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Lecture - 09 Classification of a Waste as Hazardous The TCLP Test

Hello everyone. So again welcome back to the latest lecture session. So as is customary let us have a quick recap of what we have been up to right. So we have been looking at I believe risk assessment right. In that context, we looked at I believe two approaches, one being the deterministic approach and the other being the stochastic approach right and we did look at couple of examples in the case of deterministic approach.

And I believe the primary issue or bone of contention between what is it now, this particular deterministic and the stochastic approaches is the use of point estimates in the former approach and you know treating variables as variables with mean and spread or variation in this particular context or for in the context of the stochastic approach right. So once we are done with that we did try to understand what are the issues with both these particular approaches.

As in, in the former or in the deterministic approach right, we are using point estimates to obviously try to estimate a variable right. For example, body weight, I think the example we looked at considered an average or mean body weight of 70 kgs but we do know that body weights of the relevant affected population you know can vary widely right and also exposure concentrations and so on.

So the risk that we end up or risk I guess right that we end up calculating might not be you know conveying the right information to relevant management and such right. So to take that variation or inherent variation within each of these variables into account, we come up with or we looked at stochastic approach yes. In that context, we went ahead and started looking at a particular example.

So in this context though obviously the key is that we need a lot more data right, so you need to be able to get an idea about or estimate the population mean and what we say standard deviation right and in that context we do know that obviously the sample size is an issue and thus the bigger the sample size obviously right the closer you will be to the true population mean and standard deviation.

So here again you are trying to estimate the mean and standard deviation of the population by analyzing the sample I guess right. So again in this context, we looked at a particular example I believe and we went through, so let us look at what we have here.

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So you are trying to get a histogram right showing the distribution of carcinogenic risk yes, the key is that it is carcinogenic risk and here it is the pathway being ingestion of benzene in groundwater that was the pathway and we looked at various aspects but the key was we were trying to calculate the probability of exceeding 10 power -6 risk right. So again how did we approach this particular problem or how do we go about analyzing these particular kinds of scenarios right?

We look at or consider the Monte Carlo approach right. So for each of these particular variables we generate random numbers right. That would conform to the particular mean and standard deviation and the relevant distribution I guess. So here in our context, I think we had a couple of variables distributed normally and then a couple of variables distributed log-normally right.

So log-normally what was the case in that case, for example X, if we say that it is log normally distributed as these are the data points, what does that mean? So natural logarithm of X, if I take natural logarithm of X and plot that, that will be or those values will be

normally distributed I guess right and then we you know consider X to be log normally distributed, so obviously, we looked at those cases and went ahead with the relevant analysis. (Refer Slide Time: 04:05)

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Variable	Units	Point estimate	Distribution	Point estimate location
Scenario specific data:				
Average body weight	Кв	47	Normal (47, 8.3)	Mean
Cancer slope factor:				
SF, Benzene	(kg.day)/mg	0.029	Lognormal (-4.33, 0.67)	88 th percentile

And in that context, we also had considered the variation in some of the relevant what do we say parameters such as body weight and slope factor yes. So in this case, obviously we had one which is normally distributed and the other which is log normally distributed right. So in that context, we also looked at the example in greater detail.

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So let us see what we have here. So in Monte Carlo approach what do we do obviously or what are we considering I guess? So we generated let us say a considerable set of data set that conforms to the particular distribution right. So for ingestion of water, body weight and then log values of benzene in water because obviously we had it to be log-normally distributed. Again, when we consider lognormal distribution, it is the natural logarithm.

Please keep that in mind right and from that context, we came up with benzene concentration in water. Similarly, I think you know 10,000 what we say random numbers for different such variables right. So once we calculated intake right, again 10,000 such what do we say numbers or data set let us say. We end up then using that particular intake and the relevant slope factor to calculate the risk right.

