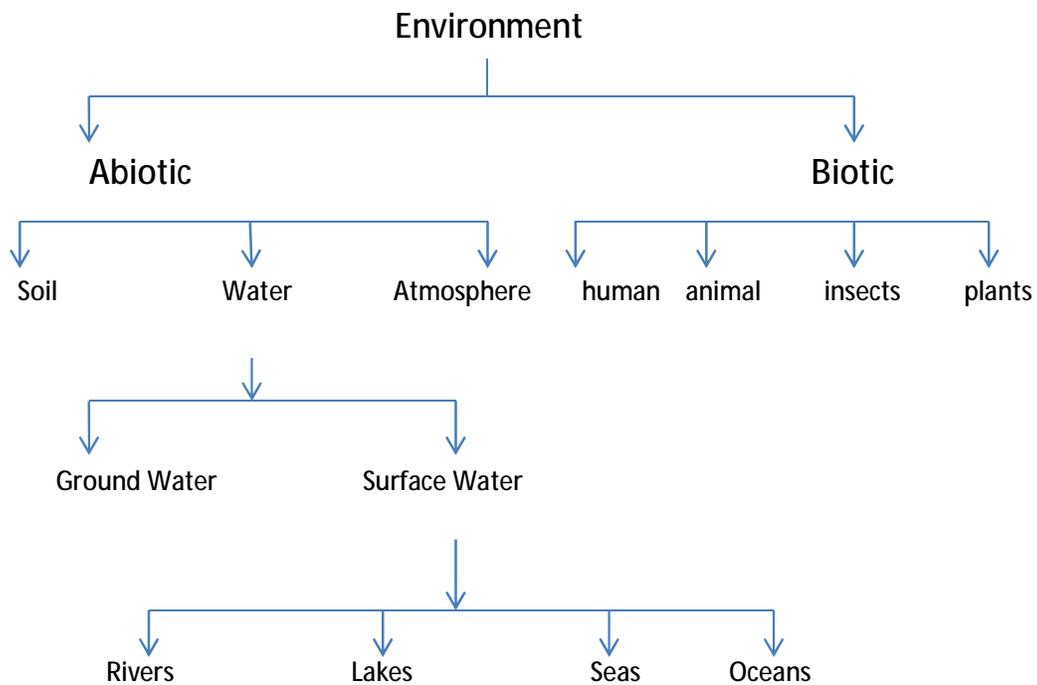


Hazardous Waste

Third Class/ Environmental Engineering Department

References

- 1- Hazardous Waste, Sources, Pathways, Receptors, Richard J., Watts.
- 2- Environmental Engineering, Gerard Kiely.
- 3- EPA Publications (Environmental Protection Agency).



Introduction

High standard of living



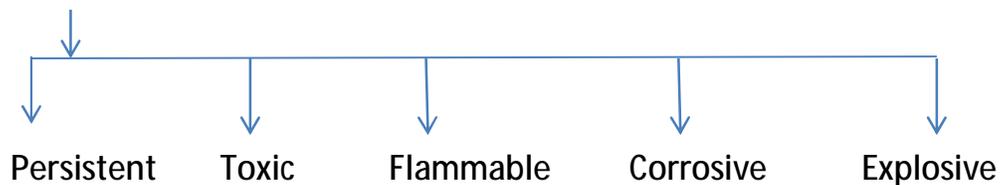
Industrial society



Manufacture of products



Generation of waste



Examples of Generated Waste

- 1- Production of computers and semiconductor components requires halogenated solvents.
- 2- Aircraft construction and maintenance activities generates petroleum, solvent and heavy metals.
- 3- Synthesis of plastics, paints and pesticides produces organic solvents, by products and sludge's.

" The Quantity of H.W have grown with the progression of technology"

Historical Review

- Until 1800's most material used in homes and industries were natural products such as lard or plant extracts.
- In 19th century the world entered the petroleum age, kerosene and other petroleum distillates were used as solvents and fuel.
- From 1930-1950 chemists discovered that the industrial properties of petroleum products could be improved by a variety of synthetic techniques.

Such as adding halogens- chlorine, fluorine, or bromine to petroleum-based chemicals.

These halogens have properties:-

- 1- Persistent for long periods of time.
- 2- Harmful to public health and environment.

H.W Characteristics

- 1- Short-term toxicity to humans.
- 2-Long-term toxicity to humans.
- 3-Ecotoxicity Ecology.
- 4-Flammability
- 5-Explosivity.
- 6-Corrosivity.

What is Hazardous Waste?

H.W came in all shapes and forms. They may be liquids, solids or sludge's (semisolids) and gases. They may be products or manufacturing processes or simple commercial products such as: house holding cleaning fluids or battery acid that have been discarded.

** Sludge contains of 97% water an 3% solid.

EPA definition

H.W: A substance considered hazardous if it exhibits one or more of the following characteristics:-

- . Ignitable- the substance causes or enhances fires.
- . Reactive- the substance reacts with others and may explode.
- . Corrosive- the substance destroys tissues or metals.
- . Toxic- the substance is a danger to health, water, food, and air.

And it is likely to result in danger to human health or the environment.

Case Studies

a- 5000 tons/year of pesticides

Produce 300 drums of 55-gallon in the year and the concentrated waste contain:

- 1- Hexachlorocyclopentadine.
- 2- Chlorophenole.
- 3- Benzene.
- 4- Chlorobenzenes.
- 5- Solvents.

They dump the drums in soil near the boundary of the plant and dig a shallow bit in which to empty the drums.

After 20 years from dumping the chemicals onto soil, benzene was discovered in a water supply well 3 miles away. Another chemical, P-dichlorophenol, was found in the well 6 months later. An environmental consulting firm, after drilling and sampling 80 monitoring wells, found almost all of the chemicals that had been disposed of.

b- Love- Canal

Niagra Falls, New York

1892-1910

Canal constructed was never completed. Industries in 1930 began using part of the unfinished canal for the disposal of chemical waste. In 1952, waste disposal into the canal ceased, and it was covered and the land sold. A school was built with the full knowledge of the authorities that chemical wastes has been disposed of on the property.

In 1979 liquid and gaseous waste migrate into the basement of the school. By inhalation of waste, the incidence of cancer and birth defects appears in the school.

C- String fellow Acid Pits

Hazardous waste landfill operated from 1956-1976. In 1970 appear bronchitis, asthma, and skin rashes.

-Heavy rains flooded the site and toxic run off flowed through the streets.

- The ground water contamination was also evident.

In 1977 two clean up options were evaluated

- 1- Total removal of the contamination.
 - 2- Contamination removal and on-site neutralization
- تم اختيار الثاني وكانت كلفته عالية جدا

D-Hardeman County, Tennessee

Pesticides production (from 1964-1972)

300000 drum of waste were buried at the site in shallow trenches

5 years after the site was closed

Residents noticed foul odors in their well water also appear

Nausea, respiratory infections.

Until 1970 50000 sites of H.W in the United States in which approximately 60 million tons of wastes had been disposed.

Lecture Two

Hazardous Waste

Past Disposal Practices

Quick and dirty disposal techniques:

- 1- Soil spreading.
- 2- Pesticides rinse and formulation area.
- 3- Underground storage tanks.

- 4- Pits/ Ponds/ Lagoons.
- 5- Sanitary landfills.
- 6- Drum storage area.
- 7- Unlined hazardous waste landfills.
- 8- Midnight dumping.
- 9- Uncontrolled incineration.

1-Soil spreading

Liquid waste (specially lubricating oils and other petroleum residues), spread on soils and unpaved roads to:

- a- Disposing of waste.
- b- Mitigation flowing dust.

- One of the problems with placing petroleum on soils is the presence of cancer- causing polycyclic aromatic hydrocarbons (PAHs).
- Petroleum products may mix with wastes solvents and pesticides causing more complicated problems.

The worst case of soil spreading with oil occurred at Times Beach Missouri.

2- Pesticide rinse and formulation areas.

Pesticides in concentrated use in agriculture received by farmers and diluted in site and because of the:

- 1- Remote nature of many of these sites.
- 2- The lack of regulatory control.

The areas have become contaminated from both past and present disposal practices because many of the pesticides, especially those

used in the 1940s through 1970s, are resistance to natural degradation processes.

3-Underground storage tanks

Throughout the 20th century 5 million Underground Storage Tanks (USTs) installed to hold, gasoline, jet fuel, solvents, heating oil.

-"Soil is a corrosive environment"

-1.8% of tanks less than 5 years old leak

-11.8% of tanks last longer than 25 years

-Most tanks age range for leakage is 11 to 25 years (the rest)

Leakage from (UST)



Saturation of soil with chemicals



Contamination of groundwater and surface water

4-Pits/ Ponds/ Lagoons

Workers dug a pit into which wastes were poured.



Wastes disappeared by seeping through the soil



Less permeable soil → waste held at the surface so these areas called ponds or lagoons.

5-Sanitary landfills



Designed to accept

Newspapers, cans, bottles, others



Other household received

Petroleum products, solvents, pesticides and transformer oils.

-Liquid hazardous waste disposed in:

1-Drums

2-Poured directly into the landfills



These sanitary landfills were unlined



Waste migrate to surface and groundwater

6-Drum storage areas

Chemicals stored in 55- gallon drums



Placing in loading docks, concrete pads



Drums stored in thin manner eventually corroded and leaked, with chemical releases to the underlying soil and groundwater.

7-Unlined hazardous waste landfills

Chemical waste were disposed in these landfills with nonhazardous solid materials.

