B.Sc. Course(Second Semester)

University of Babylon-College of Engineering

Environmental Engineering Department

Hazardous Waste Management, Assessment And Control:

The natural of some typical hazardous waste projects are:

1-Site assessment:

When a contaminated site, leaks or spill↔the contaminator must be assessed →to determine how much of the soil and ground water must be cleaned up.

Involve the collection of these data:

1. Geology of the site.
2. Soil type.
3. Surface hydrology.
4. G.W. condition and flow.
5. Land used surrounding the site.
6. Climatological condition.
7. Mineral resources in the area.
8. Vegetation cover.
9. Future land use.

2-Risk assessment:

To evaluate the potential threat to public health and the environment.

$Risk = f(exposure\ and\ hazard)$

If the waste for from the population, immobile and /or not biodegrades rapidly, this will minimize the risk.

3-Emergency response assessment and hazardous material spill control:

a. Values of acutely toxic chemicals from industries may pose potential environmental disasters.

b. Accidents and weather events often results in spills of H.W. and materials from chemical plants or during transport, resulting in potential public health threats if the spilled material is acutely toxic.

4-Soil and G.W. Remediation:

If the contaminated site often it is assessed and characterized, required clean up.

Most effective processes for remediation of contaminated sites are based on natural pathways. Which they are:

a. Biodegradation.
b. Volatilization.
c. Sorption.
d. Chemical oxidation.

5-Treatment, storage and disposal design:

Included:

a. H.W. landfills.
b. Heavy metal recycling operations.
c. Incinerators.
d. Traditional treatment (neutralization).
e. Solvent recycling facilities.

6-Waste minimization and pollution preventation:

Reducing the mass and volume of hazardous wastes by change the materials (used in manufacturing e.g. using zinc chloride instead of zinc cyanide) or change the process.

Source-Pathway-Receptor Analysis:

How to solve hazardous waste problems divided them into three categories:

1-Source:

Assessing H.W. problem by defining the waste component at their source including:

a. Concentration.
b. Properties(density, solubility , flashpoint, etc).

2-Pathway:

Focuses on quantifying rates at which the waste compounds volatilize, degrade and migrate from the source.

3-Receptor analysis:

Its effect on human health and other species.

Common Hazardous Wastes:Properties and Classification: Common Concentration Units :

Different units are used to quantify the concentration of hazardous chemicals depending on what they are present in water , soil or air.

$$ppm = \frac{mg\ of\ compound}{kg\ of\ medium} = \frac{mg\ of\ compound}{g\ of\ medium}$$

- ***In Water:***

1 lit of water has a mass of approximately 1 kg Therefore,

$$ppm = \frac{mg}{L} = \frac{mg}{kg}$$

$$ppb = \frac{mg}{L} = \frac{mg}{kg}$$

- ***In Soil:***

$$ppm = \frac{mg\ of\ contaminat}{kg\ of\ dry\ soil} = \frac{mass}{mass}$$

$$ppb = \frac{mg}{kg}$$

- ***In Air:***

$$\frac{mg}{m^3} = \frac{mg\ contaminate}{m^3\ of\ air}$$

$$ppm = \frac{1\ part\ of\ contaminate\ (by\ volume)}{10^6\ parts\ of\ air\ (by\ volume)}$$

The units of mg/m^3 and ppm may be easily converted if the temperature and pressure at which the measurement were made are known, referring to ideal gas law:

$PV = nRT$

$P = pressure\ (atm)$

$V = volume\ (L)$

$n = no.\ of\ moles\ of\ gas$

$T = temperature\ (k)$

$R = The\ universal\ gas\ constant = 0.082\ \ L.atm/mole.k$

The volume occupied by 1mole of gas at standard temp and press. $(0°C\ or\ 273k\ and\ 760\ mm\ Hg\ or\ 1\ atm)\ is\ 22.4\ L\ or\ 0.0224\ m^3 (1000L = 1m^3)$

$$vol_{contaminate}(m^3) = \frac{mass\ of\ contaminat\ (g)}{\mu\ weight\ (g/g_{mol})} \times 0.0224\ \frac{m^3}{mol}$$

For any Temp. and Press.

$$vol_{contaminate}(m^3) = \frac{mass\ of\ contaminat\ (g)}{\mu\ weight\ (g/g_{mol})} \times 0.0224\ \frac{m^3}{mol} \times \frac{T}{273k} \times \frac{760\ mmHg}{P}$$

T=ambient temp. (k) of the gas sample.

P=atmospheric press.(mmHg) of the gas sample.

