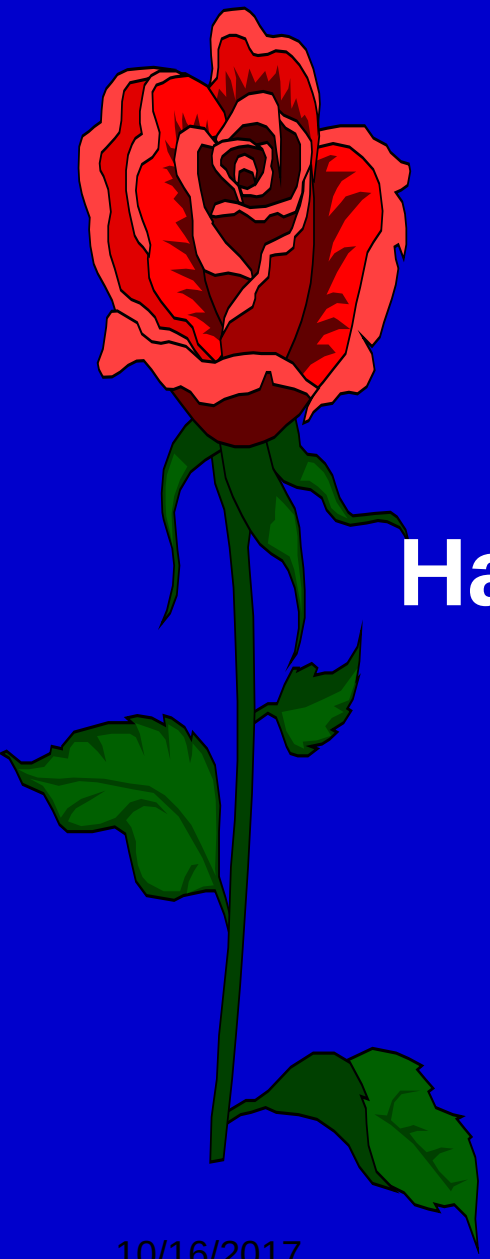


Hazardous Waste Management

By
N. RAMADOSS

INTRODUCTION

- **Hazardous Waste Management**
  - **Solid Waste Management**
  - **Plastic Waste Management**
  - **E-Waste Management**
  - **Bio-Medical Waste Management**
  - **Construction and Demolition Waste Management**

HAZARDOUS WASTE

HAZARDOUS WASTE

Minamata Disaster
Mercury - Water Contamination
WATER POLLUTION

1956

LOVE CANAL
Illegal Hazardous Waste Dump

The Love Canal Story

- Love Canal was a waterway built in the 1800s next to Niagara Falls, NY.
- Hooker Chemical Company purchased the site and used it for a chemical dump 1942-53.
- Site was sold to local gov't for $1. A housing development and school were constructed on the site in the 70s.
- Chemicals began seeping into basements.
- Housewife and resident Lois Gibbs brought problems to national attention in 1977.
- Some families moved right away, some cleanup done.

The Love Canal Story

- Of remaining families, miscarriage rate 50% higher than normal.
- Of 17 pregnancies in 1979, 2 normal, 9 had birth defects, 2 still born, 4 miscarriages.
- In adults tested, nerve impulses slower, 30% had broken chromosomes.
- 1980, government relocated everybody, started massive cleanup.
- 1990 cleanup done, new development called Black Creek Village opened. Houses cheap.

