

Environmental Remediation of Contaminated Sites
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Lecture - 39

Calculations for Fractions of Binders, Admixtures, Waste and Water used in Solidification

Hello everyone. Welcome back to latest lecture session. Again a very quick recap of what we have been up to, right, to refresh your memory.

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<u>Calc.</u>	<u>Solids & Stabil.</u>	<u>Trial & Error approach</u>										
	<u>TCLP approach</u>											
$\frac{20 \text{ mL of E.F.}}{9 \text{ g of waste}}$	$\cdot 0.1 \frac{\text{meq}}{\text{mL E.F. (1)}}$											
$= 2 \frac{\text{meq}}{\text{g of waste}}$												
$ANC_{\text{mix}} = 2 \frac{\text{meq}}{\text{g}} = \sum f_i ANC_i$		<table style="margin-left: auto; margin-right: auto;"> <tr><td style="padding-right: 10px;">11</td><td>ANC₁₁</td></tr> <tr><td style="padding-right: 10px;">10</td><td>ANC₁₀</td></tr> <tr><td style="padding-right: 10px;">9</td><td>ANC₉</td></tr> <tr><td style="padding-right: 10px;">8</td><td>ANC₈</td></tr> <tr><td style="padding-right: 10px;">7</td><td>ANC₇</td></tr> </table>	11	ANC ₁₁	10	ANC ₁₀	9	ANC ₉	8	ANC ₈	7	ANC ₇
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So we were looking at you know the relevant calculations in the context of solidification and stabilization, right. In that context, we are looking at calculations of how to calculate the various fractions. So what is the key here? It is that we are looking at TCLP approach. Obviously you can follow the trial and error approach as in just you know try out different fractions and then try to see to that does it meet you a relevant criteria or not in so on and so forth or you will see that what is the pass mark or what is the TCLP approach about.

You are just trying to pass the relevant exam now. So we will look at the pass mark or the optimum pH and how do we try to get that optimum pH now, pH as in such that because in your TCLP test, you are adding acid. You are going to decrease the pH. So you will try to see you that the pH is maintained even after addition of acid that the pH is maintained at such a level that you

know the relevant contaminants or heavy metals do not dissolve to or beyond the relevant thresholds.

So that is the approach and in that case obviously we looked at that case as in we know the 20 mL/gram, 20 mL of extraction fluid is added per gram of waste. I think we saw that it is 0.1mEq of acid/mL of extraction fluid mEq that is what we have for extraction fluid too anyway and multiply that we end up with 2 mEq/gram of waste. So this is the amount of acid that we are adding out here. So obviously you need to be able to neutralize this acid.

So your acid neutralizing capacity of the waste or the total mixture if I may say so, should be equal to 2mEq/gram. So that is what it should be. And you know that this is depend upon the different fractions that you have and their acid neutralizing capacities. So this is what we end up with. So obviously let say you know if I take cement let us say, at a particular pH let us say 11 it will have particular acid neutralizing capacity and 10, 9, 8, 7, ANC 10, 9, 8, and 7, different acid neutralizing capacity. So obviously which one will I choose.

I will choose one for that particular pH when I know that the relevant heavy metals are not going to fall below a certain or above a certain threshold. That is from your KSP or the relevant chart that we are going to use, again later on when we look at the relevant example I guess. So you are going to choose that particular acid neutralizing capacity interpolate or extrapolate if necessary and then pluck that in here and calculate that.

So more or less again we are just trying to pass the test, let us say. So let us just look at one example that I have here.

(Refer Slide Time: 04:06)

$\frac{\text{Water}}{\text{Cement}} = 0.6$
 $\frac{\text{ANC}_{pc} = 14 \text{ meq/g}}{\text{Waste contains 10\% water that is available to hydrate PC}} \quad \frac{\text{ANC}_w = -1 \text{ meq/g}}$

$$\text{ANC} = 2 \text{ meq/g} = f_{pc} \cdot \text{ANC}_{pc} + f_w \cdot \text{ANC}_w + f_{H_2O} \cdot \text{ANC}_{H_2O}$$

$$2 = f_{pc} \cdot 14 + f_w \cdot (-1) \leftarrow$$

$$f_{pc} + f_w + f_{H_2O} = 1$$

$$\frac{\text{Water}}{\text{Cement}} = \frac{f_{H_2O} + 10/f_w}{f_{pc}} = 0.6$$

So let us say we have acid neutralizing capacity of Portland cement to be 14 mEq/gram of cement and for acid neutralizing capacity of waste it is -1 mEq/gram. So obviously it cannot neutralize an acid. It itself is an acid let us say that is what we have here when we say it is -1 is the acid neutralizing capacity. It is negative acid neutralizing capacity and in this particular context to look at structural integrity and such the water and cement ratio is 0.6 and also that the waste itself contains 10% of the water that is available to hydrate the Portland cement.