So again what is the key aspect here or maybe a take-home message here? We are trying to replicate all the feasible or you know different permutations and combinations that you know can be feasible within these data sets let us say or with between these variables on the ground and I think one example I have been repeating is about a person with greater body weight being exposed to lower concentration, a person with lower body weight being exposed to higher concentration.

And thus the risks associated are going to be different right and obviously you need to be able to capture all those particular combinations right. So obviously, greater the data set you know the closer you will be to the true what do we say case out there right and you will get a smoother what we say distribution curve or distribution function here right. So in that context, we went ahead and calculated the risk right.

So we had the particular risk to be calculated here and you see the different sets of data or risk here for risks and then we end up plotting the risk but at a preliminary examination, we saw that it did not make much sense but the key was that you know looks like after we understood how excel comes up with you know the built-in function for histogram I guess. We used the built-in function for histogram to develop the histogram.

And asked it to automatically calculate the bin size right, so there are two options here. We could have given the bin range but we did not do that, we asked excel or requested excel to what do we say come up with the histogram let us say and automatically come up with the bin size. So in that context let us say looks like all the particular risk values were within a particular narrow range that is how they were distributed I guess.

And with that bin size looked like there was a skew to the left with all of them bunched together and a particular bin right but obviously you know I could have changed the bin size and such but from preliminary understanding, we see that it was or it would follow a log normal distribution right. So try to you know visualize that, we then took the natural logarithm of risk and that is out here in this column right and then we sorted them out to remove some of these non-numeric values right.

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And then we plotted the histogram and now we see that it is normally distributed. So we have a log normal distribution and then we have this particular cumulative what we say a distribution to here I guess, cumulative percentage pardon me and that is what we see out here. So again what does this tell me here let us see. So bin size you know range from -15 to -14, -14.9 to -14.09 and so on.

So this will give me an idea about let us say the risk that would be that would fall within -12.39 and -11.53. So there you are under this particular curve or the frequency I guess right. So again we have on the x-axis the bin size which in this context is the relevant risk or natural logarithm of risk right. So let us try to understand this in the context of what we have been trying to look at.

So if we can go back to the particular question, we were trying to understand what is the probability of exceeding 10 power -6 risk right. So let us try to understand that here. So here we are looking at 10 power -6 risk. Let me see what its natural logarithm is going to be is

equal to the natural logarithm of right 10 to the power of -6 right and I am going to say enter, so it looks like I come up I end up with a value of -13.81 right.

So here the question was asking us to look at or obviously you know the scenario is we are trying to understand what are the chances of this particular exposed population having an additional risk of you know contracting cancer right. Typically, as we know we look at one in a million or 10 power -6 chance right and in that context because you are looking at the logarithmic risk fear because it is log normal distribution.

We took the natural logarithm of 10 power -6 and the value that I end up with is -13.8. So if I look at that out here in this particular graph that would fall somewhere out here I guess right. So that would be somewhere out here right, so if I do consider this as a distribution function you know which I can let us say the more I get the data you know the closer it would be I guess. So if -13.8 right which corresponds to 10 power -6 risk falls out here.

And what are we trying to get at, the probability that it would, it as in the risk would be >10 power -6 but when you try to look at this graph right what do you see, you see that almost all the particular data that we have or the area under this particular graph is greater than this particular -13.8 out here right.

So what does that tell us right and this context it tells us that almost all the people that are exposed to the relevant you know this particular scenario let us say are going to have or you know >1 in a million or 10 power-6 risk of contracting cancer right. So that is what we understand from here. Obviously, we can look at you know exact value as in I can plug this in and look at that.

Or obviously because we already ordered this, again this is also log risk, column M is also log risk. We ordered this I think according to its increasing order or decreasing order. So let me try to sort it in a different manner right. So okay so as we see I try to sort it from an increasing order and so here if I am trying to look at the number of cases that have a risk of <10 power -6.

So -13.8 so I have only two cases out of 9995 cases which we looked at I guess right, 10,000those 5 non-numeric values. So the risk of contract in this particular cancer from this particular scenario what is that I guess.