BHOPAL
MIC Gas Leak
AIR POLLUTION

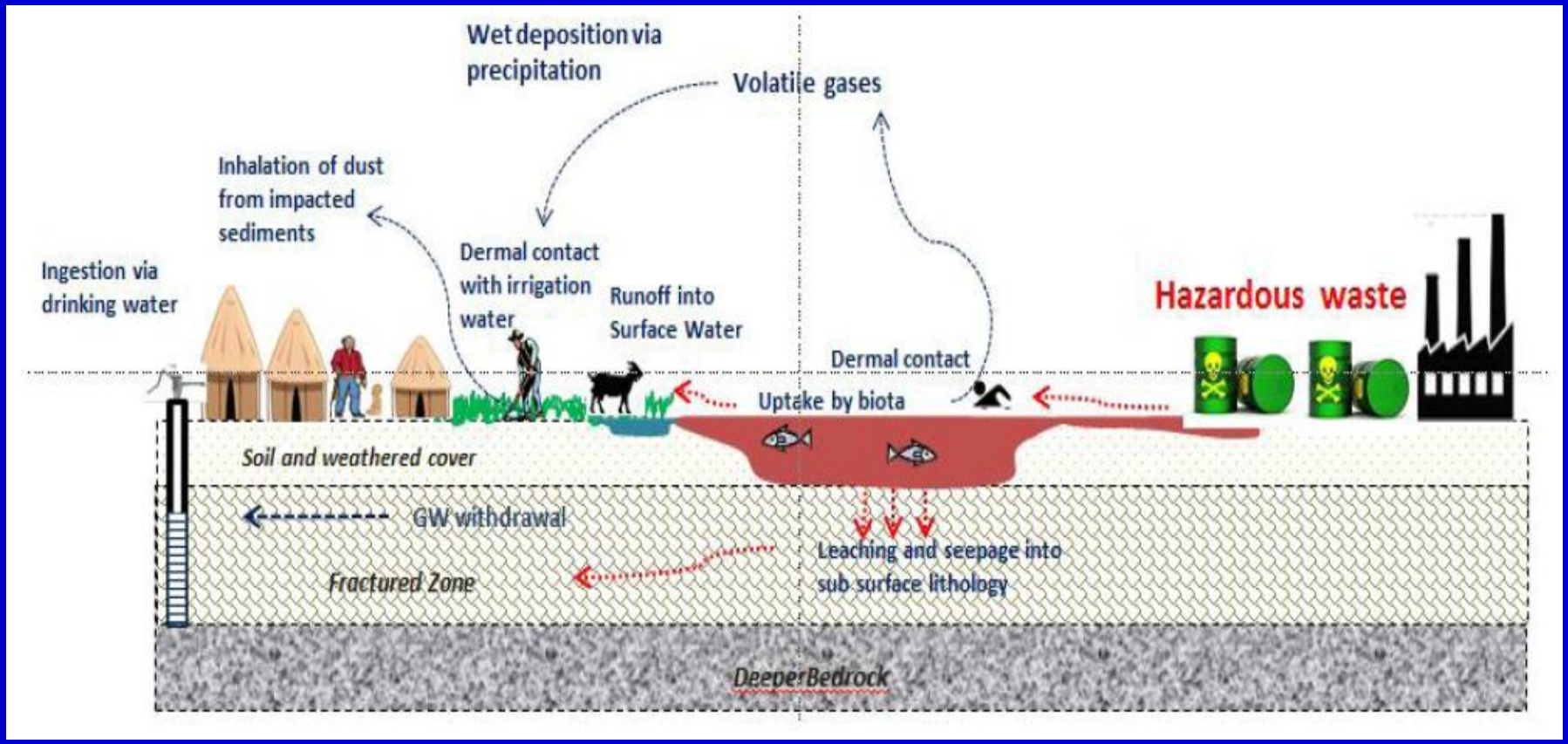
CHERNOBYL
Radiation pollution

MARINE POLLUTION

Waste

Any activity will generate waste
Nature's ability to use waste
Human's basic requirements

EFFECTS OF WASTE DISPOSAL



TYPES OF WASTES

- Industrial Wastes
  - Hazardous Waste
  - Non hazardous waste
  - Bio medical waste
- Plastic waste
- E-waste
- Construction and Demolition waste
- Solid waste Management

LEGISLATION ON WASTE MANAGEMENT

- The HW (Management, Handling & Trans-boundary Movement) Rules, 2008. Original Rules came in 1989, which were amended in 2000, 2003, 2008, 2010, and 2016
- Solid waste Management Rules 2016
- Plastic Waste Management Rules, 2016.
- Construction and Demolition waste rules
- E-Waste (Management and Handling), Rules, 2016
- The Bio-Medical Waste (Management & Handling) Rules, 1998,2003 and 2016

Identification and Characterization of hazardous wastes

Definitions

- "waste" means materials has no further use for the purposes of production, transformation or consumption.
- Explanation.- for the purposes of this clause,
- (i) waste includes the materials that may be generated during, the extraction of raw materials, the processing of raw materials into intermediates and final products, the consumption of final products, and through other human activities and excludes residuals recycled or reused at the place of generation; and
- (ii) by-product means a material that is not intended to be produced but gets produced in the production process of intended product and is used as such

Definitions

- "**hazardous waste**" means any waste which by reason of characteristics such as physical, chemical, biological, reactive, toxic, flammable, explosive or corrosive, causes danger or is likely to cause danger to health or environment, whether alone or in contact with other wastes or substances, and shall include
- (i) waste specified under column (3) of Schedule I;**(PROCESSES)**
- (ii) waste having equal to or more than the **concentration limits** specified for the constituents in class A and class B of Schedule II or any of the **characteristics** as specified in class C of Schedule II; and
- (iii) wastes specified in Part A of Schedule III in respect of import or export of such wastes or the wastes not specified in Part A but exhibit hazardous characteristics specified in Part C of Schedule III;

An Example of Schedule 1, HWM Rules, 2016

Schedule I

[See rules 3 (1)]

List of processes generating hazardous wastes

S.No.	Processes	Hazardous Waste *
1.	Petrochemical processes and pyrolytic operations	1.1 Furnace/reactor residue and debris 1.2 Tarry residues 1.3 Oily sludge emulsion 1.4 Organic residues 1.5 Residues from alkali wash of fuels 1.6 Still bottoms from distillation process 1.7 Spent catalyst and molecular sieves 1.8 Slop oil from wastewater

CLASS C : Based on hazardous Characteristics

- **Class C1: Flammable**
- **Class C2: Corrosive**
- **Class C3: Reactive or explosive-**
- **Class C4: Toxic**
- **Class C5: Substances or Wastes liable to spontaneous combustion**
- **Class C6: Substances or Wastes which, in contact with water emit flammable gases-**
- **Class C5: Oxidizing**
- **Class C8: Organic Peroxides**
- **Class C9: Poisons (acute)**
- **Class C10: Infectious substances**
- **Class C11: Liberation of toxic gases in contact with air or water**
- **Class C12: Eco-toxic**
- **Class C13: Capable,** by any means, after disposal, of yielding another material, e.g., leachate, which possesses any of the characteristics listed above

Waste Properties?

Hazardous waste is a solid/semisolid/liquid waste which because of its quantity and characteristics may pose a substantial hazard to human health or the environment when improperly treated, stored, disposed off or managed.

