

Basic Environmental Engineering And Pollution Abatement
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Lecture: 18
Sampling And Characterization 3 (Solid Waste And Soil)

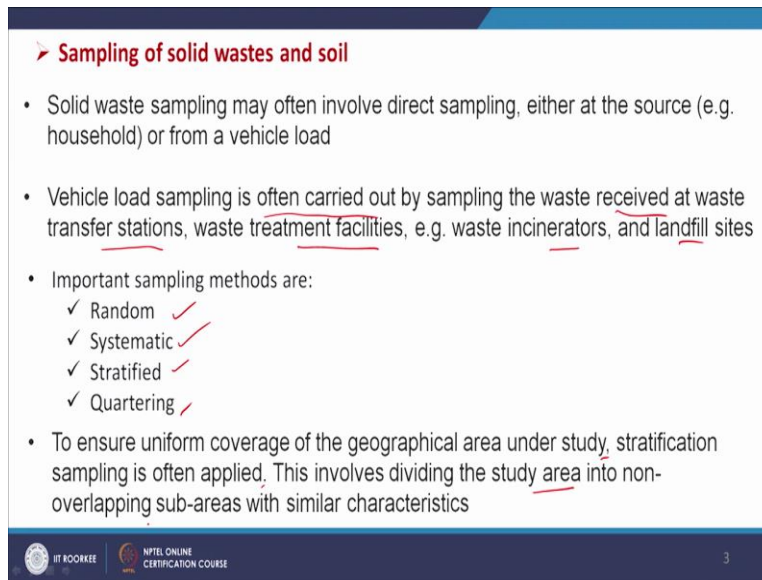
Hello everyone. Now, we will discuss on the topic Sampling and Characterization, Part 3. In this class, we will discuss sampling of solid waste and soil, characterization of solid waste that physical and chemical characteristics of solid waste and the methods for this characterization like see.

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Contents	
➤	Sampling of solid wastes and soil
➤	Characterization of solid wastes
–	Physical ✓
–	Chemical ✓
•	Proximate and ultimate analysis
•	Fusing point of ash ✓
•	Lignocellulosic composition ✓
•	Leaching properties ✓
•	Energy content: Heating value ✓

Proximate and ultimate analysis, Fusing point of ash, Lignocellulosic composition, Leaching properties and Energy content. These are the chemical characteristics.

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➤ **Sampling of solid wastes and soil**

- Solid waste sampling may often involve direct sampling, either at the source (e.g. household) or from a vehicle load
- Vehicle load sampling is often carried out by sampling the waste received at waste transfer stations, waste treatment facilities, e.g. waste incinerators, and landfill sites
- Important sampling methods are:
 - ✓ Random ✓
 - ✓ Systematic ✓
 - ✓ Stratified ✓
 - ✓ Quartering ✓
- To ensure uniform coverage of the geographical area under study, stratification sampling is often applied. This involves dividing the study area into non-overlapping sub-areas with similar characteristics

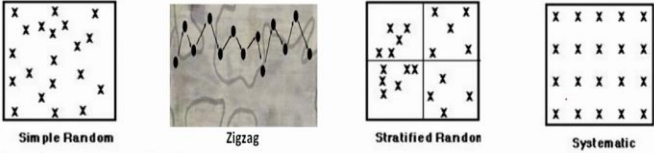
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And first we will see how to sample solid waste or soil samples. So, solid waste sampling may often involve direct sampling, either at the source or from a vehicle load. So, vehicle load sampling is open, carried out by sampling the waste received that waste transfer stations, waste treatment facilities. That is waste incinerators and landfill sites.

Important sampling methods are Random, Systematic, Stratified and Quartering. To ensure uniform coverage of the geographical area under study. Stratification, sampling is often applied this involves dividing the study area into non overlapping sub areas with similar characteristics.

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➤ Sampling of solid wastes and soil contd..




Simple Random Zigzag Stratified Random Systematic

Procedure for sample collection

- Scrap away surface litter.
- Obtain a uniform thick slice of soil from the surface to the plow depth from each place.
- A "V" shape cut to a depth of 15 cm in the sampling spot using the spade to remove 1 to 2 cm slice of soil.
- The sample may be collected on the spade's blade and put in a clean bucket.

• Samples to be mixed thoroughly and foreign materials like roots, stones, pebbles, and gravel to be removed



V shaped method of soil sampling

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If you see, this is say we are going for random sampling. So, this is our collection area or study area. So, for any point randomly we can get the samples. And here zig-zag so, in that way randomly we are taking also so, this is zig-zag nature and stratified sampling means so same area we are interested to get more accurate result or sample.

So, we can divide into four equal non overlapping area and from each area we can collect equal number of samples maybe randomly and if we want to make more accurate, then we can go for systematic sampling. So, equal distance, equal direction like this. So, that way the sampling methods are followed.

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➤ **Sampling of solid wastes and soil contd..**

Random sampling, stratified sampling, and systematic sampling methods are evaluated for precision and efficiency in soil analysis. The procedure for obtaining soil samples varies according to the purpose of sampling.

Random or Zig-Zag sampling

Each soil core is selected separately, randomly, and independently with a simple random system. Suitable for uniform fields. Samples are collected in a zig-zag or random pattern across the field.

