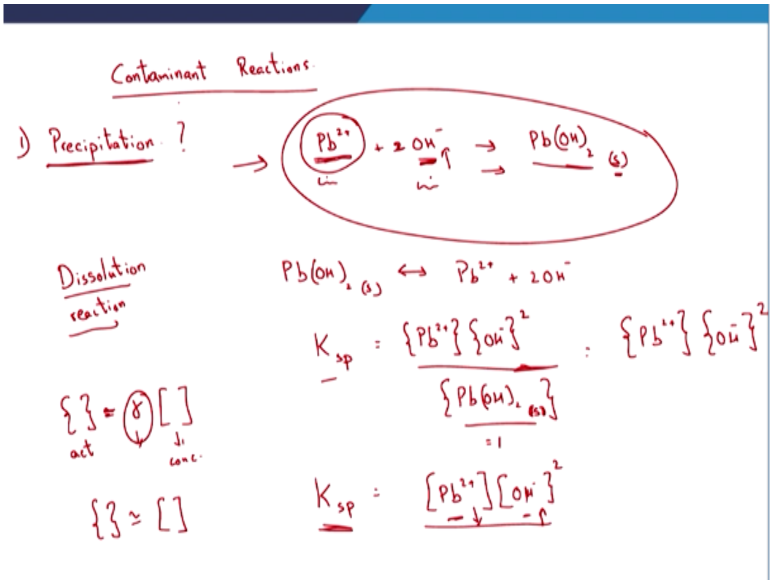
Contaminant Reactions

1) Precipitation ? → $Pb^{2+} + 2OH^- \rightarrow Pb(OH)_{2(s)}$

Dissolution reaction $Pb(OH)_{2(s)} \leftrightarrow Pb^{2+} + 2OH^-$

$$K_{sp} = \frac{\{Pb^{2+}\}\{OH^-\}^2}{\underbrace{\{Pb(OH)_{2(s)}\}}_{=1}} = \{Pb^{2+}\}\{OH^-\}^2$$

$\underset{act}{\{\ \}} = \gamma \underset{conc.}{[\ ]}$

$\{\ \} \simeq [\ ]$

$$K_{sp} = [Pb^{2+}][OH^-]^2$$

So as we what do we say solidify and stabilize this waste, how is the contaminant going to be transformed right. We briefly looked at some of them, but today we will look at that in greater detail and move on to solving the relevant examples let us say. So obviously you know, you are adding the lime right. Again as you see or if you look into the relevant reaction, you typically see that the pH typically increases, typically again right.

Again we looked at that in greater deal in the example. So again obviously pH as we know is the master variable and most of our environmental engineering related aspects or scenarios now right. So how does that particular pH or the master variable play role here now right. So here obviously we know that or we briefly discussed that the contaminant can be precipitated or precipitation of the contaminant can occur right.

So now how does that go about now right. So let us say you have particular heavy metal, let us say, we will take the example of a heavy metal and solution now right. So let us say you might have observed let us say may be with chalk or sugar or salt let us say in a particular glass or you know a glass of particular volume and if you keep adding salt or sugar and keep stirring that after particular point let say you know any other additional salt or sugar that you add is going to not dissolve further right or it is not going to be inside the solution and dissolve I guess right.

But it will precipitate out or you know settle to the bottom, if you might have observed that right again what is the key here. The key is that the particular solution can hold only a certain concentration of the relevant species or you know, there is a maximum concentration with respect to the relevant dissolve concentration or aqueous concentration for different particular species now right.

So here we are going to look at how we understand this Layman's term of maximum concentration, what are the variables that affect it and so on, right. For example, now, we are looking it lead right. So lead can, let us say again OH- in water. So this is my metal and this is my ligand, let us say electron rich, and this is electron pool right. Again it can form okay and thus can precipitate out, as means a solid which can precipitate out right. So this is something that can happen out there again for particular example of lead here.