A hazardous waste can be defined by one or more of the following characteristics:

- Ignitability
- Corrosivity
- Reactivity
- Toxicity

What is Hazardous Waste

- Any waste that has the following characteristics:
  - Ignitable
  - Corrosive
  - Reactive
  - Toxic
- Characteristics of waste

Ignitability

A waste is considered ignitable if:

- Its flashpoint is < 60º C
- It is an oxidizer
- It is a non-aqueous liquid capable of fire through friction, absorption of moisture or spontaneous chemical change.

Characteristics of a Waste

- **Ignitable**

  Flash point < 60º

  <u>Examples:</u>

  Acetonitrile, alcohols, acetone, toluene, xylene, ether, other

Characteristics of a Waste

- **Corrosive**

  pH $\leq$ 2.0 or pH $\geq$ 12.5

  Examples:

  Acids, glass cleaner, hydroxides, bases, drain cleaners, other

Reactivity

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A waste is reactive if:

- It is capable of creating toxic gases when mixed with water
- It forms explosive mixtures with water
- It is cyanide or sulfide bearing
- It reacts violently with water
- It is normally unstable
- It is capable of detonation

Characteristics of a Waste

- **Reactive**

  Unstable and may explode under certain conditions such as heat, friction or pressure

  <u>Examples:</u>

  Picric acid, peroxide forming chemicals, ethyl ethers, dinitro compounds, other

Characteristics of a waste

- **Toxic**

  Fails Toxic Characteristic Leaching Procedure (TCLP) Test

  <u>Examples:</u>

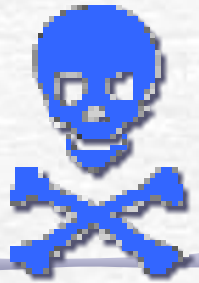
  Heavy metals: mercury, lead, silver, chromic acid, other

Toxicity

A waste is considered toxic if:

It contains –

- toxic heavy metals (such as arsenic, barium, cadmium, chromium (VI), lead, mercury, selenium etc.)
- pesticides (DDT, BHC, Heptachlor, Endrine, 2-4D etc.)
- chlorinated & non-chlorinated organics (benzene, chlorobenzene, chloroform, cresol, carbon tetrachloride, PAHs, Chlordane etc.)
- toxic inorganic compounds (cyanides, asbestos, halogens etc.)



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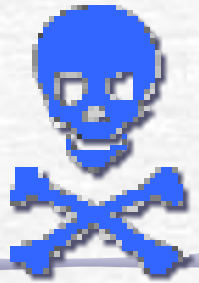


Major Sources of Hazardous Wastes

- Chemical Industries (organic, inorganic, petroleum, petrochemical, pesticides, fertilizers, paint, dye & dye intermediates, pharmaceuticals)
- Minerals & Metallurgical Industries (smelters, foundries, ore dressing, electroplating, metal surface treatment)
- Other Industries (asbestos, textiles, tanneries, pulp & paper, electronics, waste processing industries)

Some common hazardous chemicals

- Lead
  - paint, gasoline, pipes, accumulates in soil and water
  - neurological damage, slows brain development, kidney disorders; children especially vulnerable
- Mercury
  - paint, batteries, old thermometers, industrial processes, combustion of coal, dental fillings, contaminated historical mining sites
  - damages brain, kidneys, developing fetus, learning disabilities, death with high doses

Some common hazardous chemicals

- Arsenic
  - treated wood, industrial processes, contaminated soil and water
  - impairs organ, heart, and blood functions; damages nervous system
- PCBs (Ploycholorinated biphenyls)
  - industrial chemical (used in fire retartands, lubricants, insulation for electrical transformers, some printing inks)
  - carcinogenic, birth defects, lower IQ, learning disabilities, impairs neurological development

Issues w.r.t. Identification of Hazardous Wastes

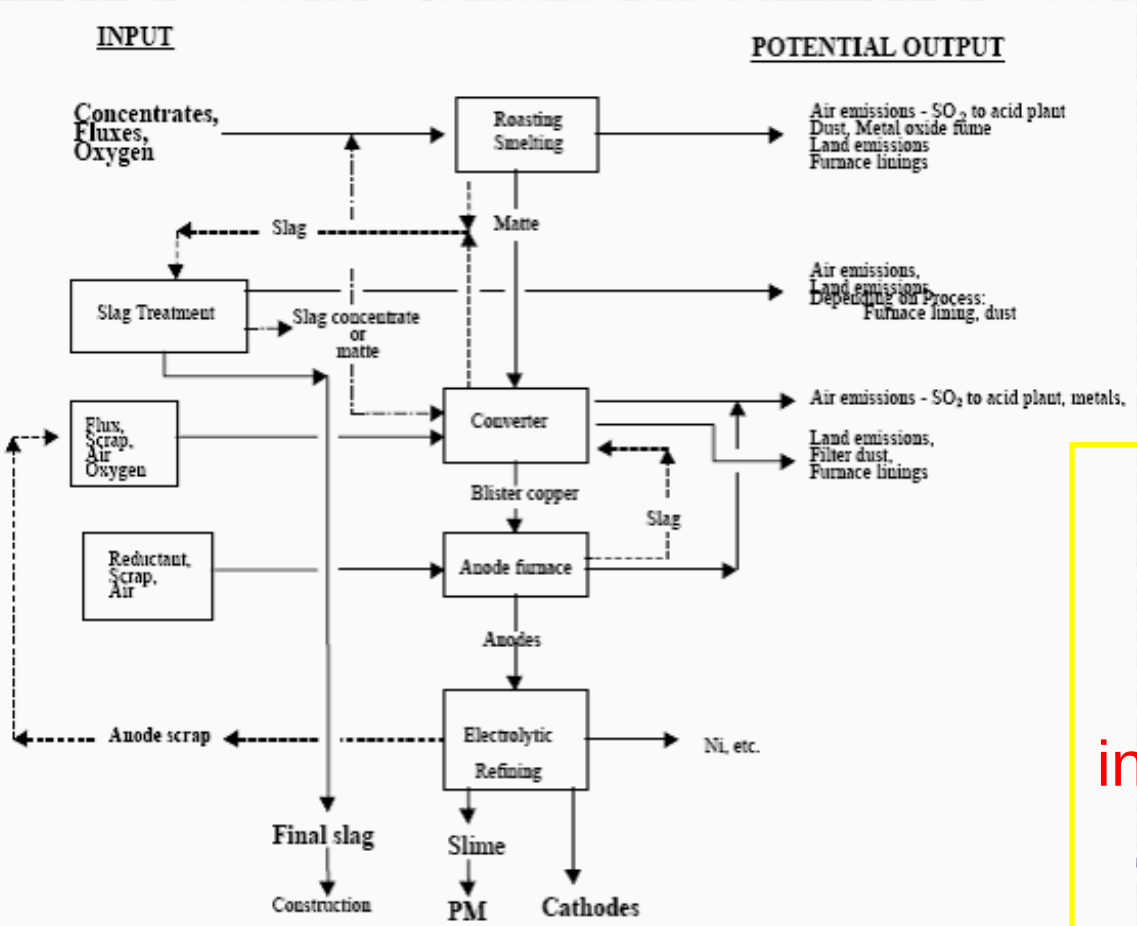
- Analytical procedures
- Identification of parameters for analysis