They leak to soil and groundwater.

8-Midnight dumping

The wastes were sometimes transported and disposed of on other property or in isolated locations such as wooded area or desert.

9-Uncontrolled incineration

Burning and incineration of some hazardous wastes (such as chlorophenols and polychlorinated biphenyls).



Result incomplete combustion, with formation of more toxic products in the ash and the emission of hazardous air pollutants.

In order to perform safe incineration:

- 1- Specific conditions of temperature.
- 2- Turbulence.
- 3- Residence time conditions.

H.W Legislation

First legislation was:

1965s → Solid Waste Disposal Act (SWA)

Expanded at

1970 to Resource Recovery Act (RRA)

-These two laws did not have a major impact on solving hazardous waste problems.

-The two laws created a series of guidelines in the area of storage and collection of solid wastes:

1- Including the operation of sanitary landfills

2-Incineration

3-Resource recovery.

جرت بعدها تحسينات للقوانين اعلاه

1976s Start Resource Conservation and Recovery Act (RCRA)

Legislation required total documentation of where a waste is generated and where it is disposed.

يتضمن وثائق منذ تكون الفضلات الى طرحها والتخلص منها وتم كتابتها بواسطة الكونغرس وكانت شاملة

RCRA:

ضمن حق مقاضاة اي صناعة من قبل المواطنين

In 1984 appeared a new legislation called:

Hazardous and Solid Wastes Amendments (HSWA).

Which contains more technical details.

Primary goals of RCRA and HSWA

- 1- To protect public health and the environment from hazardous and other solid wastes.
- 2- To preserve natural resources through resource recovery and conservation.
- 3- Control hazardous waste from "Cradle to Grave" by tracking their movement from the point of generation through transit to treatment, storage and disposal.

Definition of a RCRA Hazardous Waste

-RCRA origin from Solid Waste Disposal Act at 1965.

-Before a waste can be considered hazardous it must be classified as a solid waste. A solid waste is any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant or other discarded material including solid, liquid, semisolid, or contained gaseous materials resulting from industrial, commercial, mining and agricultural activities.

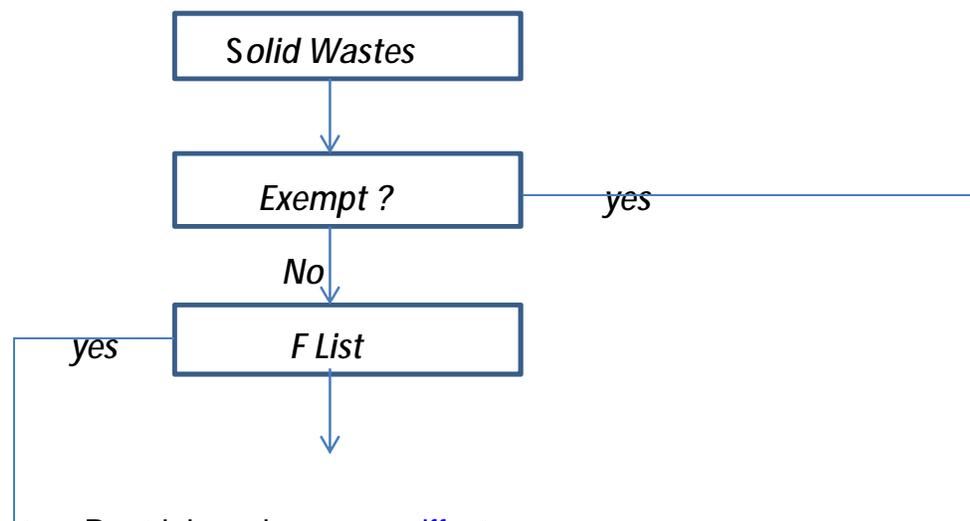
-Note that RCRA defined wastes that are gaseous, liquid and semisolids as well as solids as solid wastes.

وعلى هذا الاساس يتم تعريف النفايات الخطرة

The definition of HW due to RCRA

A solid waste or combination of solid wastes, which because of its quantity, concentration, or physical, chemical or infectious characteristics may cause or contribute to an increase in mortality or an increase in serious illness and pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported or disposed of or otherwise managed.

Figure 1 is a flow chart that provides a summary of the following discussion of the RCRA wastes identification process.



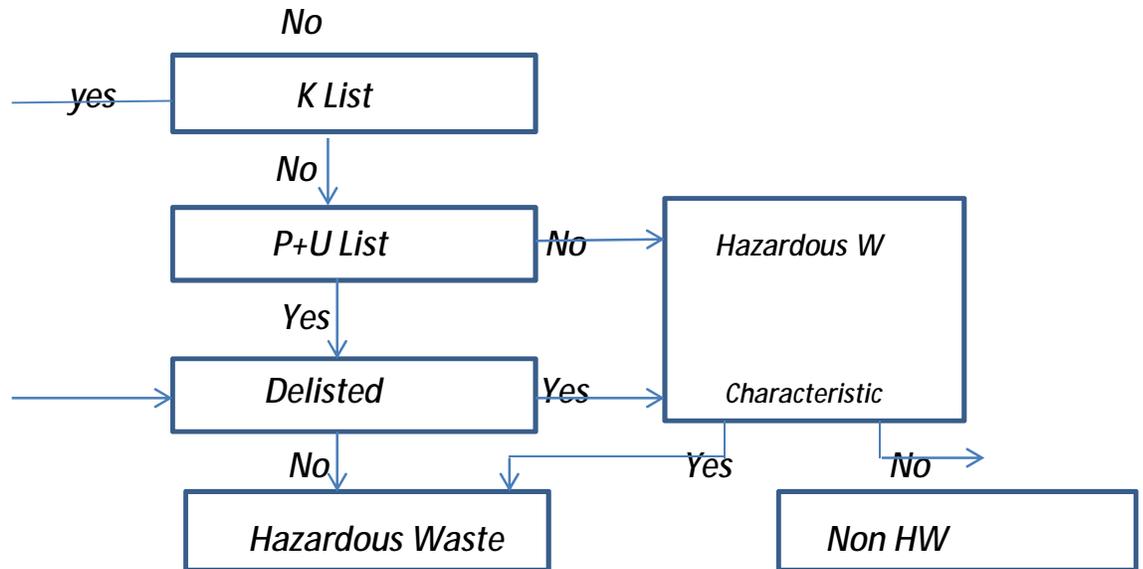


Figure 1: Critical path for determining if a waste is hazardous under RCRA.

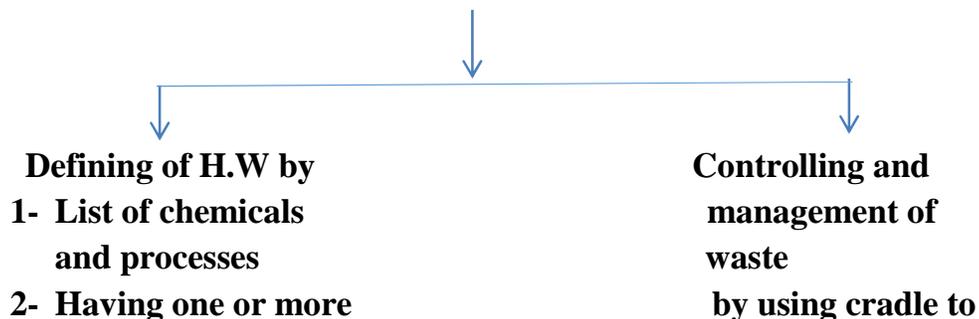
F list and K list represent waste from industrial processes.
P and U lists commercial products.

Delisting: Is usually pursued when waste characteristics are borderline, if the industry has changed unit processes to decrease the severity of the waste, or if companies are partially treating the waste.

Lecture three

Hazardous Waste

How can RCRA works?



of the following properties

- Corrosion
- Ignition
- Explosion
- Toxic

grave theory

generate

Transient

Final treatment

Storage and

Disposed facilities

Mixture rule: If a listed H.W is mixed with a nonhazardous solid waste the mixture is still hazardous waste under RCRA.

Cradle to Grave H.W Management

1- Generators

2- Transporters

3- TSD facilities (Treatment-Storage-Disposal)

Generators defined by EPA: Is any person whose act or process produces hazardous waste or whose act causes hazardous waste to become subject to regulation.

Duties of H.W generators

a- Determine if the waste is hazardous " using fig. 1 from the last lecture".

b- If they are generating a hazardous waste, it is their responsibility to obtain an EPA identification no. by filling the form (notification of H.W activity)

هناك استمارة خاصة تملأ من قبل الشخص الذي يولد النفايات

-Waste can be stored for up to 90 days before being transported off site for disposal. If the generators need a longer time to store their waste, a Treatment, Storage, and Disposal (TSD) permit must be obtained.

c- Additional responsibilities:

- 1- Licensed H.W transporter must be hired and shipment of the waste must be arranged.
- 2- A uniform H.W manifest is prepared that details the classifications and quantities of the wastes.

هناك استمارة خاصة بهذه العملية

- d- Generators must prepare the shipment of H.W in a safe manner (safe packing, labeling, marking, and placards).

وذلك بالاعتماد على تعليمات

Department of Transportation regulation (DOT)

- e- Generators must provide personnel training and contingency plans.

" Industries that generate < 1000 kg/ month were not regulated under RCRA "

HSWA deals with small quantity generators 100-1000 kg/month

** More lenient rules are provide for small quantity generator, for example:

Keeping 1000 kg of waste on their property for 180 days ----- if shipped over 200 miles ----- it may be stored for up to 270 days.

