

CHEMICAL HAZARDS AND REACTIONS

1.0 INTRODUCTION

Exposure to chemicals is the most common and may be the most significant health hazard that personnel face during field activities. Chemicals may be hazardous because they are either toxic, flammable, combustible, explosive, corrosive, radioactive, biologically active, or some combination of these and other characteristics. In addition, a chemical may combine with other chemicals to create new hazards. The use and storage of chemicals should take into account any inherent hazards posed by specific chemicals, incompatibilities, or other relevant information. This module discusses the characteristics of chemical hazards, how they are determined, and where to find more information on chemical hazards.

Learning Objectives

At the end of this module, you will be able to:

- Recognize chemical hazards commonly encountered in the field
- Provide examples of physical and chemical characteristics of contaminants
- Explain warning properties of various chemical hazards
- Describe how to evaluate and control these hazards.

2.0 CHEMICAL HAZARD RECOGNITION

The degree of hazard associated with a particular chemical will depend on its physical properties, toxicity, the way it is used, and the environment in which it is encountered. The degree of hazard represented by a chemical depends upon many factors. These factors are described in the sections that follow.

2.1 Physical Classification

Chemicals may be found in solid, liquid, aerosol, and gas or vapor form. The degree of danger varies according to the form of the chemical. For example, liquid chlorine bleach (sodium hypochlorite) can affect not only the skin, but also the eyes and respiratory tract. The toxicity of a chemical agent depends in part upon its "route of entry" (see "Toxicology"). Inhalation, ingestion, skin absorption, and eye contact, and injection are generally considered the four routes of entry.

2.1.1 Solids

The following is information regarding the physical classification of chemicals as solids:

- Not all forms of a chemical pose a health hazard. For example, a lead pipe is not a significant health hazard. However, the lead can become a human health hazard if the pipe is sanded or welded, producing lead dust or fume. The dust or fume can become airborne and be inhaled, or it can leach into water and be ingested.

- A chemical may be hazardous even in solid form. For example, individuals who are sensitized to nickel may develop dermatitis from skin contact with the metal. Fuming solids emit toxic vapors that may be inhaled. Some materials, such as pesticides, can evaporate directly from solid form.
- Some solids are not a hazard alone but become hazardous when they come into contact with other chemicals (e.g., acid in contact with iron can release hydrogen gas).

2.1.2 Liquids

The following is information regarding the physical classification of chemicals as liquids:

- Many liquids are hazardous when they contact the skin either because they damage the skin or they are easily absorbed through the skin. It is important to remember that chemicals that can damage or be absorbed through the skin will have this effect on all skin, not just the hands.
- The degree of hazard associated with a liquid depends on the characteristics of the liquid and handling practices. If, for example, inhalation is the most significant route of entry for a chemical, then its vapor pressure is important in determining the degree of hazard for the agent. Cold liquid, or liquid with a low vapor pressure, may be expected to create a low airborne concentration. Hot liquids, or liquids with a high vapor pressure, may produce high airborne concentrations. Whether the airborne concentration is hazardous will depend on the toxicity of the chemical.
- In some cases, the chemical allows other contaminants to penetrate the skin. For example, dimethyl sulfoxide (DMSO) is extremely well absorbed and is used in medicine to transport drugs through the skin.
- Liquids can present a splash hazard to the skin and eyes. Appropriate protective equipment (e.g., goggles, faceshield) and clothing (e.g., gloves, coveralls) must be worn to prevent contact with eyes and skin.
- If spilled, liquids can create a slippery surface.
- Some liquids combine easily with other chemicals to produce hazardous substances. For example, household bleach, when combined with ammonia-based cleaning solutions, produces a much more hazardous substance than either of the two original components.

