Environmental Remediation of Contaminated
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Lecture - 40
Discussion of TCLP Approach Solidification and its Example

Hello again. Welcome back to the latest lecture session. Today we are going to work out an example related to the design of let us say a particular contaminated matrix let us say, again before we read further, let us know refresh our memory with respect to the two approaches per solidification stabilization, right. So what are they?

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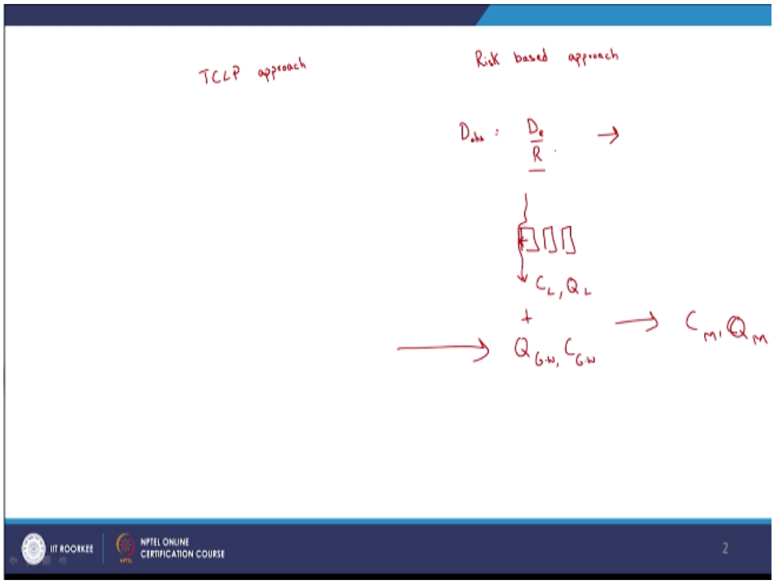

One was the case where we get the TCLP based approach and the other is the Risk based approach, right. Okay. So in this context what are the fundamental differences between both these approaches now; the example that we are going to look at today is the one related to the TCLP based approach right. So what is that we are trying to do the where we are trying to beat the test. As in why are we trying to do that?

Obviously, because how is a particular waste classified as hazardous based or such based on the TCLP test, right. So we are going to design the system and matrix in such a way that I mean we will add the relevant flyers, cement and so forth, right different add mixtures if required and see to it such that we maintain a pH that is high enough, so that even after the addition of acid in your TCLP test right you add acid in your TCLP test I believe aesthetic acid and worked out the relevant calculations and it is around 2 millie-equivalents per gram right.

So even if we add that amount of acid we will design in such a way that the pH is high enough and the acid neutralizing capacity of the system is high enough such that you know the pH will not follow below that value, let us say where let us say the solubility of this heavy metals or the compounds will be greater than the relevant standards, right. Again we are going to try to maintain the relevant pH to be relatively high enough such that you now, leaching is restricted if I may say so, right.

It should not leaching I guess I should not have use the term leaching it is that let us say heavy metals switch are precipitate let us say or you know dissolve or such, right. Again, that is the aspect related to the TCLP approach. But what is this Risk based approach about though, right. Again, this is the one that is relatively more stringent and that would be that should be the let us say if I may say so, or that is the better approach certainly.

And why is that better approach, because it is a TCLP approach, we are obviously trying to beat the test, right. We are not trying to look the actual site conditions or so on which might be worse than what the TCLP is predicting let us say, right. So in that context what do we do now we look at a particular scenario or the site where this is going to be dumped and such and we look at or consider particular De-observe you know, which will give you an idea about the rate of leachate, right.

De-observed, I think this is something what we looked at based on D effective by retardation factor, right. More or less what this give you an idea about. It gives you an idea about the rate of leeching or let us say how fast or slow is a relevant leaching now, right. That is something that we looked at. And based on that let us say or we apply the material balance on that particular compound let us say, right and we looked at the relevant solution for that, right and based on that we can come up with the relevant concentration, right. Concentration of the containment in the leachate, right.

So let us say your leachate is going through the relevant matrix, there is going to be diffusion of leaching into this particular what do you say leachate, right. And now this particular leachate is going to have particular concentration L of these particular contaminates and which has a flow rate of QL. This comes in contact with the ground water which let us say can have some concentration of the relevant contaminants.