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So here we have two cases, only two cases out of 9995 let us say, that would lead to a case or scenario where the risk is <10 power -6 or 9993 times out of 9995 times the risk is >10 power -6. Again, that is something we saw from the distribution too right and then we had something like this 10 power -6 was somewhere out here. So if I want to get the risk >10 power -6, so obviously it is going to be all this particular region or portion.

As you see, that is almost equal to 1 right, so the probability of the person in this of any person rather in this particular scenario let us say exposed to those conditions right say right having an additional chance of contracting risk when we consider 10 power -6 risk anyway is almost 1 right.

So there is almost 100% guarantee that the people there are going to be you know or exposed to you know or you know contract cancer right pardon me considering all the variations that we have taken into account. So obviously you see here that it is much better approach compared to the deterministic approach yes. So again let us say if I wanted to look at a particular any other value of risk let us say maybe 10 power -4 >10 power -4 and then I can convey that particular data to the management too.

For example, I am going to consider this hypothetical scenario let us say. As in, management considers that okay 10 power -6, we do not have the relevant resources to bring down the risk to that particular value. Maybe I am going to look at let us say 10 power -4 threshold for the risk let us say, hypothetical aspects.

So how would they go about that, obviously they will look at 10 power -4 let us say maybe here or here let us say and look at what are the chances or probability of contracting risk let us say. So here if 10 power -6 is out here let us say I am you know just drawing an accurate and inaccurate estimate here obviously. So 10 power -4, so this would be the probability of contracting cancer right if we look at or consider the case of 10 power -4 risk.

So again this particular histogram and such stochastic analysis would try to would convey the information in a much better manner and obviously you know whenever you can or whenever you can spare the resources to get the level of data required for stochastic approach, stochastic approach obviously is a better approach. For example, if I replace this particular information of the risk and such right say and the relevant distribution with just its mean value let us say right.

So obviously let us say maybe the mean would be somewhere out here let us say but that obviously would not convey the right information regarding the spread of the particular risk associated with this particular scenario right. So in that context again, we are going to wrap up this particular case as in trying to understand in which cases is deterministic approach feasible.

Obviously, let us say time and resources and also data and also we looked at or you know in which cases stochastic approach is relatively better right. So in that context, we are going to wrap up risk assessment and we are going to move on to the next topic let us say. As in, laws and regulations associated with hazardous waste and their treatment or disposal in our particular country.

So in that context, we looked at a particular set of rules right, hazardous and other ways, I think Transboundary Movement Rules of 2016. So let us move back to that particular case here.

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So I have that here, so again published in The Gazette of India right and we looked at this and how does that or how did we come about to this particular stage let us say. As in, initially the draft rules let us say were published in 2015 they say July 2015. Comments are asked from various sections let us say industry and public and such that taken into account.

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And then right powers conferred by section 6, 8 and 25 of Environment Protection Act of 1986. They replaced the 2008 or you know rules with the 2016 rules and what are the rules that we are typically concerned with right now, hazardous and other ways management and Transboundary Movement Rules of 2016 right. So in general let us say you are in industry and you are concerned with or you operate an industry let us say.

And you are concerned of your particular wastes or what do we say probably toxic wastes or such let us say or hazardous wastes let us say. How do you go about understanding whether your particular industry is generating hazardous wastes or such in the first context, so obviously you can look at the information that we are going to consider in this particular case and secondly let us say if a site is contaminated let us say, as we do understand what do we say poison lies in the dose right?

And also we looked at the risk assessment and such too but obviously how can I classify that as a hazardous waste because the two classes, one is the municipal solid waste and the other being the hazardous waste in this particular context. So there are different disposal regulations and transport regulations and such for and also handling regulations for hazardous wastes. So how do I know whether a particular waste is hazardous let us say right?

In that context, we have a few tests that need to be conducted to be able to understand or you know classify if a test is hazardous or not. So let us look at what that is about. I think we did look at that briefly right.