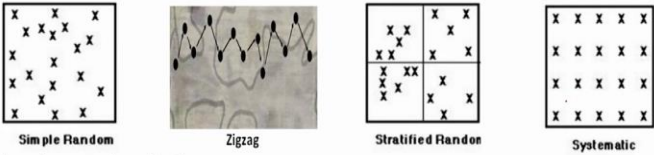
Stratified sampling

A stratified random sample is taken from a field that has been divided into several subunits or quadrants from which simple random samples are obtained.

Systematic sampling

The systematic sample is a further progression to ensure complete field coverage, similar to the change from the simple random to the stratified random. This method takes samples at regularly spaced intervals in all directions.


➤ **Sampling of solid wastes and soil contd..**



Simple Random Zigzag Stratified Random Systematic

Procedure for sample collection

- Scrap away surface litter.
- Obtain a uniform thick slice of soil from the surface to the plow depth from each place.
- A "V" shape cut to a depth of 15 cm in the sampling spot using the spade to remove 1 to 2 cm slice of soil.
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- Samples to be mixed thoroughly and foreign materials like roots, stones, pebbles, and gravel to be removed



V shaped method of soil sampling

So, random sampling, stratified sampling and systematic sampling methods are evaluated for precision and efficiency in soil analysis. The procedure for obtaining soil samples varies according to the purpose of sampling. And for random or zig-zag sampling, each soil core is selected separately randomly and independently with a simple random system.

Suitable for uniform fields, samples are collected in a zig-zag or random pattern across the field. And stratified sampling, a stratified random sample is taken from a field that has been divided into several subunits or quadrants from which random samples are obtained.

The systematic sample is a further progression to ensure complete field coverage similar to the change from the simple random to the stratified random. This method takes samples at regularly spaced intervals in all directions, then how will collect the samples. So, here scrap away surface litter so, surface litter is scrapped away.

And obtain uniform thick slice of soil from the surface to the plow depth from each place. So, here we are collecting. So, every place we will be following the same method. A 'V'-shape cut to a depth of 15 cm depth up to this. Then what we will do in the sampling spot, using the spade to remove 1 to 2 cm slice of soil.

So, one side will be taking the soil say 1 to 2 cm slice of soil. So, this is the soil sampling a typical method the sample may be collected on the spade's blade and put in a clean bucket and the samples to be mixed thoroughly and foreign materials like roots, stones, pebbles and gravel to be removed, because we will be collecting number of samples from different places, then we will mix it.

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➤ **Sampling of solid wastes and soil contd..**

- **Quartering-** Solid Waste is divided into four sections after cutting large pieces and mixing, and two diagonal sections are again mixed. These operations shown in Figure below are done several times.

Repeat several times until MSW weight is 20-30 Kg

PRIMARY SAMPLE FROM REFUSE PITS (M S W ABOUT 250Kg) → MIXING AND CUTTING → A B C D → MIXING → A D → SECONDARY SAMPLE

SEPARATION → B C

Quarter method of soil sampling

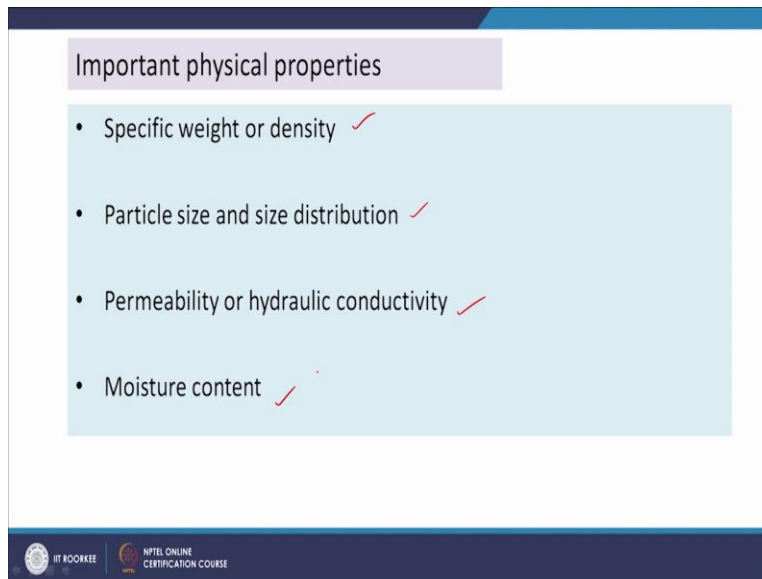
- Finally, samples are collected in a clean cloth or polythene bag.
- For analysis, the soil material is sieved through a 2 mm sieve. To determine the organic matter, it is desirable to grind a representative sub-sample and sieve it through a 0.2 mm sieve.

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And quartering another method is there that is mostly used for solid waste sampling. So, solid waste is divided into four sections after cutting large pieces and mixing and two diagonal sections are again mixed. These operations shown in figure below are done several times. So, we are made four quarter A B C D. So, these diagonals C D and A B will be mixed, again we will follow the same process again will be mixed likewise.

Number of times we will do and we will get the uniform sample that way. So, finally, samples are collected in a clean cloth or polyethylene bag for analysis the soil material is sieved through a 2 mm sieve and to determine the organic matter, it is desirable to grind a representative sub-sample and sieve it through a 0.2 mm sieve. So, these are the methods which are used for the sampling of solid waste and soil.