2.1.3 Aerosols

The following is information regarding the physical classification of chemicals as aerosols:

- Aerosol is a term used to describe fine particles (solid or liquid) suspended in air. Examples of aerosols include dust, fume, mist, fog, smoke, and smog.
- Table 1 describes some characteristics of aerosols.
- Knowing how various aerosols are generated and the expected size of the aerosol will help you anticipate where hazards may exist in the field.
- The size of the aerosol will determine where it will settle in the respiratory system.
- Aerosols may be a hazard to the eyes, skin, and the respiratory system.

2.1.4 Gases and Vapors

The following is information regarding the physical classification of chemicals as gases and vapors:

- A gas is a state of matter in which the molecules are unrestricted by cohesive forces.
- Vapors are the evaporation products of chemicals that are normally liquid at room temperature.
- Routes of entry associated with gases and vapors are inhalation, and eye or skin exposure.

Some characteristics of gases and vapors are given in Table 1.

Table 1
Characteristics of Air Contaminants in Work Places

Form	How Generated	Example/Size (micrometers)	Concentration Expressed As
Dust	From solids by mechanical means: - grinding - blasting - drilling	Quarry dust (less than 1 to 10)	mg/m ³ (1)
Fumes	Condensation products of metals and solid organics, welding on metal	Lead fume (less than 0.001 to 50)	mg/m ³
Mist	Liquid droplets formed by atomizing liquids or condensing liquids from vapors	Chromic acid mist	mg/m ³
Smoke	Products of combustion of organic materials	Incinerator (less than 0.5)	mg/m ³
Gases & Vapors			
Gases	Occupy space of enclosure, liquify only under increased pressure and decreased temperature	CO, Hydrogen H ₂ S	ppm(2)
Vapors	Evaporation products of substances normally liquid at room temperature (solvents, gasoline).	Acetone,	
Carbon disulfide, Benzene	ppm		

- (1) mg/m^3 – milligrams of contaminant per cubic meter.
- (2) ppm – parts of gas or vapor per million parts of air.

3.0 PHYSICAL AND CHEMICAL CHARACTERISTICS

Knowing the physical and chemical characteristics of the chemicals you anticipate finding during a field activity can help you recognize potential hazards and appropriately protect yourself. You can find the details on the physical and chemical characteristics by referring to the chemical's Material Safety Data Sheet (MSDS). Also, the National Institute of Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards contains basic information on many chemicals encountered in the field. Refer to “Hazard Communication,” for more information on MSDSs.

3.1 Solubility

Solubility is the ability of a solid, liquid, gas, or vapor to dissolve in a solvent. An insoluble substance can be physically mixed or blended in a solvent for a short time but is unchanged when it finally separates. The solubility of a substance is independent on its density or specific gravity. Solubility is important when determining health effects, reactivity, dispersion, and methods of cleanup and treatment. Solubility is generally expressed in parts per million (ppm) or as a percentage (0-100%).

3.2 Specific Gravity/Density

Specific gravity (SpG) is the ratio of the density of a substance (at a given temperature) to the density of water at the temperature of its maximum density.

Density of a substance is its mass per unit volume, commonly expressed in grams per cubic centimeter (g/cc). The density of water is usually accepted as 1 g/cc since 1 cc has a mass of 1 g for water at 4°C. Numerically, SpG is equal to the density in g/cc, but is expressed as a pure number without units. If the SpG of an insoluble substance is greater than 1 (the SpG of water), it will sink in water (e.g., methylene chloride). The substance will float on water if its SpG is less than 1 (e.g., oil/petroleum products). This is important when considering containment, cleanup, disposal and treatment alternatives.

3.3 Vapor Density

The density of a gas or vapor can be compared to the density of the ambient atmosphere. If the density of a vapor or gas is greater than that of the ambient air, then it will tend to settle to the lowest point. If the vapor density is close to the density of air or lower, the vapor will tend to disperse in the atmosphere.