How to select the parameters for analysis?

- Collect the list of products and raw materials from the industry
- Obtain analysis/assay reports for major raw materials (MSDS)
- Obtain and study the production route/process (eg. Mercury cell /membrane cell process for NaOH manufacture)
- Identify the sources of solid/semi-solid/liquid wastes generated from individual product stream (reactor, distillation units, filters etc.)
- Select the parameters based on raw material characteristics / assey (impurities present in the raw materials) and based on process details

Production of copper

Input materials	Quantity [t/a]	Products	Quantity [t/a]
Copper concentrates	690000	Copper cathode	370000
Copper scrap	95000	Copper salts	6500
Shredded material from electronic scraps	1200	Nickel sulphate	1800
External intermediate products	86000	Precious metals	150
		Refined lead	9000
		Sulphuric acid	660000
		Slags	410000



Smelter route

Waste Generation

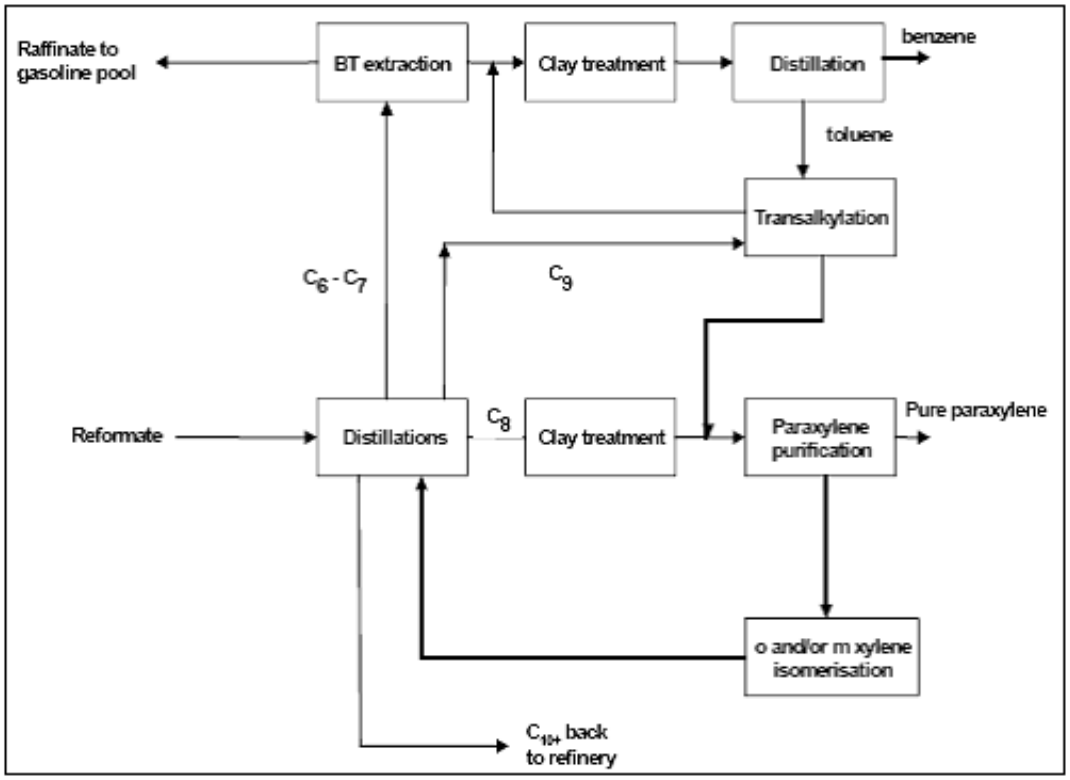
- Dusts
- Furnace linings
- Slags

Parameters to be analyzed

-Heavy metals present in the ore concentrate (As, Cd, Pb, Zn, Hg, Se, Ni, Cu)