And say after mixing right we are going to end up with C mixture and concentration of the pardon me the flow of the mixture, right. So based on again a simple mass balance we can now get what this concentration of the mixture is, right. So once we know that we can estimate what the exposure concentrations are for the relevant population, right. Again, looking at the relevant risk based approach we did which we looked at earlier in the class right.

We can calculate the different risk or you know potential risk and based on that we can take a call or one can take a call whether you need to look at other measures or you know this particular solidification stabilization is good enough for now, right. So obviously this is the better approach. In this context we would discussing about one particular aspect.

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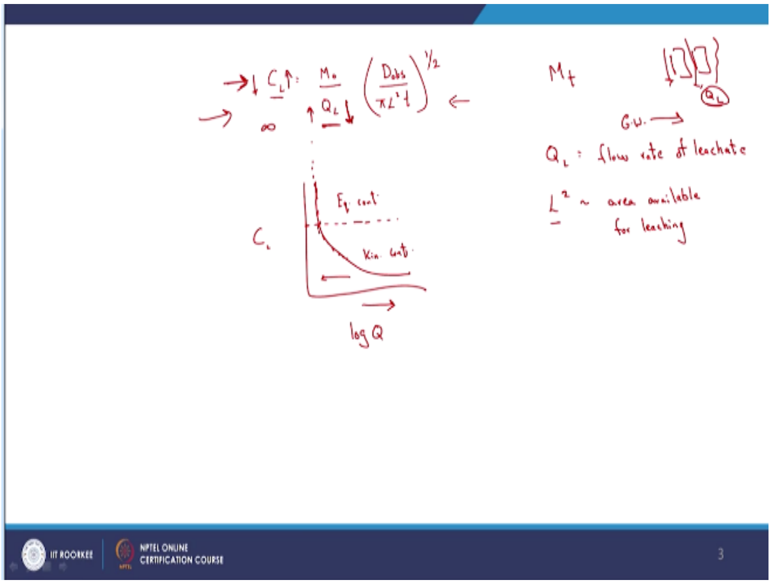

$$C_L = \frac{M_0}{Q_L}\left(\frac{D_{obs}}{\pi L^2 t}\right)^{1/2}$$

M_t

Q_L : flow rate of leachate

L^2 ~ area available for leaching

Obviously, this is the concentration the leachate; this is how we calculated that or this is how I ended up with. So how do we get this particular equation? I think we have re-equation for total, right and then took relevant differential of that with respect to time and then QL CL and so on.

So from that we have this equation. So but let us just take a quick look of what this is giving as an idea about right. So this is the QL or the flow rate of the leachate, right.

And what we have leachate mass let us say that is fine. And L square will give us an idea about let us say, what will give us an idea about area available for leaching. And as we mentioned or discussed earlier depending upon a square or rectangular block or you know is a spherical or you know what is the kind of shape of the your particular matrix let us say. It will have different ways to calculate. L square and time, time is obviously t right.

So again as QL or the you know this particular leachate decreases, so you have this flow of leachate QL which is reaching the ground water here, right. So as this particular value decreases, right what is going to happen? What is it mean more or less that you have your block here and QL is coming in contact, right. If QL is less what is that mean that now that the volume of water that is in contact with your particular matrix has enough time let us say for the system to reach equilibrium, right.

But if QL is faster right what is that means, that there is not enough time let us say for system to each equilibrium and thus you know the system will be kinetically controlled. Let us understand that from point of view of this equation here. So QL as you see as it gets higher as concentration or pardon me as QL or the flow rate increases. What is going to happen to CL obviously CL is going to be decrease, right that is obvious, right.

If you have some particular containment here and you know the flow rate of the leachate is increasing let us say, the time it has for you know, diffusion let us say is going to be obviously less and thus concentration in the leachate will be less, right. So that is something we see. But it is not as if let us say if the concentration is what do we say very high let us say what is going to happen in that case, let us say or pardon me not very high.

In the other case let us say when we have the QL to be very less, right as QL is less CL obviously decreases, right that is just the opposite of what we just discussed right now, as you know the flow rate is relatively less, this volume of water contact with your matrix as more time and let us say now you know there is greater concentration that will reach into your relevant volume of water.

But does not necessarily mean that you know, as QL decreases much further CL is going to reach infinity right it cannot reach infinity right. So there is threshold. So what is threshold? The threshold is going to be your equilibrium concentration or the one let us say for solubility. As you know, let us say for each heavy metal or different kinds of heavy metal there will be a maximum solubility or maximum concentration of that particular compound or metal that can exist an solution, right.