In settling, dense vapor (v.d. >1) creates many hazards. If the vapor displaces enough air to reduce the atmospheric concentration of oxygen below 16%, asphyxia may result. If the vapor is toxic, then inhalation problems predominate even if the atmosphere is not oxygen deficient. If a substance is explosive and very dense, the fire/explosive hazard may be in the form of vapor trails which can spread far from the liquid. Flashback can then occur if an ignition source is present.

3.4 Vapor Pressure

The pressure exerted by a vapor against the sides of a closed container is called vapor pressure. It is temperature dependent. As temperature increases, so does the vapor pressure. Thus, more liquid evaporates, vaporizes or volatilizes. The lower the boiling point of the liquid, the greater the vapor pressure it will exert at a given temperature. Values for vapor pressure are most often given as millimeters of mercury (mm Hg) at a specific temperature. Usually the higher the vapor pressure, the more volatile the substance.

3.5 Boiling/Melting Point

Boiling point is the temperature at which liquid changes to a vapor, or the temperature when the pressure of the liquid equals atmospheric pressure. The opposite changes in phases is the condensation point. A major consideration with toxic substances is how they enter the body. With high-boiling-point liquids, the most common entry is by body contact (skin absorption). Low-boiling-point liquids are most commonly inhaled.

Melting point is the temperature at which a solid, when heated, changes to a liquid. This temperature is also the freezing point, because a liquid can change phase to a solid. The proper terminology depends on the direction of the phase change. If a substance has been transported at a temperature that maintains a solid phase, then a change in temperature may cause the solid to melt. The particular substance may exhibit totally different properties depending on phase. One phase could be inert while the other is highly reactive. Thus, it is imperative to recognize the possibility of a substance changing phase due to changes in the ambient temperature.

3.6 Flashpoint

Flashpoint is the lowest temperature at which a liquid gives off enough vapor to form an ignitable mixture at standard temperature and pressure with air and produce a flame when an ignition source is present. If the ambient temperature is right, then a material may give off enough vapor at its surface to allow ignition by an open flame or spark. If the vapor does ignite, combustion can continue as long as the temperature remains at or above the flashpoint. The flashpoint is one of the types of information used to classify the relative fire hazard of a liquid and varies with different chemicals. Flashpoints of common flammable/combustible liquids are provided in Table 2.

Table 2
Flashpoint Temperatures of Flammable Liquids

Chemical	Flashpoint
Ethyl ether	-49°F
Gasoline	-45°F
Carbon disulfide	-22°F
Acetone	-4°F
Petroleum ether	0°F
Benzene	10°F
Lacquer thinner	12°F
Methyl ethyl ketone	22°F
Xylene	29°F
Toluene	40°F
Isopropyl alcohol	53°F

3.7 Autoignition Temperature

The minimum temperature required to initiate or cause self-sustained combustion in any substance in the absence of a spark or flame is referred to as the autoignition temperature. Ignition temperature varies, depending upon the test method. These temperatures are very high - commonly in the hundreds of degrees. Some approximate ignition temperatures are the following:

acetone	537.7°C (1000°F)
amyl acetate	398°C (750°F)
aniline	537.7°C (1000°F)
butane	430°C (806°F)
carbon disulfide	100°C (212°F)
ethyl ether	180°C (356°F)
phenol	715°C (1319°F)
toluene	537.7°C (1000°F)
pine shavings	265°C (507°F)
cotton batting	230°C (446°F)
magnesium powder	472°C (883°F)
nitrocellulose film	137°C (279°F)

3.8 Explosive Limits

The range of concentrations of gases in air which will support the explosive process is bounded by measurable limits called Upper Explosive Limits (UEL) and Lower Explosive Limits (LEL). The flammable range is the optimal chemical fuel concentration in air for the ignition and the sustenance of combustion. The lowest concentration of fuel in this range is the LEL or Lower Flammable Limit (LFL). The highest ratio that is flammable is the UEL or Upper Flammable Limit (UFL).