The final step is to relate the volume of contaminate to the volume of air and incorporate a factor of 10^6 based on the definition of ppm.

$$ppm = \frac{Vol.cont\ (m^3)}{Vol.air\ (m^3)} \times 10^6$$

$$C_{ppm} = C\left(\frac{RT}{p\mu}\right) \times 10^6$$

When:

$C_{ppm} = the\ contaminate\ concentration\ in\ ppm$

$C = the\ contaminate\ concentration\ in\ \ g/m^3$

$R = ideal\ gas\ constant\ (8.21 \times 10^{-5}\ \ m^3.atm/mol.k)$

$T = Temp.(k)$

$p = absolute\ press.(atm)$

$\mu = molecular\ weight\ of\ contaminat\ (g/g_{mol})$

Properties of Hazardous Wastes:

1. ***Water Solubility:***

It is the maximum concentration (saturation concentration) of substance that will dissolve in water at a given temperature.

Materials:

- Hydropholoic (hating water)
- Hydropholic (loving water)

Some substance are so finelly divided that they do not settle out. These species may remain in colloidal suspension for weeks but are not truly dissolved. Therefore, the practical analytical definition of a dissolved chemical is based on chemical analysis, it is the material that passes through glass fiber filter of 1.2mm.

Factors Affect Water Solubility:

a-Temperature

most data are obtained at 25°C (above room temp). temperature significantly affects water solubility and it is measured mg/l.

water solubility of hazardous components ranges(1-100000 mg/l).

b-Water solubility

of both inorganic and organic compounds is related to their structure and size. Very polar organic and inorganic species exhibit high water solubility.

The solubility is based on attractive forces between the solute and solvent molecules they are:

1-Van der Waals forces

(the interaction of electron orbitals between adjacent molecules).

2-Hydrogen bonding, which occurs primarily with molecules containing hydroxyle (OH) and amino (NH_2)groups.

3-Dipole-dipole interactions.

c-The size and shape

of molecules also affect its water solubility. Water solubility decrease with increasing molar volume

<u>Water Solubility Of Weak Acids And Bases:</u>

The general equilibrium expression for the dissociation of weak acid in aqueous solution is:

$$R-COOH \quad \leftrightarrow \quad R-COO^{-}+H^{+} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$(acidic\ form) \quad (basic\ form)$$

The equilibrium expression for the reaction of eq(1) is:

$$K_a=\frac{[base][H^{+}]}{[acid]}=\frac{[R-COO^{-}][H^{+}]}{[R-COOH]} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

K_a=acid dissociation constant and the brackets indicate the concentration (in mole/lit)

K_a can be written

$$K_a=\frac{[base]}{[acid]}[H^{+}] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Take (-log) of both sides of eq(3)

$$-\log k_a=-\log H^{+}+-log\frac{[base]}{[acid]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

And we have

$pH = -log[H^+]$

Also because

$-logx\ is\ defined\ as\ px$

Eq (4) can be simplified

$$pK_a = pH - log\frac{[base]}{[acid]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots....(5)$$

Rearranging eq(5)

$$pH = pK_a + log\frac{[base]}{[acid]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..\ldots\ldots\ldots\ldots.(6)$$

Eq(6) known as Henderson-Hasselblach equation values of pk$_a$ for weak organic acids are found in tables.

A weak organic base is characterized by accepting a porton.

$R + H_2O \leftrightarrow RH^+ + OH^-$

The base association constant k$_b$ is defined as

$$K_b = \frac{[RH^+][OH^-]}{[R]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots\ldots\ldots...(7)$$

And

$$K_w = [H^+][OH^-] = 10^{-14} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..\ldots(8)$$