So that will more or less be your equilibrium concentration, let us say for those particular conditions now, right. Obviously, if the conditions change the concentration will be depend upon the other relevant variables but again we are looking at the equilibrium concentration to be threshold. So in this context we can look at this particular graph, what is that? Let us say we have C here Cl and log Q out here let us say. What is the graph typically going to look like?

It is going to be look something like this let us say, right. And obviously from here on out it is equilibrium controlled, right all throughout here, above this particular dotted line equilibrium control and below it is kinetic control. Let us just try to understand that. As Q increases let us say, right Q increases, right what do you see in respect to see? CL if I may say so, it decreases, right. And why is that? The system does not have enough time for the mass to be transferred from your particular matrix into the leachate right.

Now that is what you see out here, right. But let us say if the Q decreases, what do you see, obviously that CL increases, right. But, theoretically let us say from this particular equation it means that it should keep going up and up or you know can reach infinity but that is not the case. So the maximum is obviously going to have to be the C equilibrium, right.

That is the maximum that it can go based on the physical characteristics at the, or you know of the site let us say or the water part, right. So that is something to keep in mind. So now let us look at the example that we are talking about or we are been referring to. So that is again what is it now based on the TCLP approach, okay. let us look at that.

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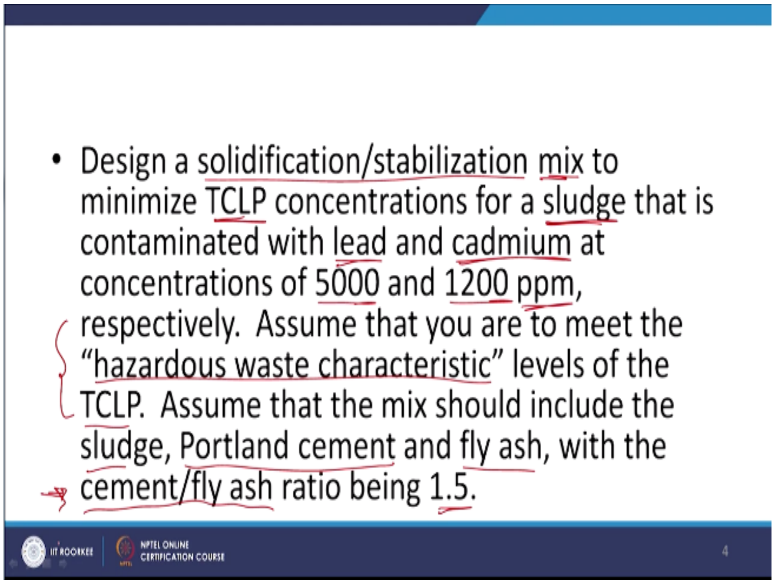

- Design a solidification/stabilization mix to minimize TCLP concentrations for a sludge that is contaminated with lead and cadmium at concentrations of 5000 and 1200 ppm, respectively. Assume that you are to meet the "hazardous waste characteristic" levels of the TCLP. Assume that the mix should include the sludge, Portland cement and fly ash, with the cement/fly ash ratio being 1.5.

So first let us understand the question. So we are going to design a mix right solidification/ stabilization mix to minimize the TCLP concentration, so obviously we are looking at the TCLP approach for a sludge okay, that is contaminated with looks like both lead and cadmium okay both are heavy metals right. At; what are their concentration now 5000 and 12000 ppm, right ppm is milligram per liter right.

So 5000 and 12000 milliliters per gram respectively. And hazardous waste characteristics as in of the TCLP test. Assume that you are to meet the hazardous waste characteristics levels of the TCLP, what does this mean? As an let us say once I conduct to this test let us say I should be able to see to it that the relevant concentration of flood and cadmium and leachate let us say in the TCLP are going to be lower than the concentrations of the threshold or the standards given in the 2016 hazardous waste and so on rules, right.

So that is something to keep in mind, right. So is what we are trying to say here, right. Assume that the mix should include the sludge, so it seems the options you have are Portland cement and fly ash and one other fact is obviously that helps you to solve the relevant system or solve for the relevant system is cement to fly ash ratio is 1.5.