Concentrations less than the LEL/LFL are not flammable because there is too little fuel; the mixture is too "lean" to burn. Concentrations greater than the UEL/UFL are not flammable because there is too much fuel and not enough oxygen. The mixture is too "rich" to burn. Fuel concentrations between the LEL/LFL and UEL/UFL are optimal for starting and sustaining fire and are called a material's flammable range. The lower the LEL and the greater the flammable range, the greater the hazard.

4 WARNING PROPERTIES

Warning properties, such as those described in the following sections, are examples of characteristics that could alert you to the presence of a chemical in the air.

4.1 Odor Threshold

The odor threshold is the airborne concentration (ppm) at which a hazardous chemical can be detected by smell. It is considered to be one of the warning properties of gases and vapors but must always be used with caution because of variations between individuals and their senses of smell. Allergies, head colds, and olfactory fatigue also can reduce one's ability to smell.

Ammonia is a good example of a chemical with a "useful" odor threshold. One reference indicates that ammonia can be detected by smell at 5 ppm which is 5 times lower than its Threshold Limit Value (TLV) and 10 times lower than its OSHA Permissible Exposure Limit (PEL). Since the odor threshold can warn you well before the TLV and PEL are reached, ammonia is said to have adequate warning properties. Another reference indicates that vinyl chloride has an odor threshold of 3,000 ppm, which is 3,000 times higher than its PEL of 1 ppm. Thus, vinyl chloride's odor is a dangerous warning property on which to rely.

Some chemicals can be detected easily by smell initially but can then cause olfactory fatigue or the loss of ability to smell the substance. Hydrogen sulfide (H_2S), rotten egg gas, is a classic example of a substance which causes olfactory fatigue. Hydrogen sulfide's odor threshold is 0.3 ppm and its PEL is 10 ppm.

At first glance these numbers indicate that H_2S has an adequate warning property. They fail to show, however, that H_2S causes olfactory fatigue and that at high concentrations, paralysis of the olfactory nerves can occur. Thus, relying on your sense of smell would provide a false and potentially fatal sense of security with an extremely toxic gas. In summary, the sense of smell can sometimes provide a qualitative indication of the presence of a substance; however, never use your nose as a quantifier of chemical concentration or as a device to determine whether or not the air is safe.

4.2 Color of Product

Color can present a visual indication of the presence of a potentially hazardous chemical. Some examples are fuming nitric acid, which creates a red cloud, and chlorine gas, which has a greenish color. Both of these materials are highly toxic.

4.3 Other Senses

Mild irritation of the eyes, nose, or throat can be a useful warning property if it occurs at a concentration that does not produce other harmful or toxic effects. Some chemicals will produce a taste before, or instead of, odor or irritation.

5.0 CHEMICAL USE

The way a chemical is used will have a significant influence on the degree of hazard associated with its use. Careful review of the process and a walkthrough inspection of the work area will provide useful information to help anticipate potential exposure points.

6.0 ENVIRONMENTAL FACTORS

The following environmental factors may have an impact on potential hazards:

- Temperature
 - Increased temperatures increase the evaporation rate of many solvents and cause a greater respiratory and flammable hazard.
 - Can contribute to heat and cold stress.
- Humidity
 - Can contribute to heat and cold stress.
 - Can increase potential for generation of static electricity, which can in turn act as an ignition source in flammable atmospheres.
- Wind
 - Can contribute to heat and cold stress (e.g., wind chill).
 - Can hinder work activities by moving vapors, gases, and dusts around (e.g., obscure vision)
- Precipitation
 - Can increase volume of spilled materials, causing greater contamination.
 - Can cause incompatible reactions (e.g., reactive substances such as metallic sodium and potassium, select acids, etc.).
 - Can cause unstable working surfaces and increase chance for slips, trips, and falls.

7.0 GENERAL CHEMICAL HAZARDS

The following general chemical hazards may be encountered during the course of field activities.