2-Transporters: defined by EPA ----- any person engaging in the off-site transportation of H.W by air, rail, highway, or water.

Responsibilities ----- Most transporters are truckers

- a- Must obtain an EPA transporter identification no.
- b- Responsible for accidental and intentional release when the waste is in their possession.
- c- If the waste is spilled, they must be prepared to clean it up after contacting local police and fire department.

3-TDS facilities: Includes

- **Landfills**
- **Incinerators**
- **Acid neutralization tanks**
- **Holding tanks**
- **Lined surface impoundments.**

Underground Storage Tank Legislation (USTs)



Because of 100 to 1000 of underground storage tanks have the potential for leaking ---- HSWA have a new section (subtitle I) to regulate the installation of new tanks and the mitigation of leaking tanks.

The definition of UST by RCRA:

"Any or combination of tanks (including underground pipes connected thereto) which is used to contain an accumulation of regulated substances, and the volume of which (including the volume of the underground pipes connected there to) is 10% or more beneath the surface of the ground.

Comprehensive Environmental Response Compensation and Liability Act (CERCLA)



Respond to spills and other release of hazardous substances to the environment, particularly those resulting from the past disposal of hazardous waste.

لمعالجة المواقع القديمة الملوثة



The purpose of the act is to provide a mechanism for the cleanup of hazardous waste contamination resulting from large-scale accidental spills or chronic environmental damage.



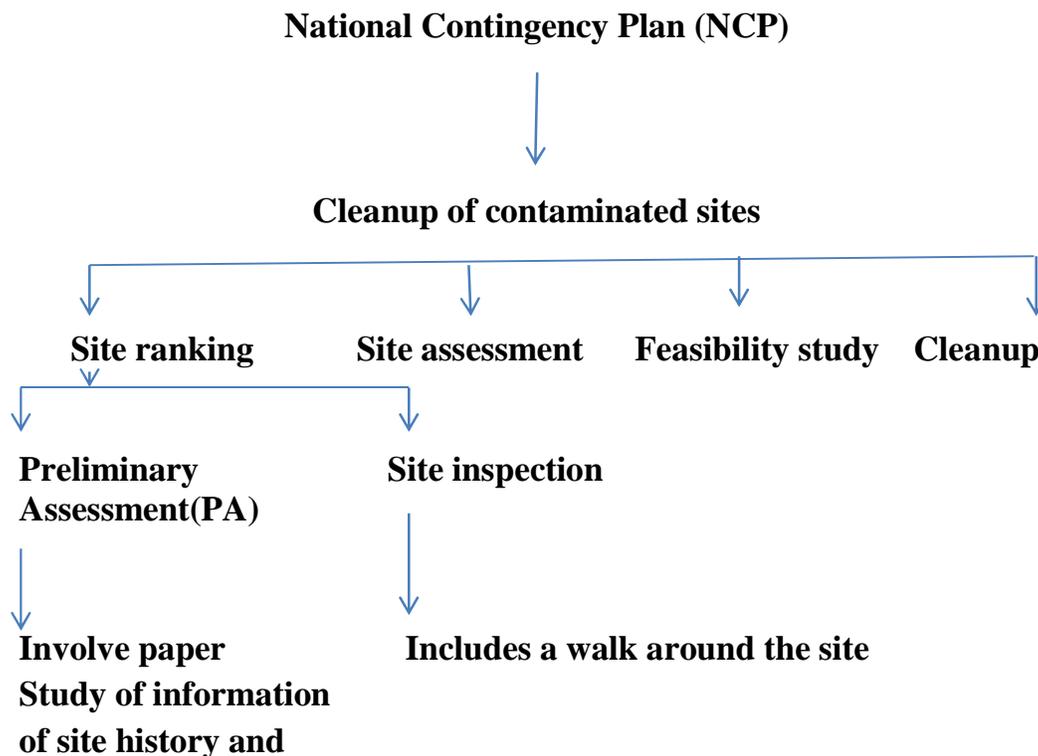
Focused primarily on contaminants at sites where disposal took place in the past.

1986 → Superfund Amendments and Reauthorization Act (SARA)



Created \$8.5 billion fund to identify hazardous sites of priority requirement to be cleaned up.

Environmental Release: Spilling, leaking or disposing of a hazardous substance into the environment.



disposal records

Liability is responsible parties to clean up the waste that was disposed

** Other Legislations:

- 1- The Clean Water Act (1979).
المياه الصالحة لعمليات الري والصيد
- 2- The Toxic Substance Control Act (TSCA, 1976).
- 3- The Safe Drinking Water Act (SDWA, 1974).
- 4- The Clean Air Act (CAA, 1970).
- 5- The Federal Pollution Prevention Act (PPA, 1990), this is to promote the minimization and source reduction of H.W.

H.W Management, Assessment and Control

For purpose of management the nature of some typical hazardous waste projects are:

1- Site Assessment

If a contaminant leaks ----- extent of contaminant must be assessed, in order to determine how much if any, of soil and ground water must be cleaned up.

It involve data collection and analysis of these data through:

- a- Geology end of the site.
- b- Soil type.
- c- Surface hydrology.
- d- Ground water condition and flow.
- e- Land used surrounding the site.
- f- Climatological conditions.
- g- Mineral resources in the area.
- h- Vegetation cover.
- i- Future land use.

2- Risk assessment is to evaluate the potential threat to public health and the environment.

Risk=f (exposure and hazard)

If the waste is:

- a- Far from population.**
- b- Immobile and/ or**
- c- Not biodegrades rapidly**



This minimize the risk

But if the waste is:

- a- Immobile.**
- b- Deep.**

Excavating the site may cause more problem better leaving the soil.

3- Emergency response assessment and hazardous materials spill control

H.W and materials transported on highways. Rail, and ships.

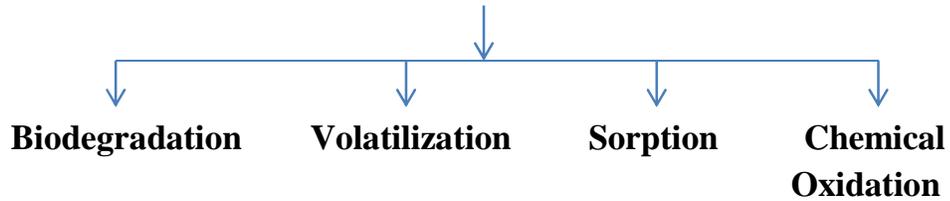
بالنسبة لمصادر التلوث

- a- Values of acutely toxic chemicals from industries may pose potential environmental disasters.**
- b- Accidents and weather events often result 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 ground water remediation

If the contaminated site after it is assessed and characterized, requires cleanup.

Soil and ground water treatment are implemented and the most effective processes for remediation of contaminated sites are based on natural pathways.



5- Treatment, Storage, and Disposal design and permitting



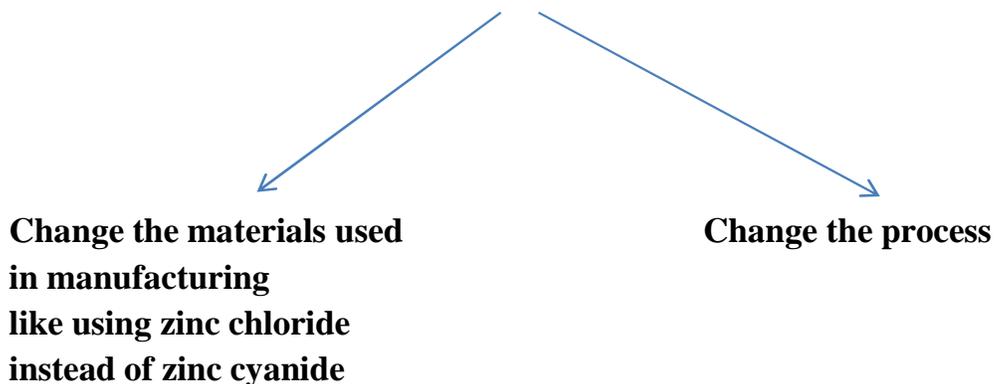
Include the followings:

- a- H.W landfills.
- b- Incinerators.
- c- Heavy metals recycling operations.
- d- Solvent recycling facilities.
- e- Traditional treatment process such as neutralization oxidation and precipitation.

6- Waste minimization and pollution prevention



Reducing the mass and volume of hazardous waste by



Source- Pathway- Receptor Analysis

How to solve H.W problems, first of all divide the problem into three conceptual categories:

1-Source

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

a- Concentration

b- Properties (density, solubility, flash point, and etc.)