It can be based on let us say aspects to the economy or the integrity or the structural integrity or the system and so on. So those two aspects typically determine how much cement to fly ash can you add and so on, right. So this is the relevant question. The take home message is I have both lead and cadmium at these concentrations and I want to beat the TCLP test, right. So let us understand what else we have here.

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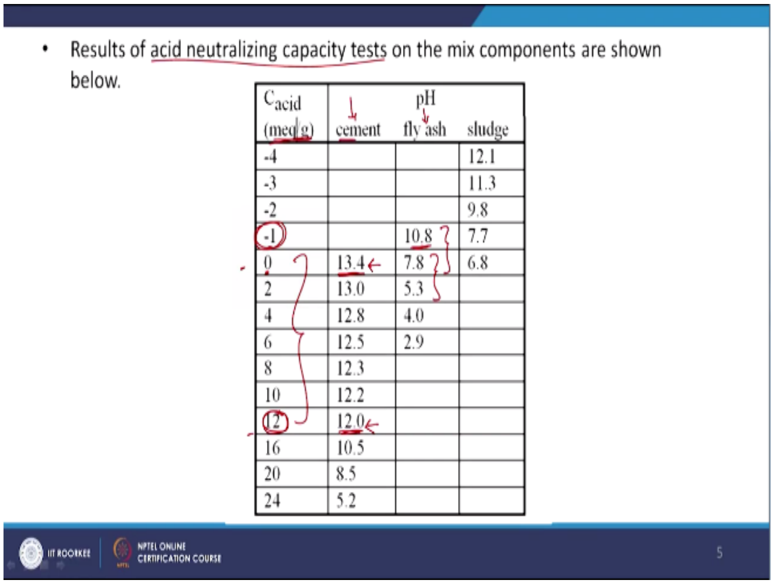

- Results of acid neutralizing capacity tests on the mix components are shown below.

C_{acid} (meq/g)	pH cement	fly ash	sludge
-4			12.1
-3			11.3
-2			9.8
-1		10.8	7.7
0	13.4	7.8	6.8
2	13.0	5.3	
4	12.8	4.0	
6	12.5	2.9	
8	12.3		
10	12.2		
12	12.0		
16	10.5		
20	8.5		
24	5.2		

So obviously, we have the acid neutralizing capacity test, right. So we have that. Again, this can be presented either in the form of a graph or in the form of a table as we have now, right. So again what is that we are going to look at, as we add an acid let us say you know, you are going to decrease the pH but it will give you an idea about the acid neutralizing capacity let us see. So for cement let us say do we have data at different pH, right.

So 13.4 and obviously no, what do we say acid neutralizing capacity. But let us say what does this mean let us see. Now 0 out here and let us say I will go 12 out here, so pH is 12 in the cement column or a column relevant to cement and 13.4 out here, so 0 out here. So what does this mean now you now, let us just try to understand.

It means that let us say 12 millie equivalent per gram let us say of the acid or millie equivalent per; millie equivalent of the acid per gram of the cement needs to be added two cement to bring down the cement from 13.4 to 12.0, right. So that is more or less you know, you are neutralizing capacity out here or that is how you can understand this particular table, right. So again similarly let us say you now you have this particular values here, right to go from 10 to 2.9 and so on right, pH 10 to pH 2.9, the amount of acid that you need to add and so on as you can see.

You know, here you need to add a base to go to; okay here you have value negative value for this fly ash. So now let us move on to fly ash, right. So here we look that cement and acid neutralizing capacity and so on and so forth. So in fly ash too we have different cases right. So let us say you go from pH 7.8 to 5.3, let us say we require 2 Millie equivalents of the acid per gram of fly ash, right. But obviously as you see you know, from this region or 10.8 you have value of -1 now right. So what is that mean now?

This fly ash itself let us say you know, is acidic in that particular region. Or you know, you can understand that in terms of the base that needs to be added to affect the pH out there, right. So that is something to consider that there. And same case with sludge, right it does not have a acid neutralizing capacity obviously as you see in this particular range now, right. So it does not have acid neutralizing capacity in that range.

So obviously, that needs to be taken into account when you mixing both the cement fly ash and sludge that I guess you know, sludge does not have you know any acid neutralizing capacity or itself is going to consume acid let us say at this particular or it is going to behave as being acidic let us say at these ranges now, right. So again that is something to keep in mind. And what else?