Production of aromatics

	Process configuration		
	Benzene from pygas[1]	Benzene from HDA of TX cuts[2]	Reformate plant[3]
1. Consumption (per tonne of feedstock)			
Fuel gas	3 [4] - 35 kg	Net production 8.0 GJ [5]	3 - 10 kg
Steam (t)	0.5 – 1	<0.1	0.5 - 1.5
Electricity (MWh)	<0.07	<0.07	<0.07
2. Production (tonnes of product per tonne of feedstock)			
Benzene	0.2 - 0.35	0.83	0.12 - 0.24 [6]
Toluene	-	-	0 - 0.30 [7]
Paraxylene	-	-	0.23 - 0.48
Orthoxylene	-	-	0 - 0.25 [8]



Waste Generation

	Source
Process A (BTX from aromatic mixture)	Catalysts
	Clay from clay treaters:
	Desiccant material
	Inert balls
	Activated carbon
	Filter cloth, etc.
Process B: (benzene from pygas)	Reactor catalyst

Parameters for analysis

-Benzene, toluene, xylene

-PAH

- Total hydrocarbons

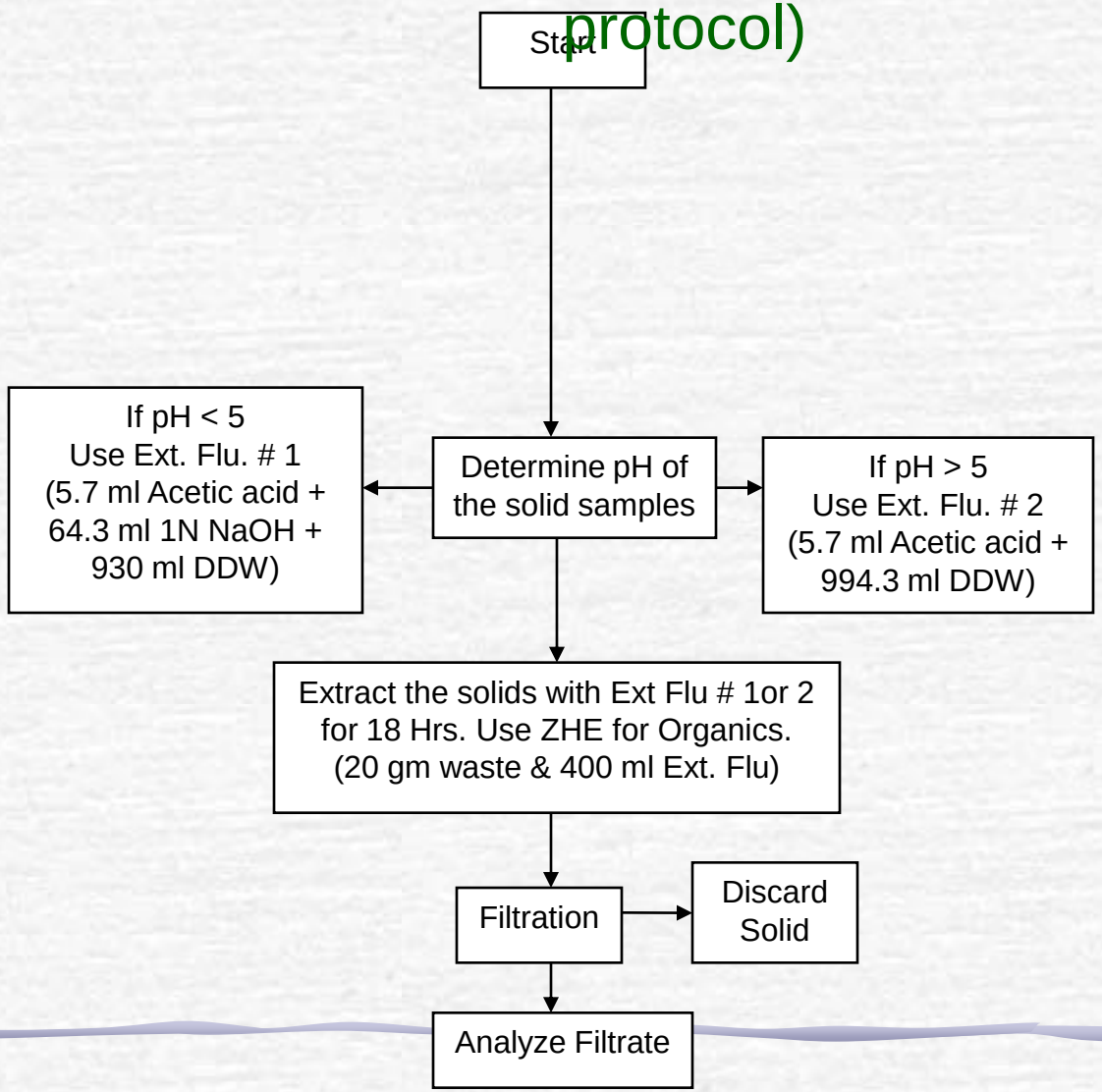
- Other hydrocarbons identified by GCMS

Important consideration for Schedule 2

- Use of Toxicity Characteristic Leaching procedure Test EPA /(ASTM D-5233-92) for determining the hazardous constituents listed in Class A to Class D
- If a hazardous constituents is present in the form of a compound the concentration limit does not apply to the compound, but only to the constituent (eg. Arsenic trioxide, sodium cyanide, barium sulphate)
- If multiple hazardous constituents from same class are present in the wastes, the concentrations are added together
- If multiple hazardous constituents from different classes are present in the wastes, the lowest concentration limit applies.