2-Pathway

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

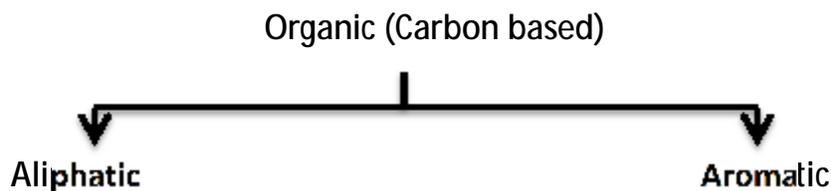
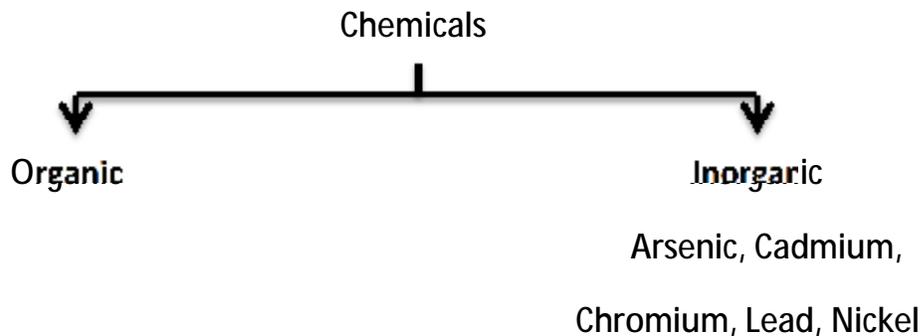
3-Receptor analysis: It's effect on human health and other species.

Lecture 4

Hazardous Waste Nomenclature

Hazardous Waste Nomenclature

Nomenclature is the naming procedure



Composed of straight or branched

Chains of carbon, classified as:

-Alkanes.

-Alkenes.

-Alkynes.

-Alcohols.

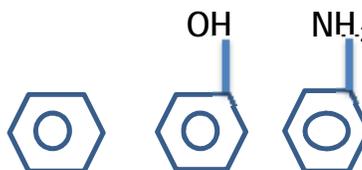
-Ethers.

-Etc.

Are characterized by

Carbon-Carbon

Based ring



Common Organic H.W

1- Petroleum:

Is a naturally occurring, complex mixture of hydrocarbons and other organic compounds of nitrogen, sulfur, and oxygen that were formed by a complex series of chemical and biochemical reactions from organic material deposited over geological time. It can be gaseous (natural gas), liquid (crude oil), and solid (asphalt) phases.

** Each source of petroleum is unique in composition and many characteristics are common among the different crude oil sources.

Petroleum products classified to

- a- Paraffin----Alkanes
- b- Olefin-----Alkenes
- c- Naphthens----Cycloalkanes
- d- Aromatics.

Source of pollution:

- a- Leaking (UST).
- b- Tanker truck accidents.
- c- Pipeline ruptures.

d- Oil rig blowout at sea.

2- Pesticides

Is a chemical, physical, or biological agent that destroys or controls pest organisms including insects, plants, fungi, rodents, fish, and nematodes (ديدان اسطوانية تتطفل على الحيوان او النبات وتعيش في الماء او (التربة).

Like DDT

Advantages:

- a- Disease reduction.
- b- Increased agricultural production.

Disadvantages:

Undesirable release of these toxic chemicals to the environment.

3- Explosives:

Is a quasi-stable chemical that rapidly changes from a solid or liquid to a gas following activation or detonation.

Advantages:

Used in:

- a- Mining.
- b- Highway construction.
- c- Quarrying.
- d- Demolition.
- e- Military applications.

Disadvantages:

Release to the environment have contaminated soils, water, and structures.

Inorganic (Metals and Non-Metals)

1- Arsenic (As)

Elemental arsenic is a gray crystalline material with a density of 5.727 g/cm^3 .

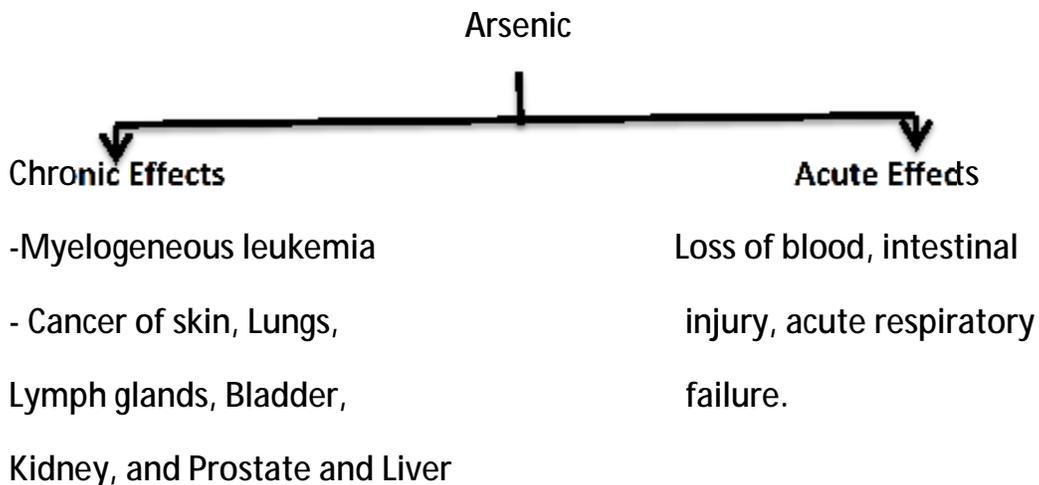
Most toxic form is AsH_3

As^{+3} ----- Characterized by intermediate toxicity.

As^{+5} ----- Least toxic form (still toxic).

Use of Arsenic:

- a- Agriculture.
- b- Manufacture of glass(remove color from glass during its production).
- c- Semiconductor industry.



Accidents

Poisoning of over 12000 Japanese children who drank milk contaminated with Arsenic resulting in 130 deaths.

2- Cadmium (Cd)

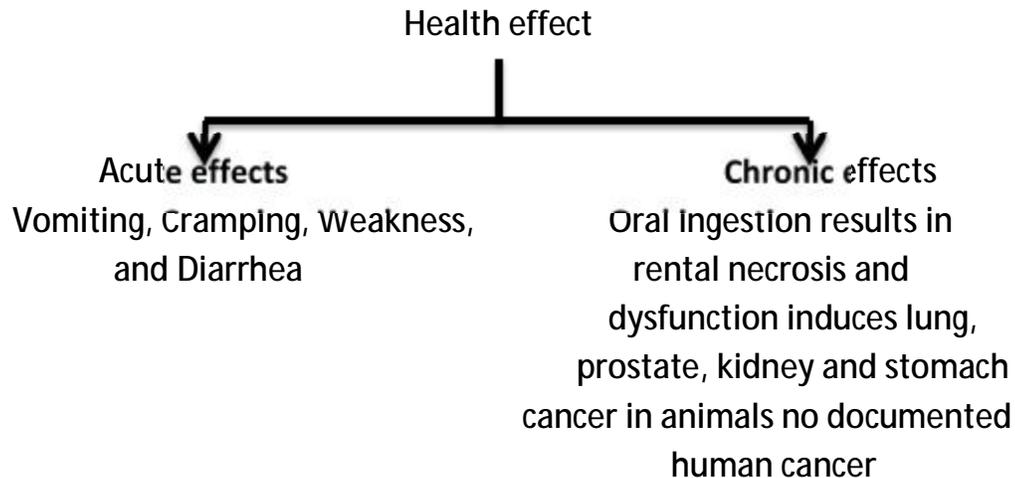
Found in +2 valence state

Cd ----- form complexes with cyanide, amines, and halides.

*Most common occurring form (CdS).

Cd is highly toxic metal used in paint pigments, electrochemical applications:

$\text{Cd}(\text{OH})_2$ serves as anode material



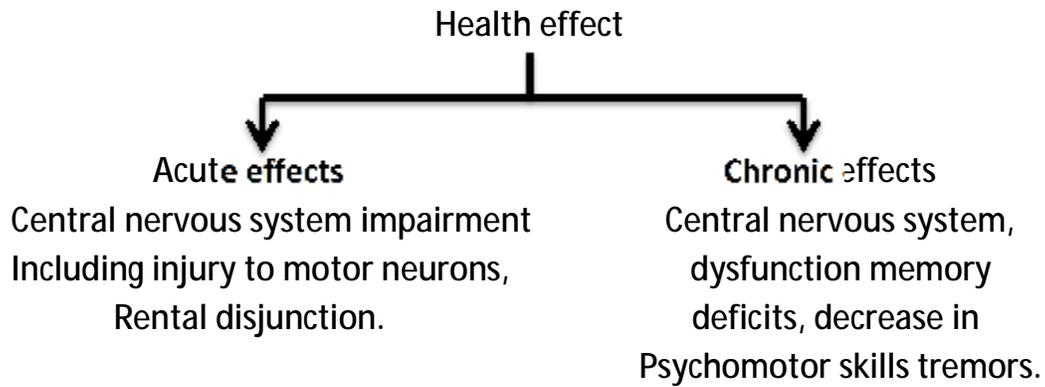
3- Mercury (Hg)

Mercury occurs naturally in the geosphere in concentrations ranging from 10 to 100 $\mu\text{g}/\text{kg}$.

Hg present as HgS

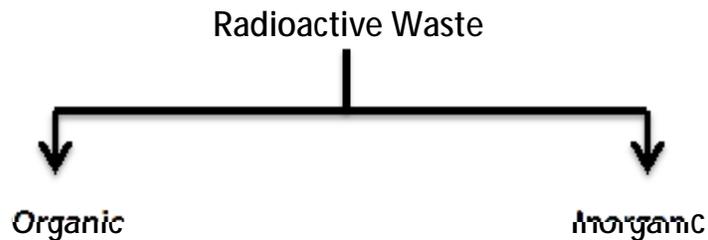
Hg uses are in

- a- Miniature batteries used in hearing aids, calculators and radio cameras.
- b- Mercury vapor lamp.
- c- Industrial catalyst in the production of caustic soda.
- d- Used in fungicide and insecticide.