So let us just try to see how to go about solvent for the relevant aspect. So what is the first aspect that you know the relevant acid neutralizing capacity of the mixture should be maintained at 2 mEq/gram. So that should be equal to the fraction of, what is the fraction, mass of this particular element, which is cement let us say by total mass.

So fraction of the Portland cement into acid neutralizing capacity of this Portland cement plus fraction of that particular waste into acid neutralizing capacity of that particular waste plus fraction of water into acid neutralizing capacity of water. In this example, we are going to assume that this is equal to 0, okay. How will this transform into? So acid neutralizing capacity of Portland cement is 14 mEq/gram plus fraction of waste into -1 that is equal to 2 mEq/gram.

So all the units match out obviously because fractions dimensionless and acid neutralizing capacity the units are all in mEq/gram now. So that is something that we have out here, but

obviously I have 3 variables what are they, 1, 2, and 3. I have only 1 equation what are the other equations. Obviously, I know that fraction of the Portland cement plus fraction of waste plus fraction of water obviously fractions, right.

So the sum of the fractions should be equal to 1 that is something that I have, but I still need one other additional equation to be able to solve for that because I have two independent equations and 3 variables, right. So obviously I need look at this particular aspect. So the fraction of water that I am going to add plus it seems 10% of the waste has the relevant water. i will have to write this as fraction of H2O+10% of fraction of waste contains water that is available to hydrate Portland cement.

That is why I have 10% here, and by cement is fraction of Portland cement that is equal to 0.6. What is this here, this is nothing but water by cement ratio, the fraction of H2O that I am adding additionally plus fraction of the water already present in the waste that seems 10% by fraction of the Portland cement is equal to 0.6. So now I have 3 equations and I will be able to solve them and I think let me look at the values that I have.

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Handwritten notes showing calculations and risk assessment criteria:

$$f_{pc} = \frac{0.197}{0.760} \approx 0.25$$

$$f_w = 0.760 \approx 0.76$$

$$f_{H_2O} = 0.043$$

$$\text{Sum} = 1$$

TCLP Trail Error N.C.R. H.I. < 1
Site charac. Risk based approach L.C.R. < 10⁻⁶

So we now have 3 equations and 3 unknowns and we can solve them and let us look at the solution that I have. So looks like the fraction of Portland cement is 0.197 or almost equal to 0.2 and fraction of the waste is 0.76 and fraction of water is 0.043 and total obviously should be

equal to 1, right. The sum should be equal to 1 that is something that you see here, but typically you want to be able to let us say you know this is the typical example that you would face.

So this is actually I believe from 1 particular site. So just let try to understand how much cement I need to add per amount of waste. So what is the ratio though, fraction of Portland cement per waste, right. So if I do that let us say, so I can see that so the fraction of this Portland cement to fraction of the waste is approximately going to be equal to, I think, 0.2 or 0.25 maybe. So you get an idea about how much cement or the binder it is that you need to add per you know waste or per gram of waste or such.

You need to add 0.25 gram of binder/1 gram of your waste now. This gives you an idea obviously. Obviously you are going to have homework that is relatively more complex and we will again solve that before we solve that again let us say, I want to look at the other approach as in what are we looked at until now. We have looked at the TCLP approach and trial and error as in very briefly discussed this trial and error which we rarely use.

TCLP approach is like you are just trying to pass the test as in you are trying to meet that particular pH value and that is it. So that you know whenever the TCLP test is conducted. The result show that this particular solidified and stabilized block is not a hazardous waste anymore, right. So what is the better approach obviously? You are going to study for the test to obviously learn for the test or do well in the test let us say.

So in that context, let us say how do you understand this particular case? So that is particularly based on side characterization, let us say, right as in risk based approach. So what is this risk based approach about. So think of this your waste can end up in any situation let us say where the conditions are such that they are worse than the TCLP, what do we say than the conditions that the TCLP test would expose your waste to.