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So list of, here we have schedule II okay and here we have list of waste constituents and their concentration limits and how do we classify them I guess or how do we look at this particular case of understanding whether a particular waste is hazardous or not. We have this particular test based on the leachate concentration limits from the TCLP or the soluble threshold limit concentration I guess.

So typically TCLP, so let us understand or try to look at what this TCLP test is about. So before we go further, what is this saying, so you are going to conduct this TCLP test on that particular waste and after analyzing the relevant concentrations of different compounds as you see here that are listed here let us say in that leachate right you are going to analyze the leachate from that after that particular test.

And if the concentration of any of the constituents listed in this particular table here or in schedule II I guess right and schedule II is higher than the concentrations given here. Then, you would classify that particular waste as hazardous waste. Obviously, there are different other classifications too but this is the primary one typically with which most of the industries are concerned with.

Other than that obviously based on the characteristics let us say we also can or you know do classify a particular waste as hazardous.

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Primarily, flammability, corrosivity right, reactivity or explosivity, toxicity right say and typically though you know though we do have this information we typically go for TCLP test and then we have some other aspects regarding their reactivity and such I guess. Again, they are listed but typically during the course of our class, we are going to be or our course pardon me we are going to be concerned with looking at the TCLP test I guess right.

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So again what is this TCLP test about? So here we have the relevant information corresponding to our particular schedule A right, so we have different compounds and the limits of what we are going to of that particular compound and the leachate after TCLP test right and here we have our particular TCLP related information. So how do we or what is this test about? Obviously, it is concerned with extraction of leachable constituents.

And it is the USEPA test method 1311 I guess, so we are going to look at that and obviously there is another more stringent test which is called the waste extraction test and that is developed by or you know available from California Code of or in the California Code of Regulations I guess right but typically we look at the TCLP test. So let us try to understand what that is about okay.





So we are moving on here, so TCLP test right so in which context are we trying to look at this particular aspect? We are trying to understand let us say for particular waste let us say or contaminated soil let us say. An example here can be treated or should be considered as hazardous waste. For example, let us say this is my soil out here and somebody dropped some chromium let us say okay.

Chromium in this particular soil okay and I have chromium in this particular soil let us say. How do I know if the particular soil can be deemed, this particular contaminated soil anyway can be deemed to be hazardous waste or not? For that obviously, I need to conduct the TCLP test right. So here I gave one example but let us try to look at the background for this TCLP test.

So what happens to the waste if you do not consider it to be hazardous waste right? It would end up in a municipal solid waste landfill right, typically if not in this example of contaminated soil typically let us say if there is an issue with you know or you need to make a call regarding a particular waste if it is hazardous or not and if you come up with the relevant or take the call that it is not hazardous waste, where will that waste end up in? Let us say in a municipal solid waste landfill and what conditions prevail in these municipal solid waste landfills now or in these municipal landfills? You have acidic conditions from the anaerobic degradation. As in, let us say over time okay assuming that this is the liner okay and the relevant leachate collection system and so on semi impermeable layer and such, very generic figure here.

Let us say if this is the landfill let us say, a very generic figure here for now or let us say if this is the landfill, I am going to have different cells and so on right. I am going to end up with this particular case let us say and let us say I cap it let us say. So now the waste does not have any access or does not or has not had any access to oxygen now right. So obviously anaerobic conditions would predominate and you are going to have anaerobic decomposition.

And in that context, you have what do we say acetic acid typically being formed right and the acetic conditions prevail. So what happens now? You have this acetic acid in contact with your waste let us say right. So let us say if there were any heavy metals let us say, what would happen to these heavy metals when they come in contact with this acid or acetic acid and such, what would happen now?

So in that context we need some environmental chemistry background. What is that about? We know that typically at higher pH let us say metals precipitate out typically anyway let us say depending on the type of ligand and such. So they are in the solid form or solid phase let us say but as the pH comes down you know depending upon type of metal and such, the metals become soluble let us say.