Obviously you have other examples of different heavy metals precipitating out with ligand OH minus or different ligands that might be present in water now right. So again OH- is always present, so that is the reason we are looking at this example now. Right here we have the precipitation, but typically we write the reaction as dissolution reaction. So Pb OH twice the solid will be in equilibrium with PB2+. What does this mean again, what are we writing now.

We are writing the relationship here right 2OH- right. So this is the equilibrium that is you know going to prevail, let us say. Again there are different stages for precipitation. It is not as if let us say, once this particular solution is slightly oversaturated you know precipitation is going to kick in. It is not going to happen like that.

There are different stages in there, but we are not going to go into that detail for now, but again keep in mind that the solution needs to be oversaturated or considerably oversaturated initially for precipitation to kick in. Again we are not going to go into that detail now. So again this is called, let us say the dissolution reaction. I guess that is self explanatory right, resolution reaction, right or if I come back to this for a given concentration of lead let us say.

Let us say my particular solution is contaminated with lead now right. That is what I have here and you know that lead as an equilibrium with PbOH twice the solid and OH- now right. So if I keep adding or increasing this particular OH- let us say, what is going to happen, the equilibrium will shift towards the right or the system would travel towards PbOH twice or the solid will be formed now.

So while the solid is being formed what will happen to the Pb2+ concentration in the water. Obviously it is going to decrease right. So by you know changing the OH- concentration, I can affect the concentration of the relevant heavy metal in that particular solution now right, again for this particular example. So again as you can see by increasing the OH- concentration what does that mean by increasing the pH right, I can precipitate the lead out here right.

So you again let us come back to the dissolution reaction. So we typically have the equilibrium constant for this reaction. We refer to that as the solubility product KSP that is equal to obviously it is the activity of the relevant reactance raised to their stoichiometric coefficient right by activity of PbOH twice the solid. Solid activity again we look at more fractions here right and more fractions again if it is a pure solid.

So the activity of this particular denominator term or the PbOH twice solid will be equal to 1 right. So that is why this is going to be Pb2+. Activity of PB2+ into activity of OH- to the power of 2, right. So you have 5, assume that the solution is relatively dilute enough such that ion extent does not play role or that what does that mean. That means that I can approximate activity by the relevant concentration right.

As you might be aware of activity is going to be equal the activity coefficient times the concentration. This is the activity here. This is the activity coefficient and this is concentration right. So for example if the solution is dilute, I can say this is relatively equal to 1 and that activity is more or less equal to or it can be approximated by the concentration now right. So that’s what we are going to assume here. Again what does activity give an idea about?

It gives you an idea about or activity gives you an idea about the ability of the relevant compound to react, let us say right. So that is what we have out here. Again so it is OH- to the power of 2. So that is what we have here right. So this is a constant, KSP is the constant right. So as you can see, this is equilibrium relationship and here we have that Pb2+ aqueous concentration in equilibrium with the OH- concentration here right.

So as you see, as you increase the OH- concentration in such the Pb2+ needs to decrease right. If I keep increasing the OH- concentration to keep the KSP to be constant; it is a constant right, what needs to happen to Pb2+. Obviously that needs to decrease now, but again keep in mind that it is not as if you know I keep increasing the pH till 14 and I end up with you know the maximal removal or every, pardon me, not every, almost all the Pb2+ or lead precipitating out.

Why is that, because we just looked the precipitation. This is something that obviously can happen within your or during your solidification-stabilization and why cannot I just take the pH up to 14 and say that okay OH- is maximum there and then you know I am going to have relevant what do we say the maximum removal of Pb2+ from the what do we say aqueous phase anyway, why is that?