Sub(8) in(7)we get

$$K_b = \frac{[RH^-]\ K_w}{[R][H^+]}$$

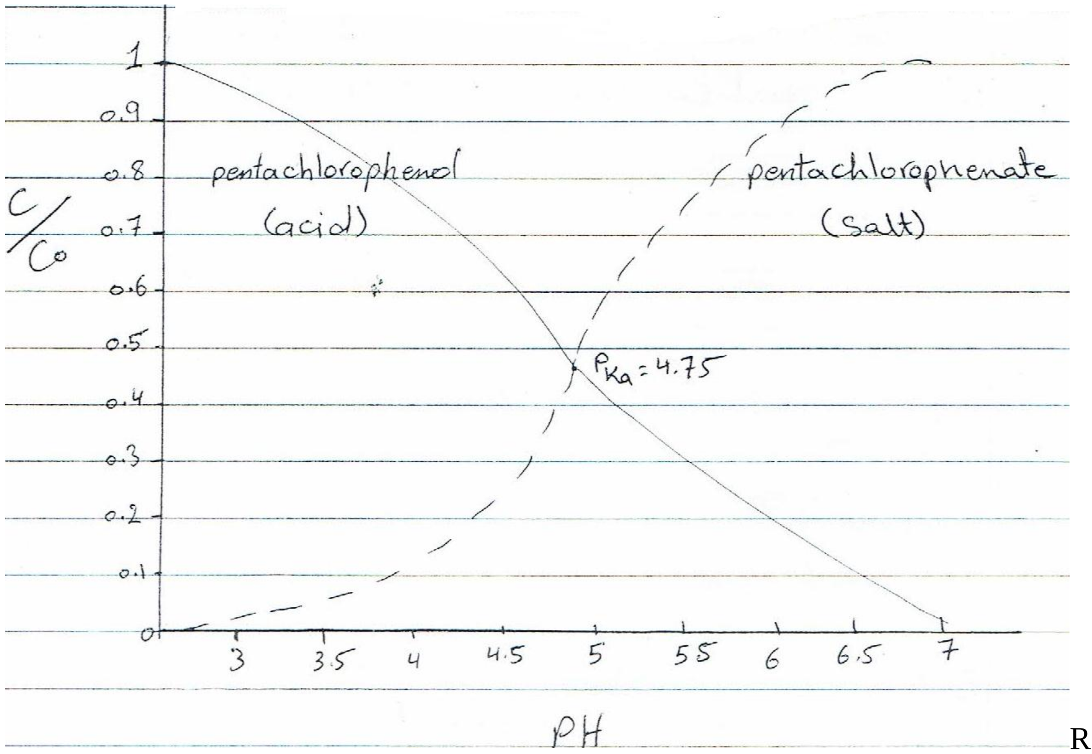
K$_b$=base association constant.

A measure of the dissociation of weak acids is the parameter α, which is the fraction of un-ionized acid.

$$\alpha = \left(1 + \frac{K_a}{[H^+]}\right)^{-1}$$

The fraction of un-ionized base , β,is

$$\beta = \left(\frac{1 + K_b[H^+]}{K_w}\right)^{-1}$$



Relative proportions of the weak acid pentachlorophenol and its salt pentachloro phenate as a function of pH.

The relative proportions of the acid form and the ionized salt of pentachlorophenol as a function of pH are shown in Fig. above.

The concentration of the acidic (unionized) form decreases with increased pH, and the concentration of the pentachlorophenate salt (ionized) form increases as the pH is raised – The two forms exist at equal concentration at the pK_a of (4.75).

2-Density and Specific Gravity:

Density is defined as the ratio of mass to volume is usually expressed in g/ml or kg/m^3.

Specific gravity: A dimension less number analogous to density.

$$S.g = \frac{density\ of\ compound}{density\ of\ water}$$

Density of water 1 g/ml at 4°C

Density is important because:

1. In assessing the behavior of nonaqueous phase in soil and ground water system.
2. In sampling of drum and storage tank contents.

- Sp.gr. range [0.6-2.9] for organic compounds
- Ethers, alcohole and esters are less dense than water.
- Metals are more dense than water.

Vapour density: Is analogous to Sp.gr. It is defined as the density of compounds in the vapour phase(with no air present) to the density of air.
Air relative vapour density=1

Vapour density important in assessing the fate of a gas e.g. chlorine gas, if allowed to escape from a tank stays close to the ground because of its vapour density is 3.8 [3.8 times more dense than air]

3-Light and Dense non agoueous phase liquid:

NAPL=Non-aqueous phase liquid.
LNAPL=Light non-aqueous phase liquid.
DNAPL=Dense non-aqueous phase liquid.

Chemicals that are dissolved in water are dispersed by Brownian motion, resulting in homogeneous distribution throughout the solution.

4-Flammability limits:

H.W defined by RCRA [may also be corrosive, explosive, flammable]

Some chemicals voltilize of stored in open drums, its vapour may then ignite in the presence of as park on open flame if they are with in a specific range of concentrations in the air.
Fire is defined as a rapid, exothermic oxidation of fuel. Elements of fire:

a. Fuel
b. Oxidize
c. Ignition

At lower vapour concentrations:[lower flammability limit (LFLs)]

Is sufficient mass is available for flame propagation (the mixture is too lean to burn or explode).

At high vapour concentrations:[Upper flammability limit (UFLs)]

There is a threshold concentration that limits combustion (the mixture is "too rich")

These concentrations usually expressed in percent %, the LFLs and UFLs for Hazardous waste listed in tables.

Most H.W. disposal and storage areas contain mixtures of chemicals that have flammability limits different from single component systems:

Le Chatelier Equation

$$LFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{LFL_i}}$$

Where,

LFL_i =lower flammability limit for component i.

y_i=mole fraction of compound i in the mixture.

n=the number of compounds in the mixture.

$$UFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{UFL_i}}$$

Where,

UFL_i =upper flammability limit for component i.

Example:Determine the LFL_s and UFL of a gaseous mixture (v/v) of 0.65% aceton, 0.2% decane and 0.3% hexane.