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The slide is titled "Important physical properties" and lists four key properties, each with a red checkmark to its right:

- Specific weight or density ✓
- Particle size and size distribution ✓
- Permeability or hydraulic conductivity ✓
- Moisture content ✓

At the bottom of the slide, there are two logos: the logo for BIT ROORKEE on the left and the logo for NPTEL ONLINE CERTIFICATION COURSE on the right.

Now, after the collection of samples you have to analyze you have to characterize this. So, for physical property assessment or physical characterization, so, specific weight or density we have seen and then particle size and size distribution, permeability or hydraulic conductivity and moisture content are important and we will discuss how to measure this?

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Specific weight or density

Specific weight/ density is defined as the weight of a material per unit volume (kg/m^3)

There are three densities associated with powders.

Absolute density (also termed the **true or skeletal density**): it excludes the volumes of pores and of the inter particle spaces.

Envelop density (sometimes called the **apparent density**) includes the pore volume but excludes inter particle spaces; and

Bulk density : it includes both pore volume and inter particle spaces. Its value changes with degree of compaction

Condition	Density (kg/m^3)
Loose MSW, no processing or compaction	90-150
In compaction truck	355-530

Measurement of density is done by true density and tap density analyzer (Pycnometer) normally by employing Archimedes' principle of fluid (gas) displacement and the technique of gas expansion.

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So, specific weight a density is defined as the weight of a material per unit volume, we know it very well. And there are three densities associated with the powders. One is absolute density or true or skeletal density and another is, envelop density or apparent density and third one is bulk density.

So, the absolute density it excludes the volumes of pores and of the inter particle spaces of the powder material. And envelop density includes the pore volume, but excludes inter particle spaces and bulk density includes both pore volume and their particle spaces, its value changes with the degree of compaction for example.

Here you see Loose MSW, no processing or compaction, it is densities 90 to 150 kg/m^3 , but if we make the compaction then in compaction truck it is 355 to 530 kg/m^3 , so the density increases. So, measurement of density is done by true density and tap density analyzer normally by employing Archimedes principle of fluid displacement and the technique of gas expansion.

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Particle size and size distribution

Particle size analysis can be done by sieve analysis, Trommels or using particle size analyzer

Sieve analysis ✓

source-
<http://www.ce.memphis.edu/1101/notes/filtration/filtration-2.html>

En.wikipedia.org

Particle size analyzer

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Now particle size distribution is very-very important, because you want to use these waste materials for different applications for recycling, then the performance of the process will be influenced by the particle size of this material. So, this can be done and for this particle size analysis can be done by sieve analysis, trommels or using particle size analyzer depending upon the size of the particles. So, bigger the particles we can go for the trommels intermediate you can go for sieve analysis or smaller and then finer particles you can go for the particle size analyzer.

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Particle size distribution

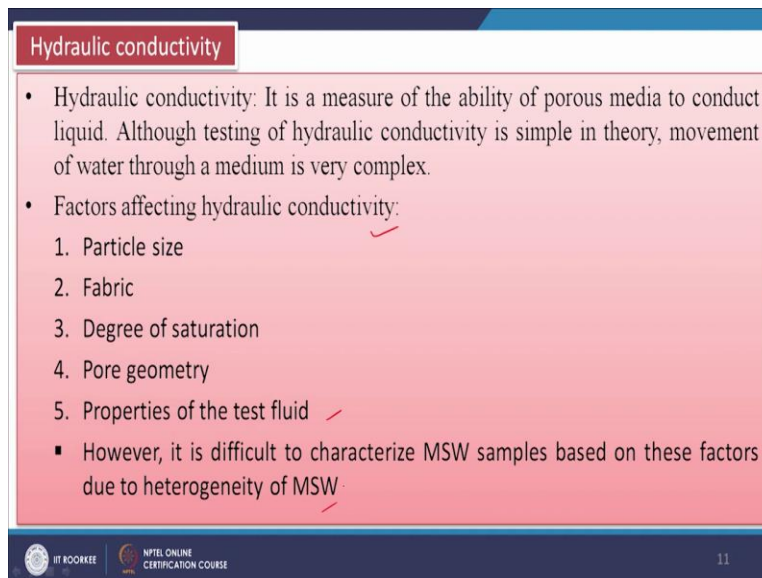
May be differential or cumulative

Average size, mm	Mass fraction
d_{avg1}	$X_1 = X_1 + X_2$
d_{avg2}	$X_2 = X_2 + X_3$
d_{avg3}	$X_3 = X_3 + X_4$
d_{avg4}	$X_4 = X_4 + X_5$
d_{avg5}	X_5

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And when we go for sieve analysis, then there are basically two major ways to represent the experimental data like say average size and mass fraction if we measure, so, that we can express in this way. So, x-axis is diameter and y-axis is cumulative mass fraction. So, we can put cumulative mass fraction so, that way you can get or simply we can put x_1, x_2, x_3, x_4, x_5 like this like trucks and we are having. So, these x_1, x_2, x_3, x_4 we can put it here or as a cumulative we can put it here.