7.1 Fire and Explosion Hazards

During field work for EPA you may be exposed to on-site materials that are flammable, burn rapidly, or are explosive. According to EPA data collected since the mid- 1980s, 55 percent of all chemical releases are materials with a principal hazard of flammability (e.g., gasoline, diesel fuel). Such materials may also be present as part of your own work: either in the emissions or discharges being monitored, in the chemicals used for field test procedures, or in the solvents used for cleaning sampling apparatus.

7.1.1 Recognition of Fire and Explosion Hazards

Recognition of fire and explosion hazards requires an understanding of:

- The types of materials that can catch fire or are reactive with air or water
- The processes by which materials burn or explode.

7.1.1.1 Combustion and Fire

Combustion is any chemical process accompanied by the emission of light and heat; typically this involves a substance that vigorously combines with oxygen. Fire is combustion that produces flame as well as light and heat. Alcohol fires are an exception because they can burn without detection during daylight; the flame of an alcohol fire is invisible.

A fire requires four elements:

- Combustible material (fuel source)
- Oxidizing substance (usually the oxygen in the atmosphere)
- Ignition energy (heat or spark)
- Chemical chain reaction (mechanism by which the fuel and oxidizing agent produce fire).

7.1.1.2 Fire and Explosion Characteristics

Many factors contribute to the occurrence of a fire or explosion of combustible materials: vapor pressure, area of material from which evaporation can occur, amount of material needed to produce flammable concentrations, temperature of the material, ambient temperature, specific gravity, vapor density, oxygen concentration, source of energy for ignition, and ventilation.

7.1.2 Identification of Fire and Explosion Hazards

Fire and explosion hazards may be identified by the presence of the following materials. (Refer to Table 2 for examples of flammable compounds and elements.)

7.1.2.1 Flammable Liquids

The U.S. Department of Transportation (DOT), the Occupational Safety and Health Administration (OSHA), and the National Fire Protection Association (NFPA) have established

definitions for flammability based on the flashpoint of a material. DOT defines flammable liquids as those liquids which have flashpoints below 140°F. OSHA and NFPA use 100°F as a cutoff point. (Refer Table 2.)

Additional information regarding storage of flammable and combustible liquids can be found in OSHA 29 CFR 1910.106 and NFPA standards (e.g., 49, 325m, 491m, and 704).

7.1.2.2 Pyrophoric Liquids

A pyrophoric liquid is any liquid that ignites spontaneously in dry or moist air or below 130°F. Examples of pyrophoric liquids are presented in Table 3.

**Table 3
Flammable Compounds and Elements**

Flammable Liquids		Flammable Solids	
Aldehydes Ketones Amines Ethers Aliphatic hydrocarbons Aromatic hydrocarbons Alcohols Nitroaliphatics		Metallic	
Magnesium dust Zirconium dust Titanium dust Aluminum dust Zinc dust		Non-Metallic Camphor	
Red Phosphorous		Water-Reactive Flammable Solids Potassium Sodium Lithium	
Flammable Gases		Pyrophoric Liquids	
Hydrogen Methane Acetylene		Organometallic compounds Dimethyl zinc Tributyl aluminum	

7.1.2.3 Flammable Gases

A compressed gas is considered flammable when a mixture of 13% or less with air forms a flammable mixture or when the flammable range with air is wider than 12% regardless of the lower flammable limit. Examples of flammable gases are presented in Table 3.

7.1.2.4 Flammable Solids

Many metals and non-metals have "fire-related" hazardous properties and nearly all will burn under certain conditions. Flammable solids can be readily ignited through friction and retained heat from manufacturing or processing.