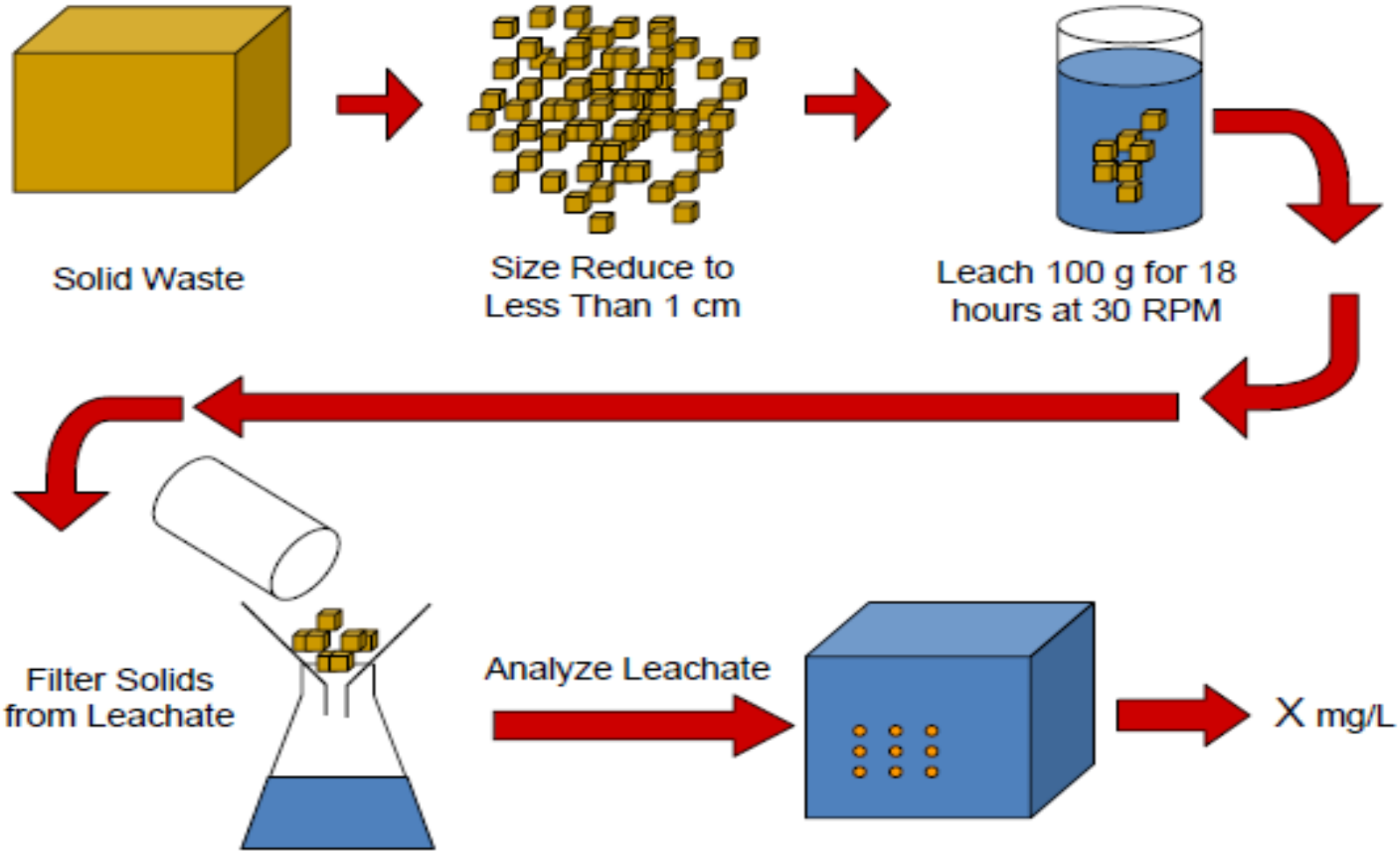
How to analyze the hazardous constituents?

(Analysis based on ASTM/TCLP test protocol)



Toxicity Characteristic Hazardous Waste

- Determined using the Toxicity Characteristic Leaching Procedure (TCLP).
- Only *leachable* concentration of pollutant is analyzed.
- In summary, a solid waste is leached in an acid solution for 18 hours and the resulting "leachate" is analyzed. If the concentration of certain pollutants in the leachate exceeds a standard in the rules, it is a TC hazardous waste (unless otherwise exempted).


Solid Waste
Size Reduce to
Less Than 1 cm
Leach 100 g for 18
hours at 30 RPM
Filter Solids
from Leachate
Analyze Leachate
X mg/L

Instruments Required for Analysis of Hazardous Waste

Parameter	Instrument/Apparatus
Iginitability	Pensky Martine Flash Point Apparatus
Corrosivety	pH Meter
Toxicity	TCLP shaker / ZHE
Calorific Value	Bomb Calorimeter
Proximate Analysis (Moisture, VM, Ash, C)	Muffle Furnace
Ultimate Analaysis (C, H, N, S, O)	CHNS Analyzer
Organics	GC, GC-MS, HPLC, LC-MS, AOX
Heavy Metals	ICP, AAS
Inorganics	Spectrophotometer, Colorimetric Methods
Sample Preparation	Microwave Digestion, Soxhalate Extraction

Analytical Protocols

- Test Methods for Evaluating of Solid Wastes- Physical/Chemical Methods (USEPA- SW846)