So what happens now let us say if in the municipal solid waste, my particular heavy metal is in the form of a solid initially and let us say my leachate so you have my solid here, metal and now leachate is formed acetic acid and that starts flowing down let us say and now my leachate comes in contact with this solid now right. So what happens in that particular context here right?

What happens now? As we know from our environmental chemistry background, you know typically anyway as you decrease the particular pH let us say of that particular solution, your equilibrium shifts and the solid phase what do we say or the heavy metal would be in the

aqueous phase and not in the solid phase right. So obviously what does that mean? It means that your heavy metal which was solid and immobile let us say is now in the aqueous phase and more mobile.

So for example, now this leachate after coming in contact with this solid or the solid phase of the heavy metal will now have greater concentrations of heavy metal let us say and that can contaminate your groundwater. For example, if this is your groundwater flow direction let us say and if your leachate collection systems and so on failed or you did not have any particularly leachate collection system let us say.

And now you are going to have contaminated groundwater right, so this is the worst case scenario that TCLP test tries to replicate that is it right. So what are we trying to do? We would replicate the worst possible conditions that would you would come across in a municipal solid waste landfill let us say right. So in that context obviously, I think we have the relevant aspects here.

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So TCLP test, so what is that about? There are two, three aspects that we need to consider here obviously leachate right. So how is that, what is that particular leachate in the municipal solid waste landfill, typically acetic acid after anaerobic digestion. So again here too we consider acetic acid okay acetic acid that is one aspect right. What else now? If the solid size is much bigger let us say compared to this particular case and leachate is in contact let us say. And I have multiple such smaller pieces in which case would I have greater dissolution of the particular solid out transfer of the relevant heavy metal from the solid phase lead to the aqueous phase. In the latter case where I have more surface area right, so the other condition that the TCLP or case that TCLP tries to replicate is the particle size right. Particle size, so typically <9 mm size is what the TCLP test prescribe.

So if your particular waste or the particles have size >9 mm, you need to crush them to a size <9 mm right. Again, we are trying to replicate the worst possible condition right. So and then again we have equilibrium conditions. So equilibrium conditions, so equilibrium and municipal solid waste can be achieved over the course of few months or years and so on let us say but here we are trying to we obviously do not have the time to what do we say wait for a few years or such.

So here we look at accelerated tests or such, so obviously what are we looking at? We are going to look at a particular case of where the solid or your particular waste which you are testing and your leachate replicate here which is the acetic acid combination of liquid which we are going to look at. They are going to be in contact and this particular tumbler is mixed end-over-end right, end-over-end for 18 hours right.

So here what are we trying to replicate? We are trying to replicate the conditions for equilibrium. So again generic aspects, so acetic acid, why do we choose acetic acid because it is what we expect to be formed in your particular municipal waste landfill, particle size smaller particle size.

Why do we need to look at that? Obviously, because the lesser the particle size the greater the surface area and thus the greater the chance of not chance I guess, the greater the kinetics of what is it now changing phase from solid phase to the aqueous phase. Again, its diffusion control typically right and again equilibrium conditions replicated by end-over-end mixing for 18 hours.

So let us move ahead, again what are we looking at test methods, where do we find this particular test? In the test methods for evaluation of solid waste and as we looked at it earlier it is called the test method or it is 1311 right and what do we have? We need to consider the

solid size, the solid size should be <9 mm before you start the test. If it is not, you need to crush it right.

And then you need to have your particular liquid phase and solid phase, again to replicate the worst possible conditions you are going to have 20 ml of your particular liquid to 1 gram of your particular solid let us say. As in, this particular container you need to have the compounds, not compounds pardon me, the relevant leachate or extraction fluid I guess in the ratio of 20 ml of extraction fluid per 1 gram of your particular solid or waste that you are trying to look at I guess.