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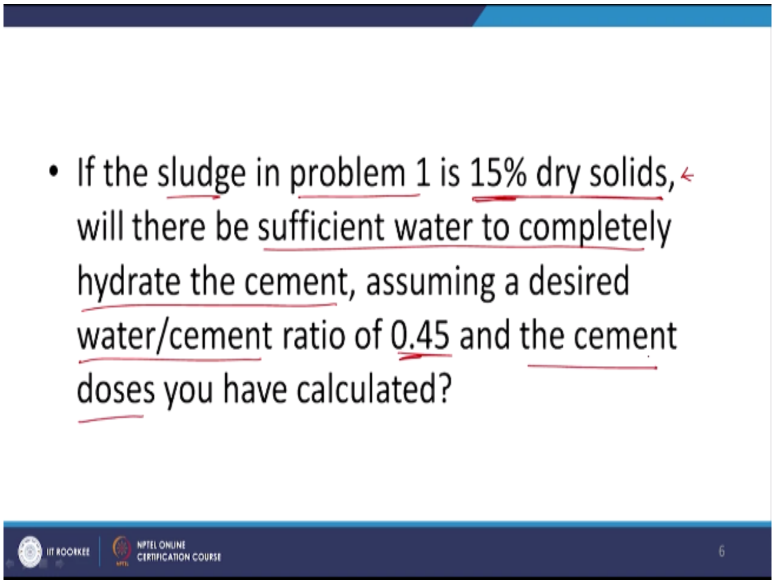

- If the sludge in problem 1 is 15% dry solids, will there be sufficient water to completely hydrate the cement, assuming a desired water/cement ratio of 0.45 and the cement doses you have calculated?

So, and in the first aspect of this problem right 15% is dry solids or the sludge is made up of 15% dry solids. So the question is do we have sufficient water to completely hydrate the cement right and this is something that we look that right, we need to maintain a certain water to cement ratio and we did look at one of the examples mire examples that we looked at right. That we have to we can add additional water and we can also see to it that the water in the sludge itself or the waste itself can be use to what we say hydrate this particular cement.

And that is the aspect that we are looking here. Looks like the it is only 15% dry solids and that you know, will there be sufficient water or you need to add the what do we say more water to be able get your water cement ratio of 0.45, right. And the cement doses what we have calculated, right. Okay. Let us move on and look at the relevant approach here obviously. So obviously, we need to be able to figure the optimum pH, right.

And this case as we just mentioned, we need to be able to balance out the concerns from both cadmium and lead. And as we know let us say there is no particular pH at which a one particular pH at which both cadmium, pardon me and lead will both be at the well to the low concentration. So let us look at the relevant graph. So this is what we have here.

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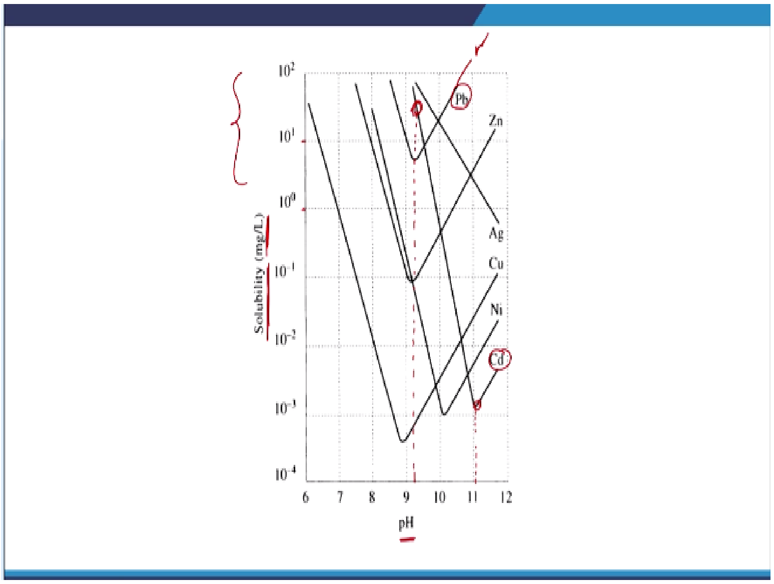

This is the standard table let us say Solubility and Milligram per liter. And keep in mind that this is the logarithmic scale, right. What is that mean? Let say here it is 10 and here it is 1, so 10 times right, so that mean unit of one difference here; if there is a difference in one unit let us say you can more or less neglect the lower value because it is 10 times less. And here we have pH obviously on the x-axis.