  (*www.epa.gov/osw/hazard/testmethods/sw846/online/*)
- ASTM
- Indian Standards Codes
- Standard Methods for Analysis of Water & Waste Water (APHA)
- CPCB Guidelines/Manuals

Comprehensive analysis

COMPREHENSIVE ANALYSIS REQUIREMENTS FOR HAZARDOUS WASTES – GENERATOR /TSDF OPERATOR

Method of Analysis	**Comprehensive Analysis is to be submitted by the Generators of Hazardous Wastes**
Physical Analysis	Physical State of the waste (liquid/slurry/sludge/Semi-solid/solid : inorganic, organic, metallic)
	Description of different phases of the wastes (in cases of solid wastes slurries and sludge) contained in aqueous/ non-aqueous liquids/solutions.
	Colour and texture
	Whether the waste is mulit-layered (Yes/No)? If yes, quantify each layer.
	Specific Gravity
	Viscosity
	Calorific Value
USEPA, SW-846; Method 1010 and 1020	Flash point
	% moisture content loss on ignition at 105° C
	% organic content loss on ignition at 550 °C
USEPA, SW-846; Method 9095	Paint Filter Liquid Test (PFLT)
Chemical Analysis	
USEPA, SW-846; Methods 9040, 9041 and 9045	pH
Method of analysis	**Comprehensive Analysis to be submitted by the Generators of Hazardous Wastes**
Inorganic Parameters Analysis	
USEPA, SW-846; Vol. 1C Part II; Test method to determine HCN released from Wastes	Reactive cyanide (ppm)
USEPA, SW-846; Vol. 1C Part II; Test method to determine H_2S released from Wastes	Reactive sulfides (ppm)
USEPA, SW-846; 9010, 9011, 9012	Sulphur (elemental)
USEPA, SW-846; Vol 1A, 1B, 1C and Vol.2	Concentration of In-organics [as per Schedule 2 of HW (M&H) Rules, 1989, as amended]
Organic Parameter Analysis	Oil & Grease
	Extractable Organic (in special cases only)
	% Carbon
	% Nitrogen
	% Sulphur
	% Hydrogen
USEPA, SW-846; Vol 1A, 1B, 1C and Vol.2	Concentration of individual organics [as per Schedule 2 of HW (M&H) Rules, 1989, as amended]
USEPA, SW-846; Method 1311, 1330	Toxicity Characteristics Leaching Procedure (For the parameters identified in **Section 2, Annexure – III** and the listed parameters as presented in Method 1311 of SW 846; USEPA)

Finger print analysis

Annexure II

FINGERPRINT ANALYSIS REQUIREMENTS FOR HAZARDOUS WASTES – TSD FACILITIES

Method of Analysis	Fingerprint Analysis by the Operators of TSD Facilities
Physical Analysis	Physical State of the waste (liquid/slurry/sludge/Semi-solid/solid : inorganic, organic, metallic)
	Identification of different phases of the wastes (in cases of solid wastes contained in aqueous/ non-aqueous liquids/solutions. slurries and sludge)
	Colour and texture
	Whether the waste is mulit-layered (Yes/No)? If yes, quantify each layer.
	Specific Gravity
	Viscosity
USEPA, SW-846; Method 1010 and 1020	Flash point
	Loss on ignition at 105° C
	Loss on ignition at 650 °C
USEPA, SW-846; Method 9095	Paint Filter Liquid Test (PFLT)
USEPA, SW-846; Method 9096	Liquid Release Test (LRT)
Chemical Analysis	
USEPA, SW-846; Methods 9040, 9041 and 9045	pH
USEPA, SW-846; Vol. 1C Part II; Test method to determine HCN released from Wastes	Reactive cyanide (ppm)
USEPA, SW-846; Vol. 1C Part II; Test method to determine H_2S released from Wastes	Reactive sulfides (ppm)

Concentration limits

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CONCENTRATION LIMITS/ CRITERIA FOR ACCCEPTANCE OF HAZARDOUS WASTES FOR DIRECT DISPOSAL TO SECURED LANDFILL

Leachate Quality *	Concentration
pH	4-12
Total Phenols	<100mg/l
Arsenic	<1 mg/l
Lead	<2mg/l
Cadmium	<0.2mg/l
Chromium-VI	<0.5mg/l
Copper	<10mg/l
Nickel	<3mg/l
Mercury	<0.1mg/l
Zinc	<10mg/l
Fluoride	<50mg/l
Ammonia	<1,000mg/l
Cyanide	<2mg/l
Nitrate	<30mg/l
Adsorbable organic bound Chlorine	<3mg/l
Water soluble compounds except salts	<10%
Calorific Value	<2500K.Cal/kg
Strength	
Transversal strength (Vane testing)	>25KN/m^2
Unconfined compression Test	>50 KN/m^2
Axial Deformation	<20%
Degree of Mineralization or Content of Organic Materials (Original Sample)	
Annealing loss of the dry residue at 550 C	<20% **by weight** (for non-biodegradable waste) <5% **by weight** (for biodegradable waste)
Extractible Lipophilic contents (Oil & Grease)	<4% **by weight**