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Hydraulic conductivity

- Hydraulic conductivity: It is a measure of the ability of porous media to conduct liquid. Although testing of hydraulic conductivity is simple in theory, movement of water through a medium is very complex.
- Factors affecting hydraulic conductivity:
 1. Particle size ✓
 2. Fabric
 3. Degree of saturation
 4. Pore geometry
 5. Properties of the test fluid ✓
 - However, it is difficult to characterize MSW samples based on these factors due to heterogeneity of MSW ✓


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Now, hydraulic conductivity, so, hydraulic conductivity, it is a measure of the ability of porous media to conduct liquid. Although testing of hydraulic conductivity is simple in theory, movement of water through a medium is very complex. Factors affecting hydraulic conductivity are particle size, fabric, degree of saturation, pore geometry and properties of the taste fluid. However, it is difficult to characterize MSW samples based on these factors due to heterogeneity of MSW municipal solid waste is heterogeneous and that is a major problem for these also.

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Moisture content

- The moisture in a sample is expressed as percentage of the wet weight of the MSW material
- It is determined by using hot air oven, where the material is heated at 105°C till constant weight is achieved.
- It is calculated by following formula:
$$\text{Percentage moisture} = \frac{\text{Loss in weight}}{\text{Weight of material taken}} \times 100$$



Globetrek engineering Corporation
Available at - commons.wikimedia.org

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Next, we will see the moisture content measurement. The moisture in a sample is expressed as percentage of the wet weight of the MSW material. It is determined by using hot air oven, where the material is heated at 105 °C till constant weight is achieved. And it is calculated with the following formula

$$\text{Percentage moisture} = \frac{\text{Loss in weight}}{\text{Weight of material taken}} * 100$$

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Chemical properties of MSW

- Proximate analysis: moisture, volatiles, ash and fixed carbon
- Ultimate analysis: C, H, N and O
- Fusing point of ash
- Lignocellulosic composition
- Leaching properties (applicable to Hazardous waste fraction in MSW waste):
- Energy content: Heating value

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Now we are going to discuss about the characterization of chemical properties or the analysis of chemical properties like proximate analysis, which includes the moisture volatiles matter ash content and fixed carbon in a sample. Ultimate analysis that gives us C, H, N, S carbon hydrogen, nitrogen, sulfur and oxygen and fusing point of ash, lignocellulosic composition and leaching property applicable to hazardous waste fractions in MSW waste. And then energy content or heating value that we are going to discuss one by one.

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Proximate analysis

- **Moisture:** Loss in weight of sample due to drying at 105°C for 24h ✓
- **Volatile matter:** Loss in weight of moisture free sample ignite in muffle furnace at 950 °C for 7 minutes in the absence of oxygen in an close crucible ✓
- **Ash:** weight of residue left after combustion of dry sample in muffle furnace at 750 °C for half an hour in the presence of oxygen in an open crucible ✓
- **Fixed carbon:** Obtained by subtracting moisture, volatile matter and ash percent from 100. ✓

Types of waste	Moisture (%)	Volatiles (%)	Fixed Carbon (%)	Ash (%)
Mixed food ✓	70.0	21.4	3.6	5.0
Mixed paper ✓	10.2	75.9	8.4	5.4
Mixed plastics ✓	0.2	95.8	2.0	2.0
Yard waste ✓	60.0	42.3	7.3	0.4
Residential MSW ✓	21.0	52.0	7.0	20.0

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Ultimate analysis

Ultimate analysis or elemental analysis (CHNS) is determined by the CHNS analyzer