It can be in different kinds of or the waste can end up different kinds of settings now. So what is that this particular approach does, it is the risk based approach as in if remember in our initial classes anyway, we talked about risks as in non-carcinogenic risk or hazard index let us say and

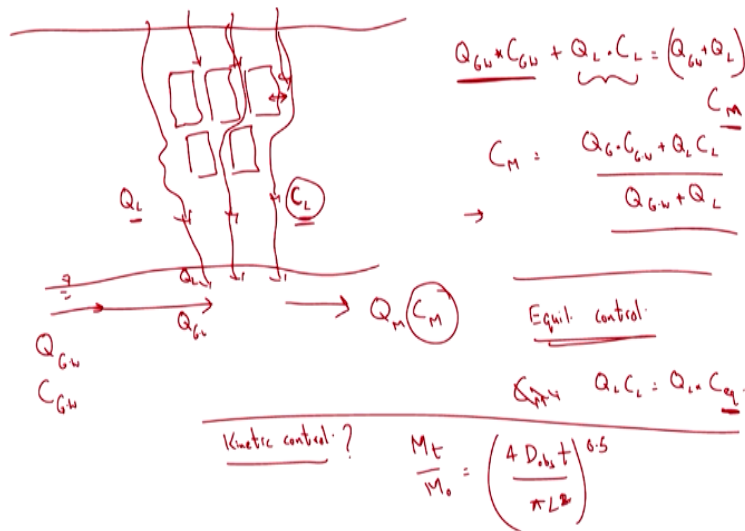
we also talked about lifetime cancer risk and the hazard index should be <1 and lifetime cancer risk, the thresholds are 10^{-6} and so on and so forth.

It should be $<10^{-6}$, hazard index is for non-carcinogenic compounds, lifetime cancer risk obviously for carcinogens obviously. So let us say, what are we going to do, let us say we know where this particular solidified and stabilized mass is going to end up in and then I am going to look at let us say, the relevant transport and the relevant pathways. Typically, what is the pathway that the leachate enters the ground water and the groundwater.

Then you know is what do we say consumed by or the relevant populations are exposed to this particular ground water and thus they are being exposed to the contaminant. So I then calculate the relevant exposure concentrations. I know the pathways. I can come up with the risks. So it is a risk based approach. so I will calculate the risks and CU is the risk less than the thresholds as is <1 and $<10^{-6}$ for the lifetime cancer risk and so on and if it is less okay that is fine.

If not, then I need to take remedial actions. So here we are actually having what do we say disposal conditions and actual site conditions in our mind and that is our objective. We are not just trying to beat the test, but we are trying to see to it that the final disposal conditions are such that they do not create any human health issues or such, right. So that is obviously the risk based approach, right. Let us just look at one aspect here.

(Refer Slide Time: 12:08)



So let us say, I have my solidified and stabilized mass blocks here and let us say this is disposed at some particular site and let us say I have my groundwater obviously flowing out here let us say. So this is subsurface and let us say you know now water permeates through and is in contact with it let us say. So the flow rate of this particular leachate, I will call this leachate is Q_L . So this leachate is now in contact with let us say you are this particular waste.

And obviously either through diffusions or advection or such, I am going to have some of these contaminants leaching into this waste. So I will call or refer to the concentration of those contaminants in the leachate as C_L , pardon me C_L and the rate of flow of this particular leachate as Q_L . This is something we can estimate and here let us say, I know concentration, not concentration, the flow rate of the groundwater and concentration of the contaminants if any in the groundwater typically we can assume them to be 0.

So at this particular point let us say or if not point in space, let us say, they are going to mix as in the leachate and the groundwater are going to mix and then I am going to end up with new Q , which is the mixture and concentration of the mixture of leachate and ground water. So obviously I will be concerned about this particular value because this is the value that the relevant population is going to be exposed to. Let us look at how we get there?

So obviously again as you see it is mass balance here. What is coming in and going out, right. So it is nothing but Q of the groundwater into concentration of the groundwater as in mass of the contaminant in the groundwater initially plus Q of the leachate into concentration of the relevant contaminant in the leachate. What is this, this is the mass of the contaminant in the leachate will be equal to the total mass after mixing. What is the total mass after mixing?

It is nothing but Q groundwater plus Q leachate into the concentration of the mixture, and so this concentration of mixture is thus nothing but Q groundwater into concentration of groundwater. Typically, we can say this is 0 plus $QLCL/Q$ groundwater + Q of the leachate. So this is the concentration of the relevant what is it now contaminant after mixing between the groundwater and leachate. So what are we observing here.