So what am I going to do? I guess in these proportions, I am going to put in that extracting fluid or that particular liquid in the mixer and also the proportionate amount of your popular waste and I am going to mix that end-over-end continuously let us say for around not around for 20 hours or 24 hours I believe right and after that I am going to let us say look at the particular concentrations of those particular listed compounds anyway in that particular leachate or the extraction fluid.

And what is it that I am trying to replicate obviously? So I am going to presume that any contaminant in that particular solid phase or adsorbed onto that solid let us say would now change phase into the aqueous or into the extraction fluid now right. So any compound or containment that was in either the solid phase or adsorbed onto the solid let us say, we are now going to presume that it is now in the leachate or the extraction fluid.

So once I analyze that particular extraction fluid for those particular heavy metals let us say or different other compounds and if that particular concentration is greater than the particular threshold given in our particular table here as we have let us say.

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•	(1)	(2)	(3)							
	A1	Arsenic	5.0							
	A2	Barium	100.0							
r -	A3	Cadmium	1.0							
	A4	Chromium and/or Chromium (III) compounds	5.0							
	A5	Lead	5.0							
	A6	Manganese	10.0							
	A7	Mercury	0.2							
	A8	Selenium	1.0							
	A9	Silver	5.0							
	A10	Ammonia	50*							
	A11	Cyanide	20*							
	A12	Nitrate (as nitrate-nitrogen)	1000.0							
	A13	Sulphide (as H ₂ S)	5.0							
	A14	1,1-Dichloroethylene	0.7							
	A15	1,2-Dichloroethane	0.5							
	A16	1,4-Dichlorobenzene	7.5							
	A17	2,4,5-Trichlorophenol	400.0							
	A18	2,4,6-Trichlorophenol	2.0							
	A19	2,4-Dinitrotoluene	0.13							
	A20	Benzene	0.5							

For example, let us say I have different compounds here. Let us look at a few examples let us say. I am analyzing for arsenic let us say and let us say my concentration of arsenic in the extraction fluid end up being >5 milligram per liter let us say right after the TCLP test obviously. Then, what do I need to do? Obviously, I need to classify that particular waste upon which I conducted the TCLP to be a hazardous waste.

And then once you classify waste as hazardous waste, there it is obviously a different ballgame and you have different other aspects that you need to look at. Again, in this context, we also need to choose the kind of extraction fluid right. There you cannot just choose acetic acid as in what concentration and so on and for what kinds of compounds for volatile and nonvolatile compounds and so on.

So we are going to look at that in greater detail but since I am out of time, we are going to wrap up today's session and move on to what do we say the relevant aspects in the next session I guess. So again as we wrap up, what have we looked at, we looked at the stochastic and deterministic approaches, we were done with that right and then we moved on to again looking at the relevant law and the relevant aspects in greater detail.

In that context, we do or we need to obviously understand whether a particular waste is hazardous waste or not, why is that, because if it is hazardous waste then you have different set of laws and regulations that deal with its handling, transport and disposal and so on right and how do I go about you know getting to this particular what we say a case let us say of

deciding whether waste can be classified as a hazardous waste, I am going to conduct the TCLP test.

And what does the TCLP test do? It tries to replicate the worst case scenario of the wastes ending up in a municipal landfill and coming in contact with the relevant leachate or a acidified leachate I guess right. So thus we have an extraction fluid of 20 ml to a solid of 1 gram ratio and then put in a particular end-over-end mixer and then equilibrium conditions replicated and end-over-end mixer, why do we have end-over-end mixing?

We are trying to create turbulent conditions so that the particular kinetics of diffusion from the solid phase into the extraction fluid or the particular liquid here or leachate are going to be higher and we assume that the equilibrium is going to be reached I guess right. So here the TCLP test tries to again replicate what would happen or what would be the worst case scenario in the municipal solid waste landfill.

And then you are going to analyze for the particular compounds in that particular extraction fluid and if the concentrations are greater than the thresholds, you would then classify it as hazardous waste. If not, you would obviously not consider that to be hazardous waste I guess right. So I guess with that I am done for today and thank you.