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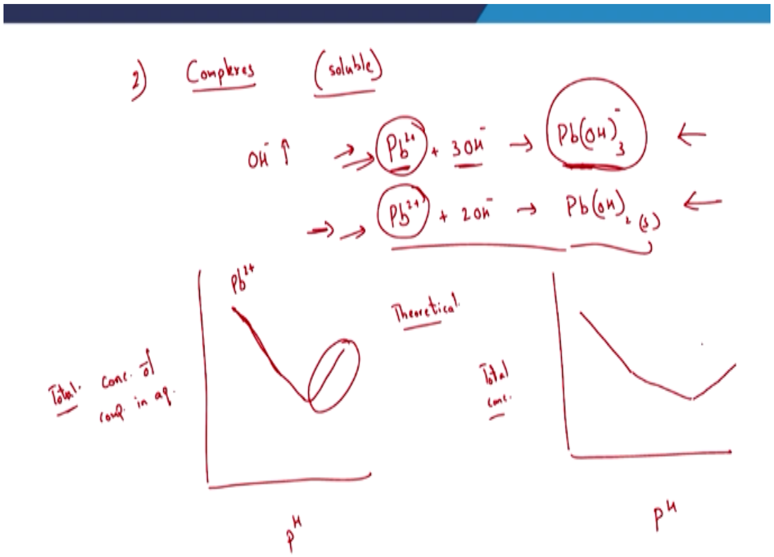

Because the metals can also form complexes right and these complexes are typically very much soluble. So what happens is as I keep increasing the OH- right, there are other complexes or there are complexes that can be formed let us say +3OH-, go into let say you know PbOH thrice and I think that is a negative charge. This is not a solid now. This is the complex here right.

So if I keep increasing the OH- simultaneously let us see when compared to this particular reaction where Pb2+ is precipitating out right, here I see that it is precipitating out, here it is the compensation occurring. Obviously both of them are going to occur simultaneously. So once I reach a certain threshold for pH and still keep increasing it further right, Pb2+ or lead will end of being more soluble.

Obviously why is that, as you see here there are complexes that the lead can form with hydroxide or OH- that are more soluble right. For example, at a certain pH or until certain threshold as you can see, lead can precipitate out right, but as you can also see here, you know as if I can just take the pH up to 14 and assume that everything is going to precipitate out, because you know have simultaneously complexes of lead that are formed which are more soluble, right.

So that is something to keep in mind, wise that again try to understand this. So this particular precipitation step depends upon the concentration of Pb2+ that is in the solution right. Pb2+ not any other complex or such, but what is happening simultaneously let us see you know the Pb2+ and 3OH-, they form a complex. So it is not as of Pb or lead is present as in free state, not free state maybe in its ionic phase let us say right.

As you can see it is in the form of a complex. So thus Pb2+ will be lesser, but you know PbOH what you say lead is still present as complex, which is again in the dissolved phase right. So that is something to keep in mind. So complexes can be formed. So typically let us say if I look at this and if I say this is the concentration of the compound in aqueous phase or in the water let us say and this is the PH.

So what is going to happen, let us say as I keep decreasing or increasing the pH from this particular reaction, I see that the concentration of lead, let us say this is for lead let us say, this keeps on decreasing now right, but once I hit a certain threshold, let us say 12 or 11 I am not sure what it is for lead, but we can check that right. You know what happens is that you again have an increase in concentration of lead.

So here is the total concentration if I can see maybe and why is this increase or why do I see this increase in concentration of lead after certain point in you know this pH let us say. Why is that because complexes are formed in this particular region let us say right or you know the lead in the form of complexes is relatively more compared to the lead that precipitates out. So that is something that you see. Again this is from the relevant theoretical aspect right.

It looks like in practice the situation is slightly different, as in you have something like this and something like this and then slight increase right. So this is again same graph pH and total concentration here right. Again this is typically the real world behavior and it is obviously because you also have other materials present out there like cement and such in your what do we say during your solidification and stabilization.

It is not just lead and hydroxide and so on. So the real world behavior is slightly different, but obviously you will make your calculations based on theory and then look at the lab tests and then you know take that for. Obviously I am not going to jump right into practice let us say from just my theory, but obviously the theory is going to be the bases for building the relevant aspects let us say right. So again we looked at how the contaminant can precipitate out. How it can form complexes right? So the other aspect is it can also be adsorbed let say right.