- The principle of CHNS analyzer depends on the tendency that all atoms prefer to be in their oxidation states. In presence of pure oxygen and high temperatures of 990°C, all carbon easily burn to become carbon dioxide, all hydrogen burn to become water and all nitrogen become N₂ gas/various nitric oxides.
- For analysis product gas mixture flows through a silica tube packed with copper granules. This zone held at about 500°C remaining oxygen is bound and nitric/nitrous oxides are reduced. The leaving gas stream includes the analytically important species CO₂, H₂O and N₂. Eventually SO₂ is absorbed at appropriate traps.

```

graph LR
    Sample[Sample] --> Combustion[Combustion]
    Carrier[carrier gas] --> Combustion
    Combustion --> Reduction[Reduction]
    Reduction --> Mixing[Mixing]
    Mixing --> Separation[Separation]
    Separation --> Detection[Detection]
  
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Show proximate analysis. So, moisture determination already we have discussed how to do it. So, that is lost in weight of sample due to drying at 105 °C for 24 hour.

And then for volatile matter so, this is the loss in weight of moisture free sample ignited in muffle furnace at 950 °C for 7 minutes in the absence of oxygen in an close crucible. That means, after the removal of the moisture, we will be taking the sample and then hit it at 950 °C for 7 minutes in absence of oxygen.

Then the vapors will be goes off that is the volatiles materials will go off. And then we will measure how much mass is remaining so, that we will calculate the percentage of the volatile matter. And for the determination of ash content, weight of residue left after combustion of dry sample in muffle furnace at 750 °C for half an hour in the presence of oxygen in an open crucible.

So, what we are getting the residue which is remaining after the volatile matter determination, we can hit it at 750 °C in the presence of oxygen. So, then also its mass will be reduced and some amount will be residual. So, that will be the basically ash content, and fixed carbon we will be measuring by getting the difference.

So, 100 – moisture content – volatile matter content – ash content. Now, some example is given a, different types of waste materials, mixed food, mixed paper, mixed plastics, yard waste and residential MSW. So typical moisture content, values is shown here.

Typical volatiles are given here, fixed carbon content, are also given typically, ash content also are provided. So, these are some typical example of different types of waste materials. Now ultimate analysis. So, ultimate analysis or elemental analysis or CHNS analysis is determined by the CHNS analyzer.

So, the principal of CHNS analyzer depends on the tendency that all atoms prefer to be in their oxidation states. In presence of pure oxygen and high temperatures of 990 °C, all carbon easily burn to become carbon dioxide, all hydrogen burn to become H₂O and all nitrogen becomes into gas or various nitric oxides.

So, nitrogen is converted to NO_x, for analysis product gas mixture flows through a silica tube packed with copper granules. This zone held at about 550 °C, remaining oxygen is bound and nitric nitrous oxides are reduced.

The leaving gas stream includes the analytically important species CO_2 , H_2O , N_2 . Eventually SO_2 is absorbed at appropriate traps. So basic concept is that we need to apply excess heat and then to convert it into the oxides of the different elements like CO_2 , H_2O , SO_2 etc., and then reduction of NO_x to nitrogen again and separate the SO_2 and analyze it.

So, sample and carrier gas combustion will take place, then reduction for NO_x to nitrogen and then it will be mixing and then separation. So, after separation you will get the detection.

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Ultimate analysis

➤ High purity helium is used as carrier gas. Finally the gas mixture is brought to a defined pressure/volume state and is passed to a gas chromatographic system. Separation of the species is done by so called zone chromatography. In this technique a staircase type signal is found. Step height is proportional to the substance amount in the mixture.

Type	C	H	O	N	S	Ash
Mixed food ✓	73.0	11.5	14.8	0.4	0.1	0.2
Mixed paper ✓	43.3	5.8	44.3	0.3	0.2	6.0
Mixed plastic ✓	60.0	7.2	22.8	-	-	10.0
Yard waste ✓	46.0	6.0	38.0	3.4	0.3	6.3
Refused Derived Fuel (RDF) ✓	44.7	6.2	38.4	0.7	>0.1	9.9

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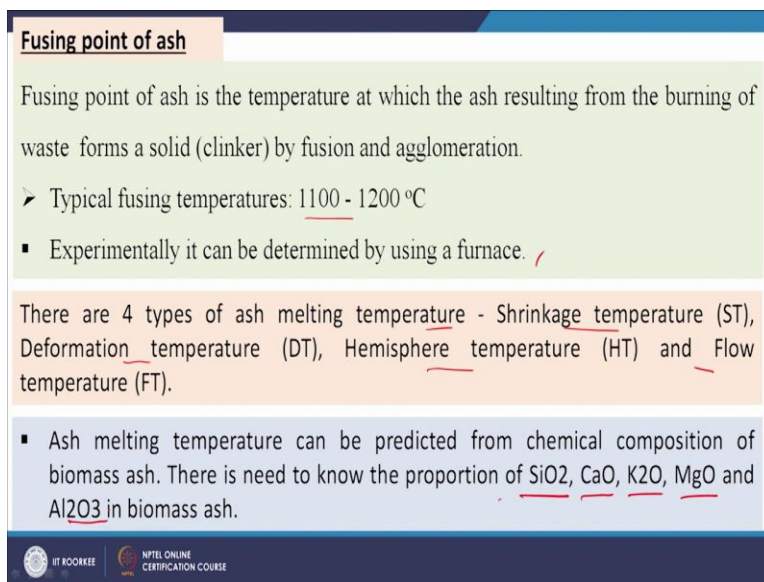
So, just like gas chromatography which we have discussed, so, on gas chromatography is used for gas analyzer also termed it is so in the same principle of gas chromatography. So, in this case depending upon the detention time different oxides like say CO_2 , H_2O , SO_2 and N_2 which is reduced the NO_x which is reduced.

They will be coming out from the column capillary at different time intervals and as NO_x is reduced to nitrogen, prior to its analysis. So, nitrogen will have no interactions it is inert gas so it will very quickly coming out it will come out very fast and we will get the peak of nitrogen as the first step.

And then carbon dioxide will come out and then H_2O will come out and then SO_2 will come out and will be able to identify these gas components. And also we will be able to determine the concentration of these gas components by calibration with some known samples.

So, high purity helium is used as carrier gas finally, the gas mixture is brought to a defined pressure, a volume state and is passed to a gas chromatographic system. Separation of the species is done by so called zone chromatography. In this technique, a staircase type signal is found. So, step height is proportional to the substance amount in the mixture. And some typical example you see say mixed food, mixed paper, mixed plastic, yard waste and refused derived fuel. So, carbon, hydrogen, oxygen, nitrogen, sulfur and ash content are provided here.

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Fusing point of ash