7.1.2.5 Explosives and Ordnance

An explosive is a substance that undergoes a very rapid chemical transformation producing large amounts of gases and heat. The gases produced (for example, nitrogen, oxygen, carbon monoxide, carbon dioxide, and steam) rapidly expand at velocities exceeding the speed of sound due to the heat produced. This creates both a shockwave and noise. There are two types of explosive hazards:

- High or detonating: Chemical transformation occurs very rapidly with detonation rates as high as 4 miles per second. The rapidly expanding gas produces a shock wave which may be followed by combustion. There are two types of high or detonating explosives:
 - Primary high explosive: Detonative wave produced in an extremely short period of time. May be detonated by shock, heat, or friction. Examples are lead azide, mercury fulminate, and lead styphnate
 - Secondary high explosive: Generally need a booster to cause them to detonate. Relatively insensitive to shock, heat, or friction. Examples are tetryl, cyclonite, dynamite, and TNT
- Low or deflagrating: Rate of deflagration up to 1000 feet per second. Generally combustion followed by a shock wave. Examples are smokeless powder, black powder, and solid rocket fuel.

When there is a possibility of the presence of unexploded ordnance (UXO) at a site, such as grenades, shells, mines, and other explosive devices, personnel and support shall be provided with equipment necessary to locate, identify, recover/remove/dispose, and consolidate all ordnance or energetic items from work areas. These efforts shall be conducted in a safe and environmentally sound manner by qualified and trained personnel (e.g., Army, bomb squad).

Prior to starting work, it is recommended that all field personnel attend general orientation sessions that include lectures and visual training aids covering the various types of ordnance.

7.1.3 Preventing Fires and Explosions

Fires and explosions can be prevented in the field by keeping ignition sources away from flammable concentrations and instituting other control measures. All possible sources of flammable concentrations must be evaluated and controlled.

7.1.3.1 Hazard Evaluation/Instruments

Four steps can be taken to identify fire and explosion hazards:

- Obtain information from reliable and knowledgeable sources
- Identify which materials may be present and get information on their hazards
- Use instruments (combustible gas indicators) to see if there is a flammable concentration of vapors or gases in the working area. (Note: Certain field equipment and instrumentation that is battery or line-powered is not safe for use in flammable atmospheres because the electrical elements are not protected from exposure to flammable vapors or gases, or combustible dusts.)
- Take precautions as if the hazards do exist.

7.1.3.2 Hazard Control

Because many chemicals and petrochemicals are highly flammable, special hazard control measures must be followed so that the hazards presented are controlled.

Fires and explosions require fuel, air (oxygen), an ignition source (heat), and a chemical chain reaction.

- Fuel. The following can be done to minimize the fuel requirement:
 - Remove the fuel source if possible
 - Ventilate the area to reduce or eliminate high vapor concentrations
 - Cover the fuel with a non-flammable substance (e.g., firefighting foam) to prevent mixture with air
 - Control vapor trails to prevent flashback
 - Control vapor emissions.
- Oxygen. Oxygen is the most difficult portion of a fire to control because it is always present (20.9%) in air. Oxygen-rich atmospheres higher than 23.5 present additional hazards (hotter burn, increase likelihood of ignition) that can be lowered by using dilution or ventilation (blowing).
- Heat. Heat/ignition sources can be controlled by the following methods:
 - Control all ignition sources by using explosion proof lighting equipment and spark resistant tools. Extinguish and prohibit open flames and spark producing equipment in the work area.
 - Control temperature when possible.
 - Bond and ground all equipment. Metal to metal contact is essential and can be accomplished by using grounding rods, metal water pipes (cold). Scrape painted surfaces to ensure "proper connections."
- Chemical chain reaction. The chemical reactions convert the fuel and oxidizing agent into

products of combustion and energy. To control this reaction, the fuel and oxidizing agent must be separated.

Because many chemicals are highly flammable, ignition sources should be carefully avoided during sampling and when handling flammable samples. Sources of ignition include matches, cigarette lighters, electrical switches and equipment, welding sparks, engines, and catalytic converters on motor vehicles.