So let us highlight, where we are or what the component that we are looking at. So this is cadmium and that has a leading to the low concentration at 11 or 11.1 may be, right. And where is lead out here, lead is somewhere out here, this is that. And as you can see here that I think comes out to be something like 9.25, 9. Something like that, right 9.25 or so. So now the key is which particular pH are you going to choose, or what is going to be your optimum pH.

As in if I choose let us say 11, right I can see that lead concentration is going to be considerably high, right. If I choose what do you say the pH at which cadmium is going to be relatively low or the lowest one. And similarly, if I choose pH 9.25 I can see that the cadmium concentration is now going to be considerably high, right. So obviously in this case there is no one particular pH that you know will solve your issue, right.

So obviously, you need to balance it out, right. So in this case let us say maybe you can give greater weightage to the relevant compound let say that is at higher concentration compare to its standard value, right. That is one case to go about it or you can look at the ratio about the equilibrium to the relevant standard and look at trying to choose that particular case where the ratio of these two variable is going to be the same. So let us look at what I have here.

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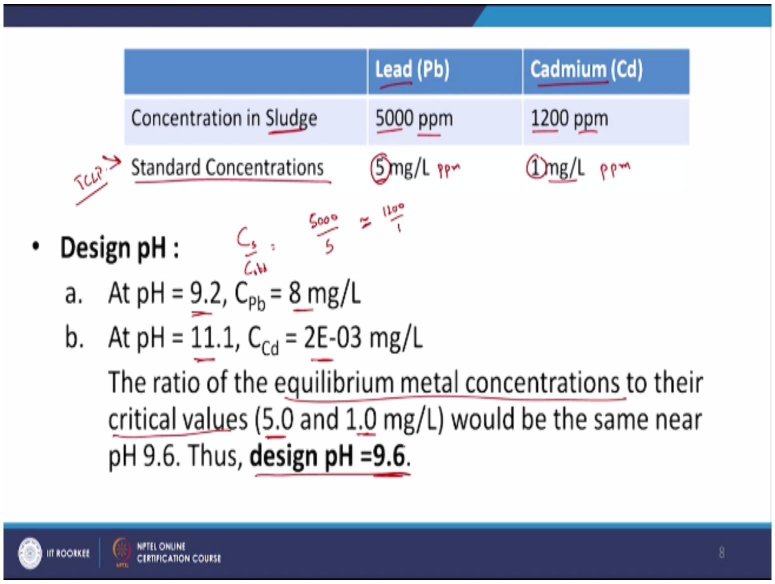

	Lead (Pb)	Cadmium (Cd)
Concentration in Sludge	5000 ppm	1200 ppm
TCLP? → Standard Concentrations	5 mg/L ppm	1 mg/L ppm

- **Design pH :** $\frac{C_s}{C_{std}} : \frac{5000}{5} \simeq \frac{1200}{1}$
  a. At pH = 9.2, C_{Pb} = 8 mg/L
  b. At pH = 11.1, C_{Cd} = 2E-03 mg/L
  The ratio of the equilibrium metal concentrations to their critical values (5.0 and 1.0 mg/L) would be the same near pH 9.6. Thus, **design pH =9.6**.

So here looks like the concentration is in the sludge, this is what we know 5000 ppm and 12000 ppm. So again here we have it in the units and these are the standard concentration from the TCLP, okay Hazardous Waste 2016 rules. And again 1 ppm right. So the relevant concentration in the leachate after you do this TCLP test should not be greater than 5 ppm for lead and 1 ppm for cadmium, right.

So one way to look at this to; you know to look at which pH to choose which you look at the concentration and the sludge or waste to concentration or the standard concentrations, right. But here I see that both the ratios are the same right 5000/5 and more or less 12000/1 more or less same, right so I cannot really use this particular ratio. So another ratio is as we just mentioned to look at the ratio of the equilibrium concentration so relevant standards let us see, right. So let us look at that.

So at pH 9.2 as we discussed it is it seems the concentration is around 8, pH 11.1 cadmium is 1 and so forth. But we see we cannot choose these pH values, right. So the ratio of the equilibrium metal concentrations to their critical values, values are 5 and 1, right. 5 and 1 concentrations would be where would they be same, looks like they would be same here 9.6, right. What are we looking at you know, we are trying to balance out both the concerns here and we are looking at equilibrium metal concentration is ratio to the critical values, right, so around 9.6 looks like.