If the data are not available for LFL , UFL in table used:

$$LFL = 0.55\, C_{st} \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$UFL = 3.5\, C_{st} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

C_{st}=the % fuel in air

$$C_{st} = \frac{100}{1 + \left(\frac{z}{100}\right)} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Z=moles of O_2/moles organic compounds lournd.

$$LFL = \frac{0.55(100)}{4.76\, m + 1.19\, x - 2.38\, y + 1} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$UFL = \frac{3.5(100)}{4.76\,m + 1.19\,x - 2.38\,y + 1} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (5)$$

Example: Estimate the LFL and UFL for aceton. Compare the estimated values to the tabulated values.

Labels And Placards:

Labels are used to identify potential dangers during transportation and storage of H.W. and hazardous materials.

1-Transportation:

Controlled by the U.S. Department of transportation (DOT).

Requires placement of placards on the outside of vehicles transporting hazardous material, to aid is assessing the potential hazard of a spill.

The DOT requires placards when 1000 pounds or more of hazardous materials are transported by rail or truck unless the materials are classified as explosive, poisons, radioactive, or flammable solid, in these cases placarding is required regardless of the quantity.

2-Storage:

Requires labels under a systems developed by National Fire Protection Association (NFPA) Drums a waiting treatment or disposal, system based on three bases to provide information of system and define hazards:

- Health
- Flammability
- Reactivity

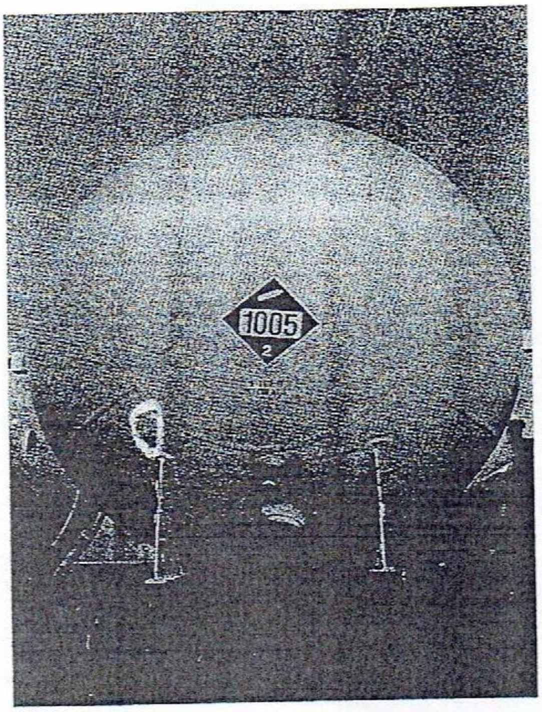


Figure5: Use of placards in transportation.

Table1: The Nine Classes of Hazardous Materials Used by the DOT

DOT Hazard Code Number	DOT Symbol	Hazard Class
1		Explosives
2		Gases
3		Flammable liquids
4 5		Flammable solids Spontaneously combustible materials Materials dangerous when wet
		Oxidizers Organic peroxides
6		Poisonous materials
		Biohazard
7		Radioactive materials
8		Corrosives
9		Other regulated materials

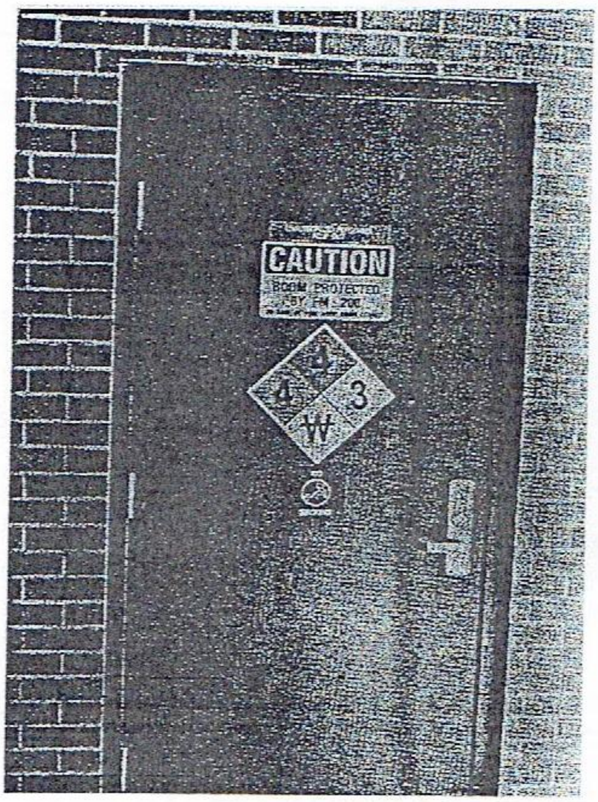


Figure6: A National Fire Protection Association placard for identifying hazards in an industrial storage area.

Figure7: A typical NFPA placard with locations of hazard