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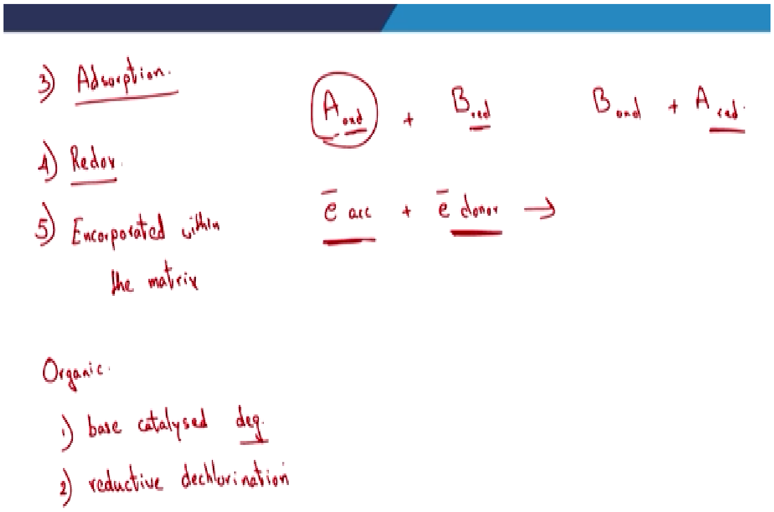

3) Adsorption.

4) Redox.

5) Encorporated within the matrix

$\boxed{A_{oxd}} + \underline{B_{red}}$ $B_{oxd} + \underline{A_{red}}$

$\underline{\bar{e}\ acc} + \underline{\bar{e}\ donor} \rightarrow$

Organic.

1) base catalysed deg.

2) reductive dechlorination

So depending upon let us say either the add mixtures that you put in let us say or even that you have the CSH matrix and such the compound can be adsorbed on to the relevant what do we say solid phase here right. So that is one way obviously. Again you can think of it slightly similar to the NAPL or the organic compound let us say adsorbing onto the organic fraction of the soil and so on. So again adsorption can occur here right.

Again it depends upon different types of aspects, as in what is the media here let us say and what is the type of contaminant and so on and so forth and the next case is one we always will have or not always, let us can have redox reactions right. So some compound let us say obviously can what do we say be or become less toxic by relevant reduction or oxidation. So obviously for that you will need to either provide the electron acceptor or electron donor right.

So redox reaction more or less, not more or less it involves the transfer of electrons. So what do you need for redox reaction to go through. You need an electron acceptor, a compound and electron donor right and then the redox reaction goes through. So electron acceptor let us say if I say A+B let say. Electron acceptor is typically the more oxidized form and this electron donor is typically the more reduced form. What will this lead to?

It will lead to formation of B, which is relatively more oxidized and A, which is relatively more reduced now right. So one of these let us say can be a contaminant. Let us say A is your contaminant and its oxidized form let us say relatively toxic to either the environment or humans let see and thus let us say you want to reduce this. So I can add an add mixture let us say, which is a reducing agent, which can degrade A to its reduced form right.

So again what we need here though, as you can see in your redox process, you need an electronic acceptor and an electron donor right, because unlike H+ electron you know cannot what do we say exist freely over there right or it cannot accumulate now. For the redox process to go through you need to have an electron donor and electron acceptor in proximity, for such that the electron transfer takes place right. So again you can add different add mixtures let us say and let the redox process take place and go through.

Second aspect is let us say it can be incorporated, or incorporate it as in the compound, incorporated within the matrix. As the CSH matrix being formed, you know the cement flyash and water, so you know part of this particular what do we say contaminant can be incorporated within the relevant matrix and let us say for organics, let us say, what can we have? So we can have let us say a base catalyzed degradation, let us say if I can call that.

So there is a part of the organic compound can be degraded let us say in the presence of what do we say the base let us say OH-. So you know that something that typically happens when this context, especially if you maintain the pH to be relatively high right. So let us look at the other aspect. So we can have reductive dechlorination. So similar to the case when we looked at I believe either natural attenuation or PRB and so on let us say.