AAS

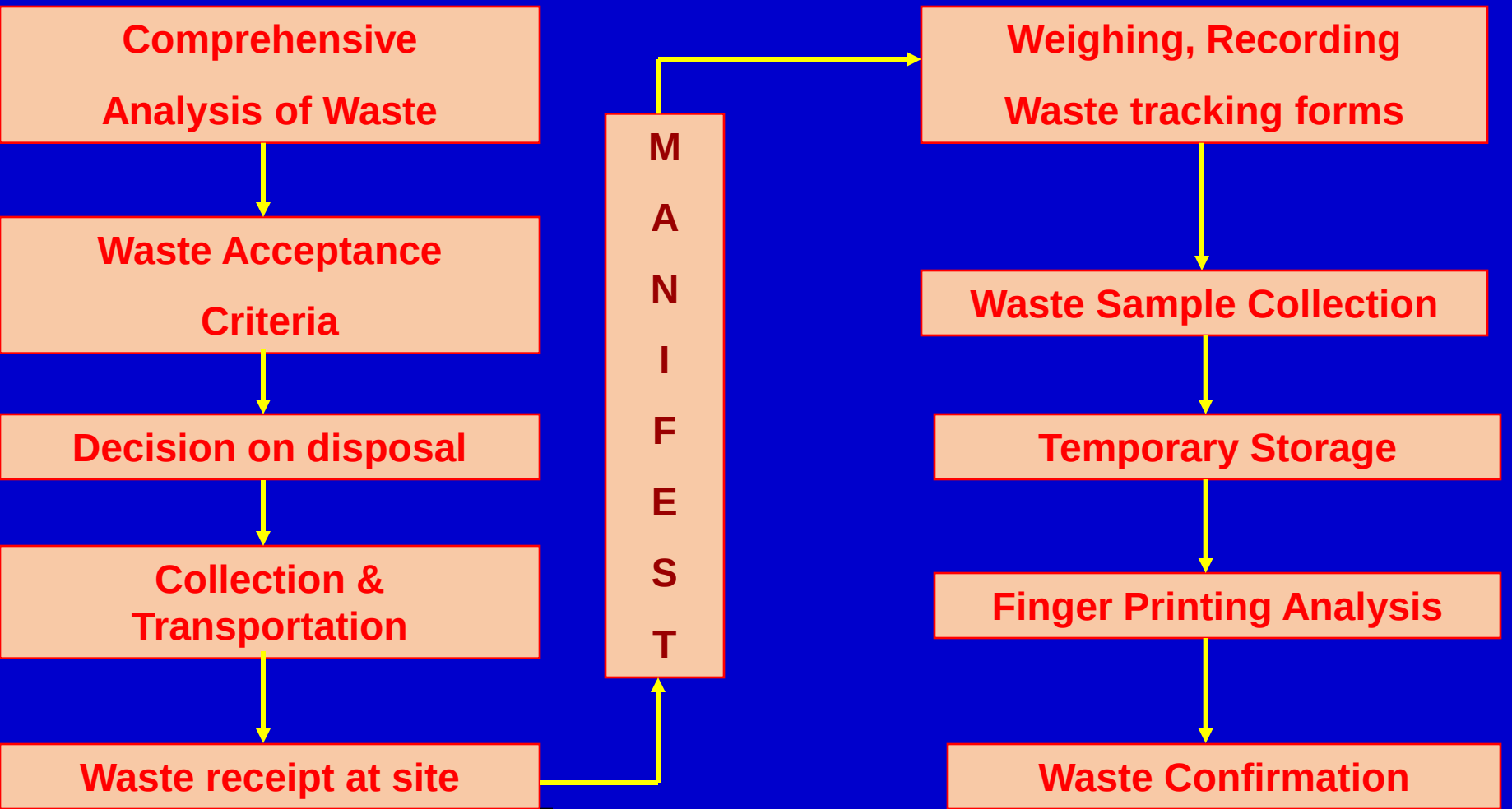

VACUUM PUMP
HAZARADOUS WASTE ANALASIS ZONE
REACTIVITY TESTS


GC-MS
GC-2010
GCMS-QP2010

DISPOSAL PATHWAYS

Flow Pathway of Wastes

Flow Path of Wastes:



DISPOSAL PATHWAYS

- Based on Comprehensive analysis
  - Disposal method is decided
  - Directly land fill
  - Land fill after treatment
  - Incinerable
    - Coprocessing
      - Raw material substitution
      - Alternate fuel

Disposal Pathways

Waste

Criteria

Biodegradable organics < 5%

Non-biodegradable Organics < 20%

Calorific Value < 2500 Kcal/kg

No Toxics

DIRECT LANDFILL

Criteria

Biodegradable organics < 5%

Non-biodegradable Organics < 20%

Calorific Value < 2500 Kcal/kg

HAS TOXICS LIKE METALS

LANDFILL AFTER STABILIZATION

Criteria

Biodegradable organics >5%

Non-biodegradable Organics > 20%

Calorific Value >2500 Kcal/kg

DUAL CHAMBER INCINERATION

Hazardous Wastes - Types

- ETP Sludge – Physico- Chemical and Biological
- Spent Catalysts and resins
- Discarded/ Off-Specification Products
- Salts and Soluble Substances
- Contaminated Glass Wool, Wiping Cotton…
- APCS Residues and Dusts
- Incineration Ash
- Iron Sludge
- Gypsum Wastes
- Still Bottom and High Vacuum Distillation Residues
- Spent Solvents
- Spent Carbon
- Tarry and Oily Wastes
- Waste Oils
- Paint Sludge

DISPOSAL PATHWAYS

- Landfillable directly
- Landfillable after treatment
- Non-landfillable – Alternates
  - Recovery/ Reuse of liquids
  - Recovery/ reuse of solids
  - Incineration
  - Co processing

INCINERABLE WASTES

- Co processing
  - AFRF
  - Raw material substitution

END