So let us move back to that particular figure, so somewhere around 9.6 let us say. Let us say this is 9.5, 9.6 so cadmium is somewhere out here, say around 9.6 let us say. Though it looks like the point of intersection that is not that seems to be a lucky or coincidence if I may say so. But again we are just trying to what do we say balance both of them out as an equilibrium to the critical concentration.

So you can either plot a graph or you know or the ratio of cadmium to the relevant standard and nickel; not nickel lead to lead at equilibrium to standard and plot it and see the point of intersection or you can try to look at it from this particular graph, right. Again that is something to look at. And based on that I guess we end up with the relevant pH to be around 9.6, right. So now that we have pH 9.6 what is the next step, right? We need to be able to design the what do we say different fractions. Let us look at what we have here.

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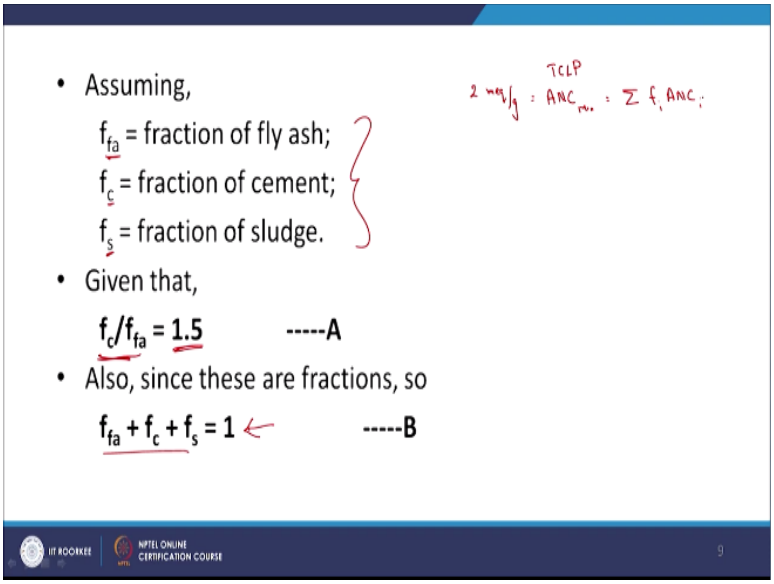

- Assuming,

  f_{fa} = fraction of fly ash;

  f_c = fraction of cement;

  f_s = fraction of sludge.

- Given that,

  $f_c/f_{fa} = 1.5$ -----A

- Also, since these are fractions, so

  $f_{fa} + f_c + f_s = 1$ ← -----B

$2\ \text{meq/g} = \overset{\text{TCLP}}{ANC_{mix}} = \sum f_i ANC_i$

So obviously, we are going to look at three aspects one is the fly ash, cement and sludge or waste here. So here right now we are not considering water here at this particular stage let us say, right. So what are the different what do we say equations that we already have? Because there are fractions this sum should be equal to 1, so obviously you know this sum of all the fractions should be equal to 1 that is something that we have.

And we know that you know, cement to fly ash ratio is already given at 1.5 right that is under independent equation. But obviously, we have three variables and we need one another independent equation. So where do we get that from? Obviously, that is based on the relevant aspects with relevant aspect to our particular case which is the acid neutralizing capacity. So how do we do that?

Obviously, we know that to we are adding 2 millie equivalents of acid per gram right and the relevant case of what do we say that TCLP test and this is what we need to be able to neutralize right. So this needs to be the acid neutralizing capacity of your mixture, right. And that will be depend upon the three fractions let us say fraction into the acid neutralizing capacities of each of these fractions.

So looks like we are almost out of time, so we will look at these aspects or the; you know, we will finish up this particular sum in the next session. But again, what is the crux here? What is one of the take home message is that we looked at here? Is that as you see you know just the case in the case when we looked at just 2 pH, 2 metals pardon met, we could not or there is no what do we say one pH value but we could choose, right.

Obviously, we have to look at different combinations or different ratios, one ratio was to look at which concentration must maybe relatively higher compare to its particular standard value. So to look at that let us say or when we looked that back we saw that both the ratios were cadmium and lead was the same. So then we looked at the equilibrium concentration to the standard value ratio and we arrive at pH of 9.6 and we are looking at the relevant cases. So since I am out of time, we will continue this in the next session and thank you.