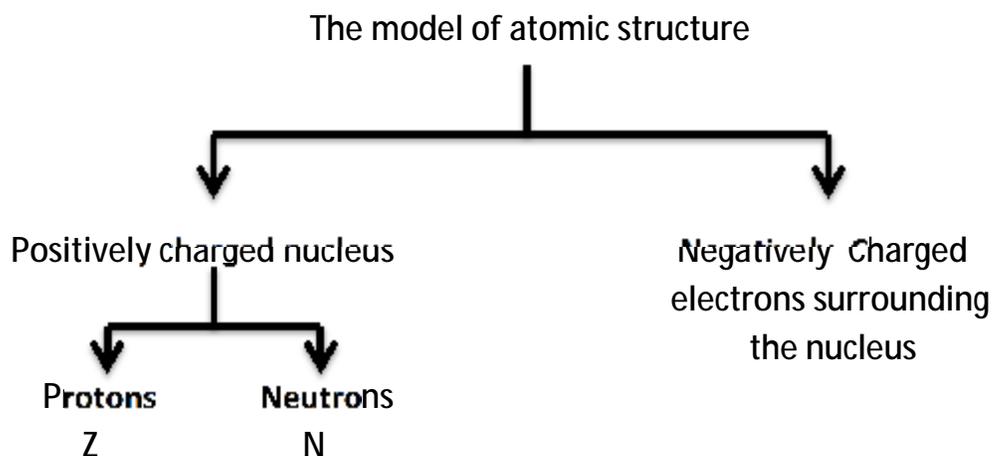
Nuclear Wastes

Radioactive waste management regulated by:
Nuclear Regulatory Commission (NRC).
Under Atomic Energy Act on 1954.



Radioactive waste pose hazard by emitting ionizing radiation

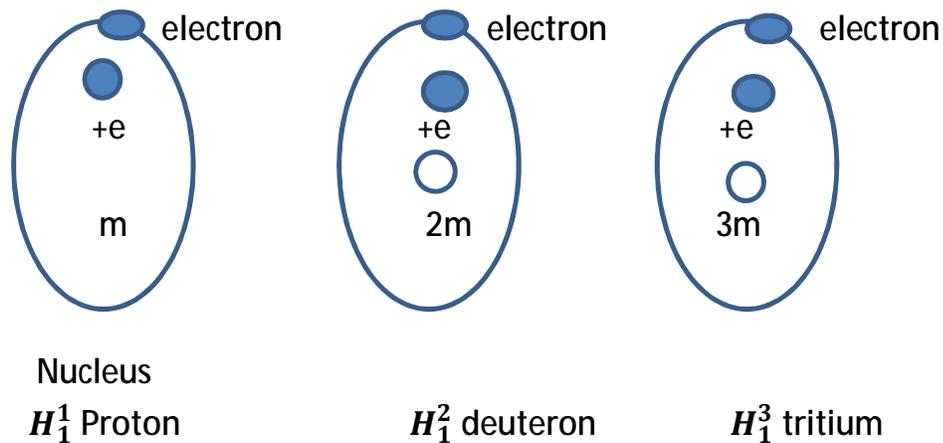
Radioactivity: Is the release of particles or radiation from the nucleus of an atom.



$$A=Z+N$$

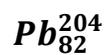
A: The atomic weight of the element.

*Species with the same no. of protons but different no. of neutrons are called isotopes.



The atomic structure of 3 hydrogen isotopes

Example:



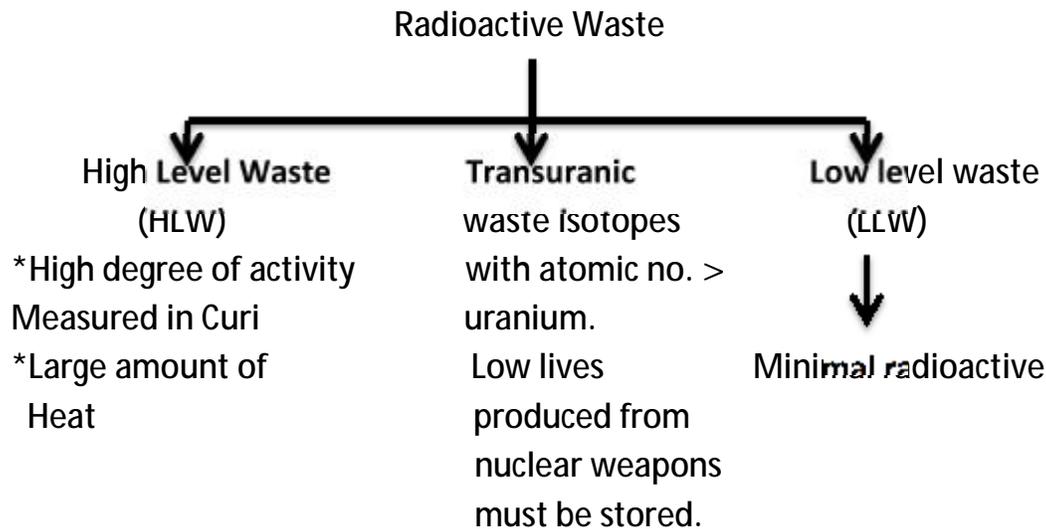
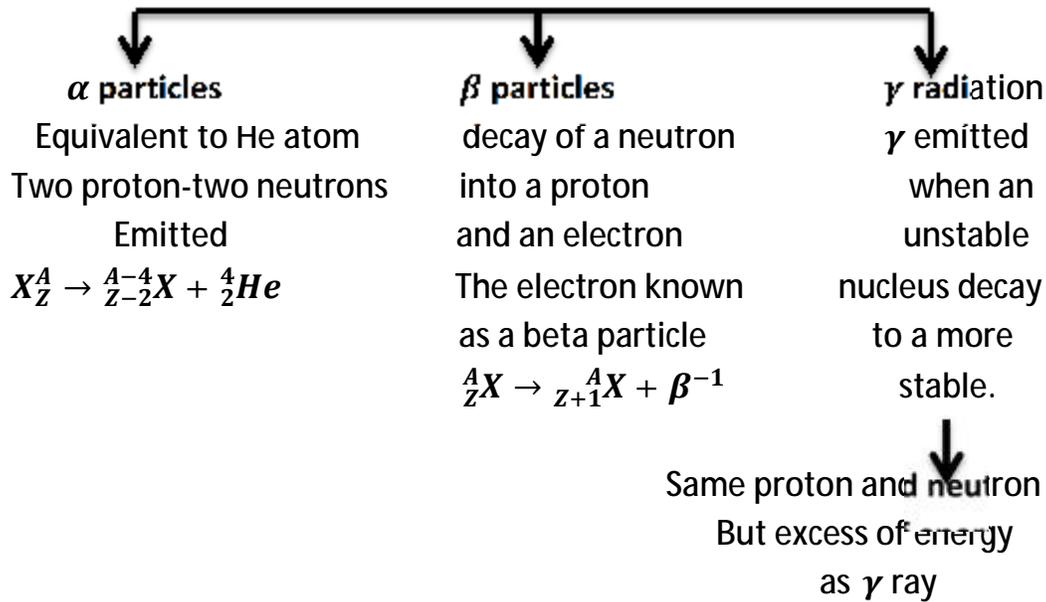
$$Z=82$$

$$A=204$$

$$N=204-82=122$$

Three types of radiation are emitted from nuclei

↓



Radioactive waste originate from:

- 1- Mining and milling activities.
- 2- Commercial sources (hospital, universities).
- 3- Nuclear reactors.
- 4- Nuclear weapons.

Advantages: (1) Many radioactive isotopes such as C^{14} , I^{131} , and P^{32} , have been used extensively in industry and research as tracers.

(2) Fuel in Nuclear Power Plant.

Disadvantages: Treatment because of the half life time of decay.

Chapter Three

Common Hazardous Waste Properties

- Concentration of hazardous chemicals depends on:
Whether they are present in:
 - 1- Water
 - 2- Solid
 - 3- Air

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

1-Concentration in water

For 1 L of water has a mass approximately 1 kg therefore :

$$\frac{\text{mg}}{\text{L}} \approx \frac{\text{mg}}{\text{kg}}$$

At 4°C , Specific gravity =1, and

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

At 20°C Density of water =0.998 g/cm³

And 1 $\frac{\text{mg}}{\text{l}}$ solution = 1 ppm

2-Concentration in soil and sludge (solids)

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

For solid the concentration is $\frac{\text{mass}}{\text{mass}}$

3-Concentration in air

$$\frac{\mu\text{g}}{\text{m}^3} = \frac{\mu\text{g of contaminant}}{\text{m}^3 \text{ of air}}$$

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

For air the concentration is $\frac{\text{volum}}{\text{volum}}$

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^3)

n=moles of gas

T=Temperature (K^0)

R= the universal gas constant (0.082 L. atm/mol. K)

The volume occupied by 1 mole of gas at standard temperature and pressure (0C^0 or 273K^0 and 760 mmHg or 1 atm) is 22.4 L or 0.0224m^3 ($1000 \text{L} = 1\text{m}^3$).

$$\text{Vol. of contaminant (m}^3) = \frac{\text{mass of contaminant}}{\text{molecular weight (g/mole)}} \times 0.0224 \frac{\text{m}^3}{\text{mole}}$$

$$n = \frac{\text{weight}}{\text{molecular weight}}$$

For any temperature and pressure:

$$\text{Vol. of contaminant} = \frac{\text{mass of contaminant}}{\text{M. weight}} \times 0.0224 \frac{\text{m}^3}{\text{mol}} \times \frac{T}{273\text{K}^0} \times \frac{760\text{mmHg}}{P}$$

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

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

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

C_{ppm} = The contaminant concentration in ppm

C = The contaminant concentration in g/m^3

R = Ideal gas constant $8.21 \times 10^{-5} \left(\frac{\text{m}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}^\circ} \right)$

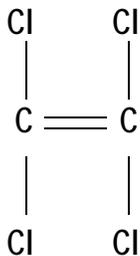
T = Temperature K°

P = Absolute pressure (atm)

M = Molecular weight (g/mol)

Example

During routine air sampling, the concentration of perchloroethylene (PCE) near a hazardous waste site was 120 mg/m^3 . The temperature was 16°C , and the atmospheric pressure was 730 mmHg. What was the PCE concentration in ppm?