If you have an organic compounds that is let us say chlorinated solvent let us say right or such, obviously that is relatively more oxidized form of the organic compound right and what can you have, obviously depending upon the add mixture that you can have reductive dechlorination right. Obviously you need to provide now, what you need to provide, you need to provide the electron, the donor because the organic compound that is chlorinated is the electron acceptor right.

So that is something can happen now right. So these are the ways let us say how the contaminant can be transformed or the relevant contaminant reactions typically occurring within this or during this solidification and stabilization right. So now let us look at transport let us say right.

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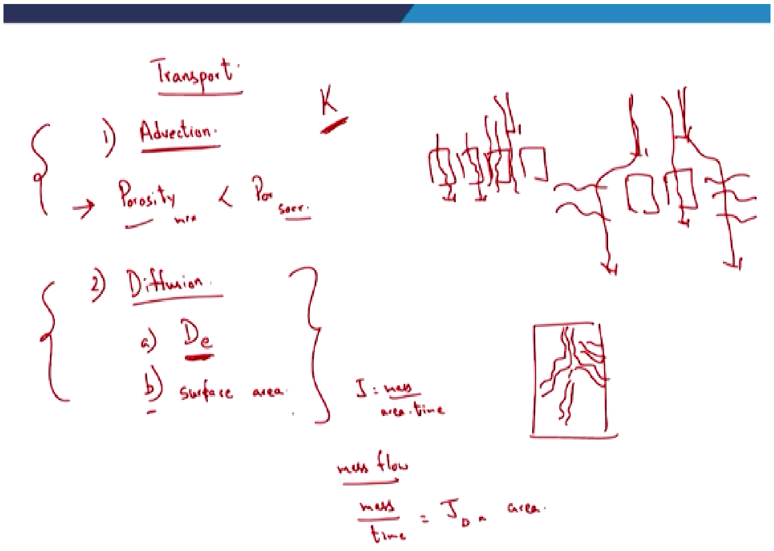

Transport

1) Advection

→ Porosity mix < Por sorr.

K

2) Diffusion

a) D_e

b) surface area

$J : \frac{mass}{area \cdot time}$

mass flow

$\frac{mass}{time} = J_D \times area$

Transport of the relevant contaminant right, so obviously what is one way that the contaminant can be transported, it is obviously by advection, right. As in let us say, you have your solidified and stabilized monolithic blocks here let us say right and either rainfall or any other leachate coming in contact with it right or even flowing through it let us say, because there will be considerable pore space.

As you know cement once it hardens to right, you know you will have considerable pore space right you know you are going to have the leachate coming in contact with your relevant what do we say compound or right. So if it is in the aqueous phase and such let us say you know your compound is going to be transported along with this net flow of fluid and that is more or less advection now.

So in this context to what is something that you want to aim for, especially with respect to the porosity and thus let us say the permeability let us say of the relevant solidified and stabilized mixture. You wanted such that let us say the porosity or even permeability right to be lesser than this is the porosity of your mixture let us say should be less than the porosity of the surrounding what do we say material now.

Why is that, because let us say the porosity of these blocks, let us say your leachate is coming out here and porosity here is relatively less than porosity and this media surrounding it. So what is the water or the leachate going to do. It is going to take the path of least resistance. So it is going to flow around the solidified material rather than flowing through it right. So that is something that you will aim for as in with respect to porosity or the permeability of that particular block now right.

So again keep in mind that advection is something that can typically or will take place and the second aspect is by diffusion let us see right. Again we know how diffusion works let us say. Again you have let us say your compound, any equilibrium here again right and even if there is no net flow of fluid and if you have let us say water in contact with this particular solution or the compound here in your solidified and stabilize matrix right.

You can have diffusion as in because the concentration is higher you know at the solid or near the solid and you know less and the relevant leachate let us say. Even though there is no net flow of the leachate through diffusion, the contaminant will want to be transported from here to out here right. So that is something that you see and upon what factors is this dependent now. So it is going to be dependent upon obviously the diffusion coefficient.