Fusing point of ash is the temperature at which the ash resulting from the burning of waste forms a solid (clinker) by fusion and agglomeration.

- Typical fusing temperatures: 1100 - 1200 °C
- Experimentally it can be determined by using a furnace. ✓

There are 4 types of ash melting temperature - Shrinkage temperature (ST), Deformation temperature (DT), Hemisphere temperature (HT) and Flow temperature (FT).

- Ash melting temperature can be predicted from chemical composition of biomass ash. There is need to know the proportion of SiO_2 , CaO , K_2O , MgO and Al_2O_3 in biomass ash.

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Now, we will discuss fusing point of ash. So, fusing point of ash is the temperature at which the ash resulting from the burning of waste forms a solid or clinker by fusion and agglomeration, the typical fusing temperature is 1100 to 1200 °C. Experimentally it can be determined by fusing by using a furnace.

So, there are 4 types of ash melting temperature, if we apply heat to the ash, then initially after a certain temperature, it will shrinkage and that is shrinkage temperature then it will deform. So, that is deformation temperature further reading or more temperature. So, we can get a hemispherical form that is hemisphere temperature.

And further reading and then we can see the flow of the ash so, that is called flow temperature. So, these different types of temperatures are phenomena we can see by the application of heat on the ash. And ash melting temperature can be predicted from chemical composition of biomass ash.

There is a need to know the composition of SiO₂, CaO, K₂O, MgO and Al₂O₃ in biomass ash there is an empirical relationship that can be used to determine the ash fusion temperature of the ash.

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Analysis of cellulose, hemicellulose lignin and extractives

➤ For determination of **extractives**, dried sample (m_0 , g) is leached with benzene and ethanol mixture with volume ratio of 2:1 at a fixed temperature for 3 h. After leaching the residue is dried in hot air oven at 105°C to a constant weight. Then the dried sample is cooled in a desiccator and weighted (m_1 , g). The mass percent extractive (W_1) is:

$$W_1 = \frac{m_0 - m_1}{m_0} \times 100$$

Fuel Processing Technology 85 (2004) 1201 – 1211

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Now, we will discuss analysis of cellulose, hemicellulose, lignin and extractives in the lignocellulosic biomass. So, for the determination of this at first we determine the extractives and basically, some solvent is used that is benzene and ethanol mixture and the sample is taken into this.

And then after vigorous mixing with volume ratio of 2:1 and a fixed temperature for 3 hour. After leaching the residue is dried in hot air oven at 105 °C to a constant weight. Then the dried sample is cooled in a desiccator and weighted that is m_1 we are getting. So, the mass percent extractive is W_1

$$W_1 = \frac{m_0 - m_1}{m_0} * 100$$

So, when we are using the solvent, the volatiles will come into the solvent, then we are vaporizing the solvent and then the remaining will be the mass and what mass we are losing. So, that will be the mass loss due to the volatile matter and that $[(m_0 - m_1)/m_0] * 100$ will be the percentage of the volatiles.

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➤ For determination of **hemicellulose** the residue m_1 after extractive is put in a flask with 150 ml NaOH solution (20g/l). Then the mixture is boiled for 3.5 h with recycled distilled water. After that the residue is washed with distilled water till no sodium ion present in wash liquor and dried it to a constant weight. The dried sample is cooled in a desiccator and weighted (m_2 , g). The mass percent of hemicellulose (W_2) is:

$$W_2 = \frac{m_1 - m_2}{m_o} \times 100$$

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Then for the determination of hemicelluloses, so, after the determination of extractives the remaining material, will treating or will react it with anyway solution and that is 150 ml NaOH solution 20 g/L. Then the mixture is boiled with 3.5 hour with recycle distilled water. After that the residue is washed with distilled water till no sodium ion present in wash liquor and dried it to a constant weight. The dried sample is cooled in a desiccator and weighted that is m_2 gram the mass percent of hemicellulose W_2

$$W_2 = \frac{m_1 - m_2}{m_o} * 100$$

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➤ For determination of **lignin** about 1g of residue after extractive analysis is dried to a constant weight. Then the sample is cooled and weighted (m_3 , g). After that the sample is mixed with 30 ml sulfuric acid of 72 percent (v/v) concentration and kept at 8-15°C for 24 h. The mixture is diluted with 300 ml of distilled water and boiled for 1h with recycled distilled water. After cooling and filtration the residue is washed with distilled water till no sulfate ion present in liquor, which is detected by 10% barium chloride solution. Then the residue is dried to a constant weight and cooled in a desiccator and weighted (m_4 , g). The mass percent of lignin

$$(W_3) \text{ is : } W_3 = \frac{m_4(1-W_1)}{m_3} \times 100$$

➤ **Determination of cellulose** The mass percent cellulose (W_4) was calculated as per equation

$$W_4 = 100 - (W_1 + W_2 + W_3)$$

Fuel Processing Technology 85 (2004) 1201 - 1211



So, then we will see the lignin concentration and for that, about 1 gram of residue after extractive analysis is dried to a constant weight. Then the sample is cooled and weighted there is m_3 gram after that the sample is mixed with 30 ml sulfuric acid of 72 percent concentration and kept at 8 to 15 °C for 24 hour.

The mixture is diluted with 300 ml of distilled water and boiled for 1 hour with recycled distilled water. After cooling and filtration, the residue is washed with distilled water till no sulfate ion present in liquor which is detected by 10% barium chloride solution. Then the residue is dried to a constant weight and cooled in a desiccator and weighted m_4 gram the mass percent of lignin W_3