Solution

To find the molecular weight of PCE

$C=12$, $\text{Cl}=35.5 \text{ g/mol}$

$\text{M.Wt}=2(12)+4(35.5)=166 \text{ g/mol}$

$\text{K}^\circ = \text{C}^\circ + 273$

$$T = 16 + 273 = 289 \text{ K}^{\circ}$$

$$730 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.961 \text{ atm}$$

Convert the concentration $\frac{\text{mg}}{\text{m}^3}$ to $\frac{\text{g}}{\text{m}^3}$

$$\frac{120 \text{ mg} \times \frac{\text{g}}{1000 \text{ mg}}}{\text{m}^3} = \frac{0.120 \text{ g}}{\text{m}^3}$$

$$C_{\text{ppm}} = \frac{0.120 \text{ g}}{\text{m}^3} \times \frac{8.21 \times 10^{-5} \frac{\text{m}^3 \text{ atm}}{\text{mol K}^{\circ}} \times 289 \text{ K}^{\circ}}{0.961 \text{ atm} \times 166 \frac{\text{gm}}{\text{mol}}} \times 10^6$$

$$= 17.8 \text{ ppm}$$

- Radioactivity

Is not measured by mass/volume, but as the rate of decay of nuclear particles.

Unstable radioactive elements reach stability by emitting α or β particles ----- This process is known as decay.

Activity: number of unstable nuclei present which is measured in directly by the rate of radioactive decay.

Units of activity:

Curi: amount of radioactive material containing unstable atoms characterized by 3.7×10^{10} disintegration/ second.

Example:

A 10 gm sample of dry sludge contains mixed hazardous wastes (radionuclides as well as hazardous inorganic and organic chemicals) in which β particles are emitted at a rate of 3×10^8 dps. Determine the specific activity of this sample.

Solution:

Convert the emission rate to Curi (Ci)

$$3 \times 10^8 \text{dsp} \times \frac{1 \text{ Ci}}{3.7 \times 10^{10} \text{dsp}} = 8.11 \times 10^{-3} \text{ Ci} = 8.11 \text{ mCi}$$

$$\text{Specific activity} = \frac{8.11}{10 \text{ gm}} = 0.811 \text{ mCi/gm}$$

Example:

How much energy will be released when two deuterons (H_1^2 nuclues) combine to form an alpha particle ($H_1^2 + H_1^2 \rightarrow H_2^4$)

Given atomic mass of $H_1^2 = 2.01474$ amu

And atomic mass of $H_2^4 = 4.00387$ amu

Solution:

$$\text{Energy released} = 2H_1^2 - H_2^4 = 2 \times 2.01474 - 4.00387 = 0.02561 \text{ amu}$$

And

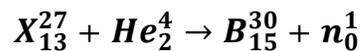
$$1 \text{ amu} = 931 \text{ Mev}$$

$$= 0.02561 \times 931 = 23.8 \text{ Mev}$$

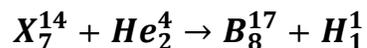
Example:

Complete each of the following by writing the nuclear reaction equation?

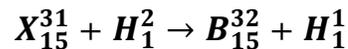
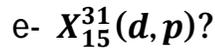
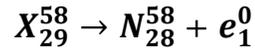
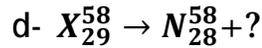
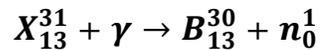
a- $X_{13}^{27}(\alpha, n)$?



b- $X_7^{14}(\alpha, p)$?



c- $X_{13}^{31}(\gamma, n)$?



Common Hazardous Waste properties

- 1- Water solubility.
- 2- Density and specific gravity.
- 3- Light and dense non aqueous phase liquids.
- 4- Flammability limits.
- 5- Flash point and ignition temperature.
- 6- Chemical incompatibility.

1-Water solubility

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

-Water solubility controls the environmental fate of waste

في حالة حصول تلوث للمياه الجوفية بمادة الكازولين فأنها تطفو فوق السطح وبالتالي لانها لاتذوب بالماء تنفصل في طبقة الى الاعلى بينما الميثانول الذائب لايطفو على السطح

Materials



Hydrophobic
Water hating

Hydrophilic
Water loving

$$\text{Water solubility} \propto \frac{1}{\text{sorptionity, bioaccumulation, and volatilization}}$$

Main Factors That Affect Water Solubility

1-Temperature

تزداد الذوبانية بازدياد درجة الحرارة ولذلك معظم القياسات تكون تحت درجة حرارة 25 درجة مئوية وهي اعلى قليلا من درجة حرارة الغرفة.

Water Solubility measured in mg/l for hazardous waste starts

From 1 mg/l to 100000 mg/l

2- Water solubility of both inorganic and organic compounds is related to their structure and size.

Water is highly polar \longrightarrow Charged and very polar organic and inorganic species exhibit high water solubility.

The solubility is based on attractive force between the solute and solvent molecules. They are:

- a- Van der Waals force
(the interaction of electron orbitals between adjacent molecules)
- b- Hydrogen bonding, which occurs primarily with molecules containing hydroxyl (OH^-) and amino (NH_2^-) groups.
- c- Dipole-dipole interactions

-Also size and shape affect its water solubility (WS)

$$WS \propto \frac{1}{\text{molar volume}}$$

-The presence of some functional groups (COOH, I, B..) decreasing water solubility.

Water Solubility of Weak Acids and Bases

كل الحوامض العضوية تعتبر حوامض ضعيفة وكذلك القواعد العضوية مقارنة باللاعضوية التي تعتبر حوامض وقواعد قوية مثل (HCL) وغيرها.

For dissociation of a weak acid in aqueous solution:



Acidic form basic form

Equilibrium expression:

$$K_a = \frac{[base][H^{+}]}{[acid]} = \frac{[RCOO^{-}][H^{+}]}{[RCOOH]}$$

Where K_a (ثابت تفكك الحامض الضعيف)

$$K_a = \frac{[base]}{[acid]} [H^{+}]$$

$$pH = -\log [H^{+}]$$

-As the pH scale applies only to aqueous media

-Since most organic compounds are insoluble in water (slightly), therefore organic reactions and associated acidity are usually carried out in non-aqueous solutions.

The expression K_a may easily converted to PK_a

Because $-\log x$ is defined as Px

PK_a , used as a more appropriate value or measure for organic compounds.

$$PK_a = -\log K_a$$

From:

$$K_a = \frac{[base]}{[acid]} [H^+]$$

نأخذ (-) اللوغاريتم للطرفين

$$-\log K_a = -\log [H^+] + \left(-\log \frac{[base]}{[acid]}\right)$$

$$PK_a = pH - \log \frac{[base]}{[acid]}$$

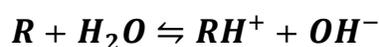
$$pH = PK_a + \log \frac{[base]}{[acid]}$$

The above equation is Henderson- Hasselbalch equation

A weak organic base is characterize by accepting a proton base association constant K_b is defined as:

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

Where K_b (ثابت تفكك القاعدة الضعيفة)



$$K_w = [H^+][OH^-] = 10^{-14}, \text{ where } [OH^-] = \frac{K_w}{[H^+]}$$

$$K_w = 10^{-14} : (\text{ثابت تفكك الماء})$$

Or

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

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

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

The fraction of un-ionized base

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

Example:

What are the concentrations of 2, 4,6-trichlorophenol and 2, 4, 6-trichlorophenolate. of a 0.1 mM . 2, 4, 6- trichlorophenol solution is adjusted to a pH of 7.0? Also determine α for these conditions?

Solution:

PK_a of trichlorophenol=6.15, At pH 7.0 (given from tables)

$$pH = PK_a + \log \frac{[base]}{[acid]}$$

$$7.0 = 6.15 + \log \frac{[trichlorophenolate]}{[trichlorophenol]}$$

$$\frac{[trichlorophenolate]}{[trichlorophenol]} = 7.08 \text{ (من المعادلة اعلاه وناتج الطرح نأخذ له عكس اللوغارتم)}$$

$$[trichlorophenolate] + [trichlorophenol] = 0.1mM$$

Then

$$[\text{trichlorophenate}] = 0.0876 \text{ mM}$$

$$[\text{trichlorophenol}] = 0.9124 \text{ mM}$$

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

$$PK_a = -\log K_a$$

We take - anti log of 6.15 to find K_a

$$K_a = 7.08 \times 10^{-7}$$

$$\alpha = \left[1 + \frac{7.08 \times 10^{-7}}{1 \times 10^{-7}} \right]^{-1} = 0.124$$

Where:

$$K_w = 10^{-14} = [H^+][OH^-]$$

2- Density and Specific Gravity

Density: is defined as the ratio of mass to volume and is usually expressed in *g/ml* or *kg/m³*.