We are observing that the leachate is contaminating the groundwater and this particular what do we say contaminated groundwater will then be, you know, taken in by different, what do we say, people out there in that locality and then I can calculate the relevant risks based on exposure concentration, age, body weight, let us say, exposure frequency, exposure duration, exposure time and so on and we did look at these calculations in great detail in the earlier class.

So we are obviously not going to go there again, but let us look at this scenario here now, the 2 scenario as in equilibrium could have already been reached or there is enough time let us say that the equilibrium can be reached between both the leachate and the what do we say now, the contaminant within the solidified matrix now or within the pore space in the matrix, right or it can also be under kinetic control when the equilibrium has not been reached.

So there are 2 cases, 1 case when the equilibrium has been reached, so that I will call to be equilibrium controlled. So how will that more or less be affected here. Let us say C_L itself is the equilibrium concentration. So I can plug this in here and then get this concentration as C mixture is equal to $QLCL$ or let us say you know. Let me simplify this further, I am trying to get this $QLCL=QL$ *the C equilibrium obviously, the equilibrium concentration itself.

So that is something straight forward, but what is the other way though. If there is not enough time for the system to reach equilibrium as in equilibrium of what now, equilibrium of the contaminant between the leachate and the what do we say, contaminant in the what do we say pore space within the solid now. So if there is not enough time for equilibrium to be reached, it is going to be under kinetic control, right. So how do I get this?

Typically, you know we might be under kinetic control, right. So how do I get this though, right. For example, we know that we have MT/M not is equal to I think what now, $4D$ absorbed time/ πL square to the power of 0.5 or square root, I believe we have this, right.

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$$M_t = M_o \left(\frac{4 D_{abs} t}{\pi L^2} \right)^{0.5}$$

$$Q_C = Q_L \frac{dM_t}{dt} = Q_L \left\{ M_o \left(\frac{D_{abs}}{\pi L^2 t} \right)^{0.5} \right\}$$

$t^{0.5}$
 $\frac{1}{2} t^{-0.5}$
 $\frac{1}{2} \frac{1}{\sqrt{t}}$

Let us just check that here, right. We have that, so $MT = M$ naught * $4D$ absorbed T πL square, right. So in kinetic control what is that I am going to have $Q * C$ or $Q_L * C_L$. The C_L will be dependent upon this particular mass that time T . So that is going to be equal to $Q_L * DMT$, let us say with respect to DT because its kinetic control. Equilibrium has not been reached and what is that going to be equal to $Q_L * M$ not and all the other what do we say aspects are constants, right.

$4D$ absorbed πL square but T to the power of 0.5, right derivative of that will be again I will end up with T to the power 1/2 and $1/T$ square, okay or nothing but $1/2 T$ to the power of -0.5. So that is going to be equal to πL square T , and 4 and 1/2 are going to cancel if I bring them out. So that is going to be equal to D absorbed, right. So this is going to be the power of 0.5. Let us just

check this. So it is supposed to be equal to $1/2 T$ to the power of -0.5 is nothing but $1/\sqrt{T}$, right.

So that is what I have here. So that is fine out here and so $QLCL = QL * M$ not D absorbed/ πL square T to the power of 0.5 , but keep in mind that you know this particular value or this CL here calculated by this particular set of variables cannot be greater than the C equilibrium value, because obvious the maximum can be only the C equilibrium and how do we get the C equilibrium, we have the relevant equilibrium constant and so on and so forth.

So again that is the relevant aspect that we need to consider here. So typically again there is going to be a phase when it is going to be between, what do we say, equilibrium control and kinetic control. So that is something also you will also need to be concerned about when it is equilibrium controlled and when it is kinetic controlled, let us say. So that is something to keep in mind.

So if there is enough time or let us say the flow is relatively slow such that the equilibrium can be reached typically we have equilibrium control, but if that is not enough time what is going to happen you are going to have kinetic control because there is not enough time for the system to reach equilibrium. So the concentration in the leachate will be relatively less than the concentration that would be in the leachate, if the system can reach equilibrium.

So that is something that we need to keep in mind. So depending on these 2 approaches, what are the TCLP approach and the risk based approached, we can look at how much you know concentrations of the waste or fractions of waste, cement and so on and so forth need to be added and we can get that done. So I guess I am slightly out of time to be able to explain the whole example here. So we will do it in the next session.

So again we are going to look at a relatively more complex example and look at the TCLP approach, right and maybe you can then used that to solve the relevant homework questions I guess and I guess with that that is it from me for today and thank you.