Typically, we are going to write the effective diffusion coefficient taking into account the tortuosity or the retardation and so on and so forth, but typically we are going to take into account tortuosity. What is the tortuosity now, as in similar to our ground water case let us say you know, you are going to have different flow paths possible right? So dispersion can take place right.

So again taking that into account rather than just having the diffusion coefficient we are going to have the effective diffusion or dispersivity coefficient I guess right. Again diffusion coefficient what does it depend upon. For example, let us say, I think one example we might have look at there is a opening a scent bottle here. So the person sitting at the back of this room can sense the compound or smell it rather right after certain period of time, why is that?

Even though there is no net transport, the compound will travel from here to there because of diffusion let us say right. Again diffusion is random in nature, that is something to keep in mind right, but if I keep this in let us say water let us say, it might take less time, more time depending upon the type of contaminant. Why is that again, because you know the diffusion coefficient depends upon both the media.

The media here is air and the compound which is the scent I guess. So in the second case the media is water and again the compound is still the scent right. So this diffusion coefficient depends upon both the media and the relevant compound here right. Again that is something to keep in mind and then the next aspect upon which diffusion depends upon is obviously surface area, right or particle size and so on, why is this important now?

As in you know that flux equal to mass per area per time right. So this is flux. So if I just want to know the mass flow or how much contaminant is leaching out per time, as in I want to know how much of the contaminant is leaching per time right. So that is equal to the flux let us say due to diffusion into the area let us say right or the total surface area available. So the greater the surface area available, the greater the diffusion let us say right.

That is what something that you here so particle size place relatively important role in this particular context now right. Again with respect to transport, we need to look at advection and diffusion right and different aspects within here. Again hydraulic conductivity right is an important parameter here. So here in this context, we will look into porosity, permeability and obviously typically hydraulic conductivity.

And again diffusion is obviously always plays a role right and what are the other aspects that we need to keep in mind. Obviously we need to look at the physical integrity let us say or physical characteristics right.

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Physical integrity.

→ U.C.S. US. E.P.A: 50 psi

Freezing & Thawing.

Leaching.

So how do we test for this physical integrity let us say of this particular matrix now or your solidified and stabilized mass. You are going to look at the unconfined compressive strength typically right and typically I think USEPI anyway right and that is obviously very good standard to typically refer to typically anyway right. I think it says that it should be minimum of 50 pounds/square inch right, the unconfined compressive strength.

Obviously this solidified blocks should be able to sustain its own what do we say weight and also any weight above it and any water or saturate, right. So again you need to have structural integrity let us say or your mass should have structural integrity right. So in this context obviously we need to look at the unconfined compressive strength right and another aspect here is that again maybe not greatly relevant in all parts of India, but depending upon where we are let us say.

So the effects of freezing and thawing let us say, right. As in you are going to have this solidified mass let us say and let us say depending upon where you live let us say you know you can have freezing of this relevant material and then again thawing of this relevant material let us say right. So during this time obviously there are going to be changes because obviously you have water, changes in the structural properties of your material let us say.

Again you have water, again the volume changes when it is solid and when it is aqueous or when it is fluid right. So again you are going to have issues with what we say the integrity of your particular mass let us say or the solidified and stabilized mass and so that is something to keep in mind let us say. The effects of freezing and thawing on this particular aspect need to be looked at right and then we are going to move on to leaching.

But looks like I am almost out of time, so we will just talk about this very briefly though right. So leaching is something we need to take into account, as in I want to know or want to be able to estimate let us say at least theoretically the rate at which the mass that will leach out, let us say particular point in time given that I assume that diffusion occurs or maybe there are other reactions occurring or so on and so forth right.

So for that we will obviously have to look at what now, it is going to be a material balance right or mass balance again on the relevant compound right. So that is something we are going to look at in the next session and then maybe we will, not maybe and then we will move on to looking at how do we see to it that I maintain a certain pH or what pH I need to maintain right and thus what is that water cement, flyash and the solid ratios that I need to add and so on and so forth right and I guess with that I end today’s session and thank you.