Specific gravity: is dimensionless number analogous to density.

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

Density of water=1 g/ml at 4C^o

Density of a compound=specific gravity × density of water

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.

Specific gravity ranges (0.6-2.9) for organic compounds.

-Ethers, alcohol and esters are less dense than water.

- Metals are more dense than water

Vapor density: is analogous to specific gravity. It is defined as the density of a compound in the vapor phase (with no air present) to the density of air.

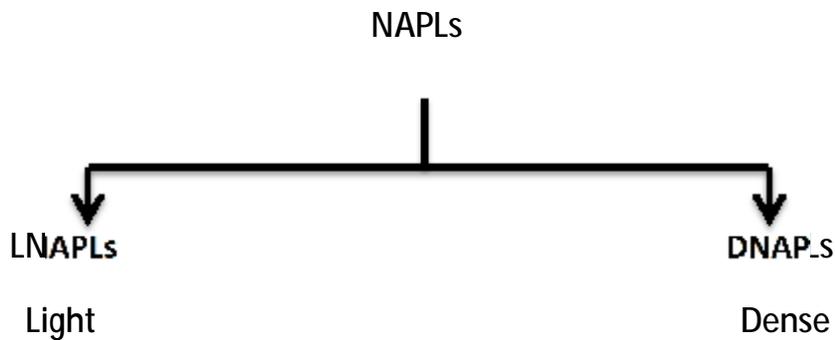
Air relative vapor density=1

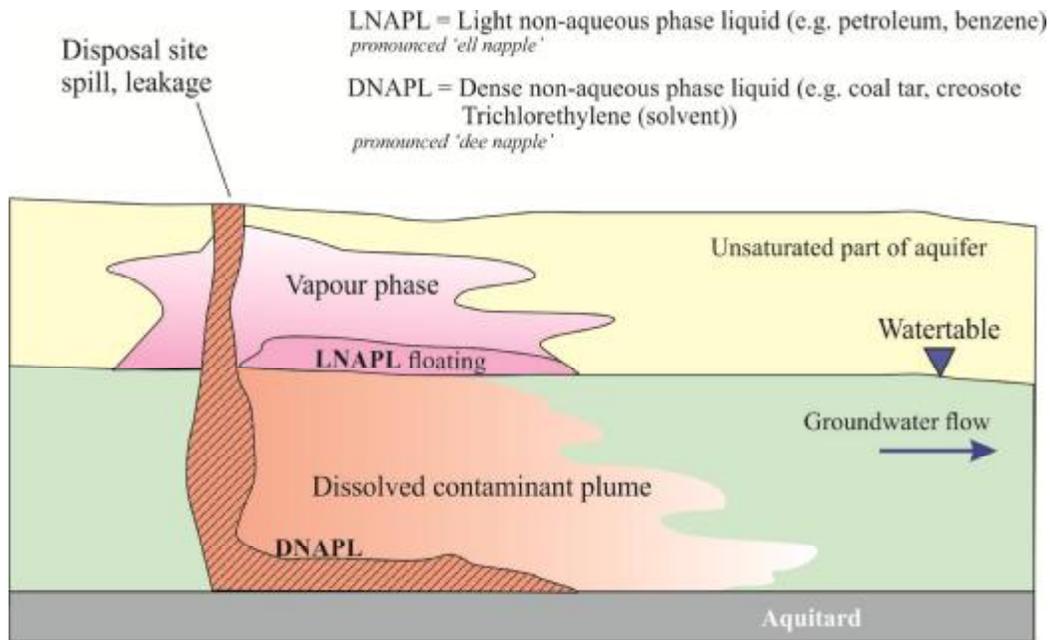
Vapor density is important in assessing the fate of a gas

Example: Chlorine gas, if allowed to escape from a tank stays close to the ground. Because its vapor density is 3.8

3.8 times more dense than air.

3- Light and Dense Nonaqueous Phase Liquid





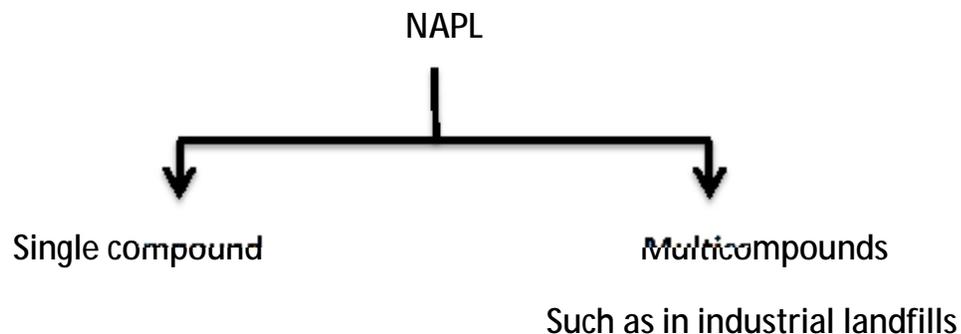
Organic contaminants, like petroleum fuels and solvents may be present as a free liquid, dissolved liquid (in water) and as vapour

Fig above shows the light and dense NAPLs

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

For LNAPLs the chemicals are:

- 1- Float on the surface of ground water.
- 2- Observed by visual inspection of well samples, soil core, or well cuttings.



Example:

A 208 L (55 gal) drum of TCE has spilled into a 10000 L (2640 gal) covered water storage reservoir. If volatilization losses are negligible and TCE dissolves to the level of its approximately determined water solubility, estimate the proportion of TCE in both the NAPL and the dissolved phases. Where will the NAPL phase be found at the top or the bottom of the reservoir? S.g of TCE=1.464, water solubility of TCE=1310 mg TCE/L water.

Solution:

$$\text{Density of TCE} = 1.464 \frac{g}{ml} = 1.464 \times \frac{1 kg}{1000 g} \times \frac{1000 ml}{1L} = 1.464 \frac{kg}{L}$$

$$208 L \times 1.464 \frac{kg}{L} = 305 kg TCE$$

$$10000 L \text{ water} \times 1310 \frac{mg TCE}{L \text{ water}} \times \frac{kg}{10^6 mg} = 13.1 kg \text{ dissolved}$$

Therefore the proportion of TCE dissolved is

$$\frac{13.1 kg \text{ aqueous phase TCE}}{305 kg \text{ total TCE}} \times 100\% = 4.3\% \text{ dissolved}$$

$$100\% - 4.3\% = 95.7\% \text{ in the NAPL phase}$$

The NAPL phase would be found at the bottom of the reservoir because the s.g of TCE (1.464) is greater than the s.g of water which is 1.

Dissolution: The transport of a compound from its insoluble phase into the water, it is the mechanism that controls the rate at which pollutants move into aqueous systems.

This process is the rate-limiting step in the remediation of contaminated ground water.

Dissolution occurs when the chemicals within an overlying (light) or underlying (dense) pool of NAPL move across the NAPL-water phase boundary.

The potential for dissolution is α to the difference between the water solubility and the actual concentration in the aqueous phase.

$$\frac{dc}{dt} \propto (c_s - c)$$

$$\frac{dc}{dt} = \text{rate of change of dissolution} \frac{mg}{L/min}$$

$$c_s = \text{contaminant water solubility} \left(\frac{mg}{L} \right)$$

$$c = \text{residual contaminant concentration} \left(\frac{mg}{L} \right)$$

$$\frac{dc}{dt} = k(c_s - c)$$

$$k = \text{a mass transfer coefficient} (min^{-1})$$

K increased through:

- 1- Increase mixing.
- 2- Increase surface to volume ratio.

في هذه الحالة نريد تقليل (k) لتقليل الجريان وال (dissolution)

- The solubility behavior of a mixture of NAPLs is more complex than that of single- component system.
- In this system effective solubility is the true solubility under real world conditions which is less than the water solubility of a single compound in the laboratory.

$$S_i^e = X_i S_i \gamma_i$$

X_i : mole fraction of compound i in the NAPL mixture

S_i^e : effective solubility of compound i $\left(\frac{mg}{L} \right)$

S_i : environmental water solubility of i in a single component

$$\text{system } \left(\frac{\text{mg}}{\text{L}}\right)$$

γ_i : *correction factor that normalizes solubility based on field conditions and water chemistry*

Example:

A release of gasoline from an underground storage tank (UST) has resulted in the presence of a large lens of an LNAPL on the surface of an aquifer. Estimate the effective solubility of benzene in the aquifer if $X_{benzene} = 0.06$ and $\gamma_{benzene} = 0.5$ and water solubility of benzene = 1770 mg/l.

Solution

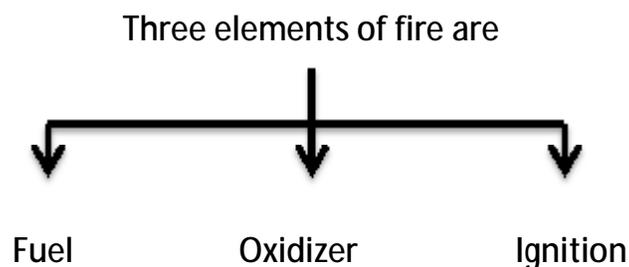
$$\begin{aligned} Si^e &= X_i S_i \gamma_i \\ &= 0.06 \times 1770 \times 0.5 \\ &= 53 \text{ mg/L} \end{aligned}$$

4- Flammability Limits

-Hazardous waste defined by RCRA may be also corrosive, explosive and flammable.