$$W_3 = \frac{m_4(1 - W_1)}{m_3} * 100$$

So, we can calculate the percentage of cellulose by difference that is

$$W_4 = 100 - (W_1 + W_2 + W_3)$$

So, that can be calculated like this. So, W_1 , W_2 , W_3 extractive hemicellulose and lignin.

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Leaching test (*Toxicity Characteristic Leaching Procedure* or *TCLP*)

The *TCLP* mimics conditions found in landfills when groundwater percolates through buried materials.

The *TCLP* is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphase wastes.

8 Heavy Metals

- ❖ Arsenic
- ❖ Barium
- ❖ Cadmium
- ❖ Chromium
- ❖ Lead
- ❖ Mercury
- ❖ Selenium
- ❖ Silver

12 Organic Solvents

- ❖ Benzene
- ❖ Carbon tetrachloride
- ❖ 2,4-dinitrotoluene
- ❖ Hexachloroethane
- ❖ Methyl ethyl ketone
- ❖ Nitrobenzene
- ❖ Tetrachloroethylene
- ❖ Trichloroethylene
- ❖ Pyridine
- ❖ Chloroform
- ❖ Vinyl chloride
- ❖ Cresol(s)



Leaching test (*Toxicity Characteristic Leaching Procedure* or *TCLP*)

17 Pesticides

- ❖ Chlordane
- ❖ 2,4-Dichlorophenoxyacetic acid
- ❖ Chlorobenzene
- ❖ 1,4-dichlorobenzene
- ❖ 1,2-dichloroethane
- ❖ 1,1-dichloroethylene
- ❖ Endrin
- ❖ Heptachlor

- ❖ Hexachlorobenzene
- ❖ Lindane
- ❖ Hexachlorobutadiene
- ❖ Methoxychloro
- ❖ Pentachlorophenol
- ❖ Toxaphene
- ❖ 2,4,5-trichlorophenol
- ❖ 2,4,6-trichlorophenol
- ❖ 2,4,5-TP (Silvex)



Now we will discuss about the leaching test that is *TCLP* toxicity characteristic leaching Protocol, or *TCLP*. This mimics conditions found in landfills when groundwater percolates through buried materials. So, we will be generating some synthetic solution, and then we will be putting the waste material in it.

And we will be providing some seeking arrangement and for certain time. So, that the leaching will take place and we will see the concentration of the pollutants in the solvent.


So, the TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphase wastes. So, different heavy metals as shown here. So, heavy metals, organic solvents, different organic solvents, as shown here.

Arsenic, Barium, Cadmium, Chromium, Lead, Mercury, Selenium, Silver here Benzene, Carbon tetrachloride, 2,4-dinitrotoluene, Hexachloroethane, Methyl ethyl ketone, Nitrobenzene, Tetrachloroethylene, Trichloroethylene, Pyridine, Chloroform, Vinyl chloride, Cresol. These are the different pesticides as mentioned here, those can also be tested for leaching purpose.

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- **Agitation apparatus:** Capable of rotating the extraction vessel at 30 ± 2 rpm
- **Extraction vessel:**

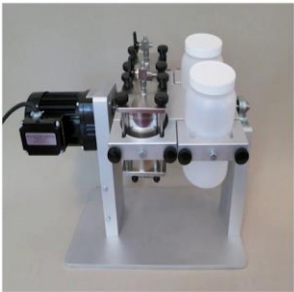
Zero-Headspace Extraction Vessel (ZHE):
This device is for use only when the waste is being tested for the mobility of volatile analytes like Acetone, Benzene, n-Butyl alcohol, Carbon disulfide, Carbon tetrachloride, Chlorobenzene, Chloroform etc.



With permission from Analytical testing corp
available at (<http://www.tclp-equipment.com/zero.htm>)

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Bottle Extraction Vessel: When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.



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available at-<http://www.tclp-equipment.com/zero.htm>

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And for this we have two types of apparatus and two types of solvent also. So, one apparatus is Zero-Headspace Extraction Vessel. So, Zero-Headspace, we are not providing any headspace particularly when we are interested to get the extraction properties or the leaching properties of the components which can be easily vaporized in that case we will be using this type of setup.

So, this device is for use only when the waste is being tested for the mobility of volatile analytes like Acetone, Benzene, n-Butyl alcohol, Carbon disulfide, Carbon tetrachloride, Carbobenzene, Chloroform, Chlorobenzene, Chloroform, etc.

And Bottle Extraction Vessel in this case we do not have any headspace when the waste is being in this case. We have headspace when the waste is being evaluated using them nonvolatile extraction a jar with significant capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel. So, this is the photographs, then will be giving some rotation it maybe horizontally or maybe shafts maybe vertically. So, that can be done.

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Reagents and extraction fluids

- Reagent grade chemicals shall be used in all tests
- **Reagent Water:** Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest.
- **Extraction fluid:**
 - Extraction Fluid (1):** 5.7 mL glacial acetic acid (CH_3COOH) is added to 500 mL of reagent water, added with 64.3 mL of 1N NaOH, and diluted to a volume of 1 liter. When correctly prepared, the pH of this fluid becomes $4.93 + 0.05$.
 - Extraction fluid (2):** 5.7 mL glacial acetic acid (CH_3COOH) is added with reagent water to a volume of 1 liter. When correctly prepared, the pH of this fluid is $2.88 + 0.05$.

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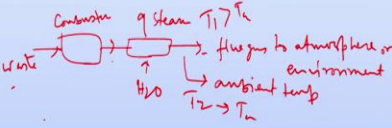
And as I mentioned, so, two types of solvent we can get that is with relatively higher pH and relatively lower pH. So, extraction fluid 1 that is pH is $4.93 + 0.05$ and in this case $2.88 + 0.05$. So, lower pH. So, in this case pH increased by addition of NaOH and basically the glacial acetic acid is used to get this 2.88 pH. So, 5.7 mL glacial acetic acid is added with reagent water to a volume of 1 liter.

When correctly prepared the pH of this fluid is $2.88 + 0.05$. And in this case 5.7 mL glacial acetic acid is added to 500 ml of reagent water added with 64.3 ml of 1N NaOH and diluted to a volume of 1 liter. When correctly prepared the pH of this fluid becomes $4.93 + 0.05$. All reagent used will be certainly analytical grade.

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Heating value determination

- **Heating value** (or calorific value) of a substance, is the amount of heat released during the combustion of a specified amount of it. It is measured in units of energy per unit of the substance, usually mass, such as: kJ/kg, kJ/mol, kcal/kg, Btu/lb.