-Some chemicals volatilize if stored in open drums, the vapor may then ignite in the presence of a spark or open flame if they are within a specific range of concentrations in the air.

-Fire is defined as the rapid, exothermic oxidation of fuel.



-At low vapor concentrations, insufficient mass is available for flame propagation (the mixture is " too lean" to burn or explode)



Lower flammability limits (LFLs)

-At high concentrations, there is a threshold concentration that limits combustion(the mixture is "too rich")



Upper flammability limits (UFLs)

-These concentrations, usually expressed in percent%.

The LFLs and UFLs for Hazardous Waste compounds usually listed in tables.

-Most HW disposal and storage areas contain mixtures of chemicals that have flammability limits different from single component systems.

Le Chatelier equation:

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

Where:

LFL_i = the LFL for component i.

y_i = mole fraction of component i in the mixture.

n= the number of components in the mixture.

And

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

Example:

Determine the LFL and UFL of a gaseous mixture (v/v) of 0.65% acetone, 0.2% decane, and 0.3% hexane? Given LFLs; 2.6, 0.8, and 1.1 for acetone, decane, and hexane and UFLs; 12.8, 9.2, and 7.5 for them respectively.

Solution

- 1- Calculate the mole fraction of each species, based on the Ideal Gas Law, the number of moles of each gas directly proportional to its volume:

$$X_{acetone} = \frac{0.65}{0.65 + 0.2 + 0.3} = 0.565$$

$$X_{decane} = \frac{0.2}{0.65 + 0.2 + 0.3} = 0.174$$

$$X_{hexane} = \frac{0.3}{0.65 + 0.2 + 0.3} = 0.261$$

- 2- Given values of LFLs and UFLs:

$$LFL_{mixture} = \frac{1}{\frac{0.565}{0.6} + \frac{0.174}{0.8} + \frac{0.261}{1.1}} = 1.49\%$$

$$UFL_{mixture} = \frac{1}{\frac{0.565}{12.8} + \frac{0.174}{9.2} + \frac{0.261}{7.5}} = 10.2\%$$

Although LFL, and UFL, are available for hundreds of hazardous chemicals .

If the data are not available empirical relationship may use.

$$LFL = 0.55 C_{st}$$

$$UFL = 3.50 C_{st}$$

Where C_{st} = the % fuel in air

(defined by combustion stoichiometry)

The combustion of most organic compounds



And

$$z = m + \frac{x}{4} - \frac{y}{2}$$

Where:

$$z = \frac{\text{moles of } O_2}{\text{moles of organic compound burned}}$$

$$C_{st} = \frac{\text{moles of compound}}{\text{moles of compound} + \text{moles of air}} \times 100\%$$

And

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

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

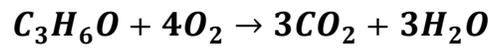
Example

Estimate the LFL and UFL for acetone

Solution



or



m=3

x=6

y=1

z=4

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

$$LFL = \frac{0.55(100)}{4.76(3) + 1.19(6) - 2.38(1) + 1} = 2.74\%$$

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

$$UFL = \frac{3.5(100)}{4.76(3) + 1.19(6) - 2.38(1) + 1} = 17.5\%$$

5- Flash Point and Ignition Temperature

Flash point: The minimum temperature at which a compound emits sufficient vapor to form an ignitable mixture with air.

An ignitable mixture: A vapor-air combination within the flammability limits capable of propagation a flame away from a source of ignition.

Flash point determination:

1- EPA Method 1010 (EPA is Environmental Protection Agency)

To determine the flash point for hydrocarbon mixtures, solids suspensions and other liquids.



Pensky-Martens closed-up testing system

Stirred sample is heated at periodic time. The stirred is stopped, a small flame is directed into the cup. The lowest temperature the flame ignites the vapor in the cup is the flash point of the sample.

2- EPA (1020) Method (Seta Flash Closed Tester)

Used for jet fuel, paints ..etc. with flash point between (0 and 145)°C.

Samples is injected into the system temperature is increased until flash is observed.

3- Tag Closed Tester

To evaluate liquid with flash points lower than 93°C.

4- The Cleveland Open Cup Tester used for petroleum products (flash point less than 79°C)

5- Tag Open Cup System (for low flash points).

6-Chemical Incompatibility

When combining HW, these materials must be combined and stored in a manner so that mixing does not result in chemical reactions that cause safety and health hazard, these reactions result from chemical incompatibility.

The consequences of these chemical reactions are:

- 1- Fires.
- 2- Explosion.
- 3- Evolution of heat and toxic gases.

Chemical Incompatibility can result from the heat evolved by mixing two incompatible solutions

$\Delta H_{mix} = 0$ for ideal mixing

Where ΔH enthalpy infinite dilute acid and base

Non ideal mixing, when $\Delta H \neq 0$

Heat evolving

Labels and Placards

Used to identify potential dangers during transportation and storage of HW and hazardous materials.

1- Transportation

Controlled by the U.S. Department of Transportation (DOT) and requires the placement of placards on the outside of vehicles transporting hazardous material to aid in assessing the potential hazard of a spill.

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

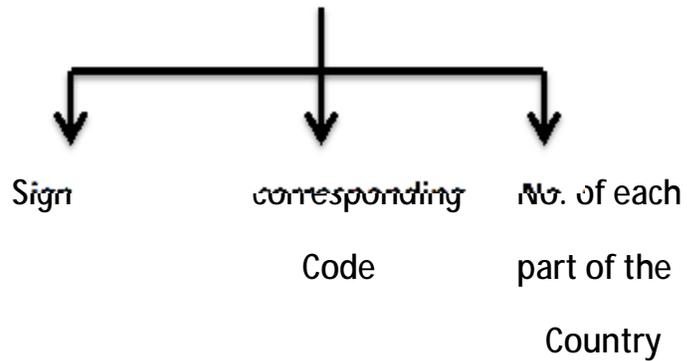
توضع العلامة لاكثر من 1000 باوند ماعدا الحالات الاربعة اي كمية تضاف

DOT classified materials based on 9 hazardous classes.





The placard is of diamond shape have colored background



رقم المنطقة الى الاسفل

2- Storage

Requires labels under a system developed by National Fire Protection Association (NFPA).



Drum awaiting for treatment or disposal



System focuses on 3 categories in defining Hazards

1-Health

2-Flammability

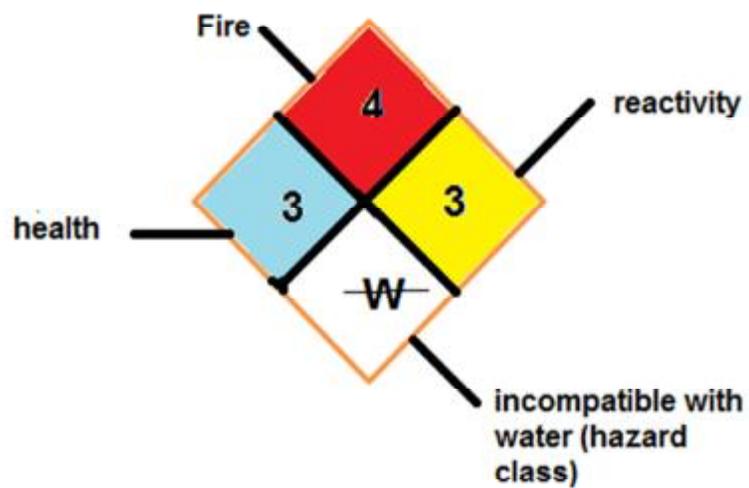
3-Reactivity

Each 5 levels of hazards, and the 5 levels ranging from 0 to 4

0= no hazard

4= severe hazard

Also in diamond shape



0=No hazard

Health= blue

Reactivity=Yellow

Fire=red

4=Extremely hazardous

Hazard Class= white

Hazardous waste site assessment

Site assessment divided into 3 phases

1- Phase I

or level I and contains the followings:

- a- Studies involve paper research (record research)
- b- Historical document (newspapers reports of spills ..etc)
- c- On-site inspection (walk through the site).

2- Phase II

Study to confirm or deny the presence of HW at the site involve

- a- Sampling (wells to find GW)
- b- Chemical analysis
- c- Path ways and receptors

3- Phase III

Investigation the extent of contamination in the area, volume and contamination concentration

Overall to provide criteria for the design of remedial processes.

Example

A 1890 L tanker containing a 40% formulation of 2,4-D in acetone has spilled, contaminating an area of soil approximately 200 m^2 and 50 cm deep. If the soil bulk density is 1800 kg/m^3 , estimate the 2,4-D concentration in soil?

Solution

The volume of 2,4-D spilled= $1890\text{L} \times 0.4 = 756\text{L}$

Given specific gravity of 2,4-D=1.416 g/ml

$$756\text{ L} \times \frac{1000\text{ml}}{\text{L}} \times \frac{1.416\text{g}}{\text{ml}} = 1.07 \times 10^6\text{g} = 1.07 \times 10^9\text{mg}$$

Determine the volume and mass of soil:

$$200\text{m}^2 \times 0.5\text{m} = 100\text{m}^3$$

$$100\text{m}^3 \times \frac{1800\text{kg}}{\text{m}^3} = 180000\text{kg}$$

$$\text{The estimated concentration} = \frac{1.07 \times 10^9\text{mg}}{180000\text{kg soil}} = 5960 \frac{\text{mg}}{\text{kg}} \text{ of } 2,4 - \text{D}$$