- Heating value unit conversions:
 $\text{kcal/kg} = \text{MJ/kg} \times 238.846$
- **Higher heating value (HHV) or Gross calorific value (GCV):** is determined by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any vapour produced. Such measurements often use a standard temperature of 15 °C (59 °F; 288 K).



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Now, we will discuss heating value. So, heating value when we are talking about the waste material so, if we combust this waste material, then it will be converted to flue gas. So, flue gas will be having high temperature. So, when we will use this flue gas to generate steam so, then the heat available in the flue gas will be converted to the steam.

And the heating value is defined is the amount of heat released by the combustion of unit mass of the material. So by knowing the amount of heat released and how much material has been used, we can calculate the heating value. So, heating value of a substance is the amount of heat released during the combustion of a specified amount of it.

It is measured in units of energy per unit of the substance usually mass such as kJ/kg, kJ/mole, kcal/kg, Btu/lb and heating value unit conversion is also there. So, that kcal/kg to MJ/kg*238.846 so, in that case, we have to use this conversion factor. And we know there is two types of heating value one is high heating value and another is low heating value and high heating value is also called gross heating value and low heating below is also called net heating value.

So, how can we explain these and how can we determine, how can we explain these say we have a waste sample we are combusting it here then flue gases coming out. So, flue gas we are using some water so, it is converted to steam so, this is our waste this is your combustor. So, then this

is our high temperature flue gas it is coming water is converted to steam and then this is going as flue gas to atmosphere or environment.

Now, if we have certain amount of material then heat is generated here then after changing the heat transferring the heat if the flue gas temperature here it is come down to ambient temperature which we had here at the start up the reaction the same temperature then we can assume how much heat was available here that is completely recovered in this tape.

But, if this flue gas is getting into the environment at higher temperature, so, this is your T_1 and this is T_2 . So, T_2 is your ambient temperature T_a and if T_1 is greater than T_a in that case, some amount of energy is already associated with this flue gas which is coming into the environment and we are not able to take that heat out from it for our useful application.

So, in this case, when we are able to extract the energy available in the flue gas, which are generated to the combustion of the materials then that heating value per 1 unit of this waste material will be higher than this value. So, this is called high heating value. So, high heating value is determined by bringing all the products of the combustion back to the original pre combustion temperature.

And in particular condensing any vapor produced such measurements often use a standard temperature of 15 °C that we are talking about that this is our standard how much temperature was there.

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Lower heating value (LHV or LCV) or Net calorific value (NCV): is determined by subtracting the heat of vaporization of the water vapour from the higher heating value. This treats any H₂O formed as a vapour. The energy required to vaporize the water therefore is not released as heat.

A common method of relating HHV to LHV is:

$$\text{HHV} = \text{LHV} + H_v(n_{\text{H}_2\text{O, out}} / n, \text{fuel})$$

Where
 H_v = Heat of vaporization of water
 $n_{\text{H}_2\text{O, out}}$ = moles of water vaporised
 n, fuel = number of moles of fuel combusted

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Heating value determination

- **Heating value** (or calorific value) of a substance, is the amount of heat released during the combustion of a specified amount of it. It is measured in units of energy per unit of the substance, usually mass, such as: kJ/kg, kJ/mol, kcal/kg, Btu/lb.
- Heating value unit conversions:
 $\text{kcal/kg} = \text{MJ/kg} \times 238.846$
- **Higher heating value (HHV) or Gross calorific value (GCV):** is determined by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any vapour produced. Such measurements often use a standard temperature of 15 °C (59 °F; 288 K).

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And lower heating value is determined by subtracting the heat of vaporization of the water vapor from the higher heating value. This treats H₂O formed as a vapor, the energy required to vaporize the water therefore, is not released as heat. So, in this case, this temperature is higher say 100 °C.

So, if this temperature is 500 °C or 600 °C here I am getting say 150 °C. So, this amount of, we are losing some amount of energy here and water which was produced here due to the combustion that is available in steam form.

But here if it is condensed its temperature is ambient temperature that water will be condensed. So, that will be basically the difference in this high heating value and low heating value. A common method of relating HHV to LHV is

$$\text{HHV} = \text{LHV} + H_v(n\text{H}_2\text{O out}/n, \text{fuel}).$$

So, H_v is the heat of vaporization of water and $n\text{H}_2\text{O out}$ is the moles of water vaporized and n is the fuel that is equal to number of moles of fuel combusted. So, how many moles of fuel is combusted and how many moles of water is produced by the combustion of this 1 mole of fuel multiply it with the latent heat of vaporization of water then we add it with the LHV that will be HHV.

Because we are assuming that the moisture which you are generated that is in steam form it is not condensed. So, that energy additional here we are not able to take it out. So, if we add with this energy with this LHV so we will get the HHV so, after this in this class. Thank you very much for your patience.