7.1.4 Static Electricity

Static electricity is generated by contact and separation of materials, such as particulates moving through a stack, gas issuing from a nozzle at high velocity, or pouring or spraying of nonconducting liquids or solids. Static electricity is also generated when materials flow through pipes, hoses, or ducts; when a belt runs over a pulley; or when a person walks across a floor. Static electricity accumulates to higher voltages in atmospheres with low humidity and during dry weather.

It is important to recognize activities that generate static electricity since it can provide sufficient energy to ignite flammable concentrations of gases and vapors. Practical measures to prevent accumulation or discharge of static electricity in field activities include the following:

- Grounding all probes used for stack sampling
- Providing a bonding connection between metal containers when flammable gases or liquids are transferred or poured
- Wearing footwear with adequate conductivity for the conditions.

7.2 Corrosive Hazards

Upon contact, a solid, liquid, or gaseous corrosive material may destroy body tissues or other materials, such as metals or plastics. Common corrosives are halogens, acids, and bases. Per EPA RCRA regulations, a waste material is considered corrosive if its pH is less than or equal to 2.0 (acidic) or greater than or equal to 12.5 (basic). Table 4 lists examples of halogens, acids, and bases.

**Table 4
Corrosives**

Halogens	Acids	Bases (Caustics)
Bromine Chlorine Fluorine Iodine	Acetic acid Chromic acid Chlorosulfonic acid Hydrochloric acid Hydrofluoric acid Nitric acid Perchloric acid Sulfuric acid	Ammonium hydroxide Potassium hydroxide Sodium hydroxide (caustic soda, lye)

7.2.1 Corrosion/pH

Corrosion is a process of material degradation. The corrosiveness of a material is based on its ability to dissociate in solution. Acids will dissociate to form hydrogen ions (H^+) and bases will form hydroxide ions (OH^-). The concentration of hydrogen ions is used to determine the pH of a material. The more H^+ ions, the more acidic; the more OH^- ions, the more basic. The pH scale ranges from 0 to 14 and is logarithmic. This means that pH is not proportional to the concentration of H^+ .

7.2.2 Halogens

Halogens will most likely be encountered in the gaseous state. They are considered corrosive because contact can lead to burns, irritations, and destruction of organic tissues such as skin and lungs.

7.2.3 Acids

Corrosives that form the greatest number of hydrogen ions are the strongest acids. Acids are on the lower end of the pH scale and range from 0 to 6, where 0 is the most acidic.

7.2.4 Bases

Corrosives that form the greatest number of hydroxide ions are the strongest bases and are measured from 8 to 14, 14 being most basic. Bases are also called alkaline materials or the generic term "caustic."

7.2.5 Practical Considerations

When dealing with corrosive materials in the field, it is imperative to determine:

- How toxic is the corrosive material? Is it an irritant or does it cause severe burns?
- What kind of structural damage does it do? What other hazards can it lead to?

- What protective equipment is needed to minimize exposure?
- Are emergency flushing facilities or equipment nearby (e.g., safety showers, eyewashes)?
- What specific handling procedures can be used to minimize exposure?

7.3 Reactives

A reactive material is one that can undergo a chemical reaction under certain specified conditions. The following are some examples of reactive materials.

7.3.1 Oxidizers

An oxidizer is any material that spontaneously releases oxygen. They are extremely heat and flame sensitive and may provide oxygen to an existing fire causing a "hotter," more intense burn.

7.3.2 Organic Peroxides

Organic peroxides are a type of oxidizing substance that can be shock/heat sensitive, flammable, and potentially explosive.

7.3.3 Water Reactives

These reactive materials are usually flammable solids that will react in varying degrees with water or humid air.

7.3.4 Pyrophoric Materials

These materials are capable of igniting spontaneously when exposed to moist or dry air at or below 130°F. They will also ignite in air at or below normal room temperatures in the absence of added heat, shock, or friction.

Table 5 presents examples of the common types of reactive materials.

**Table 5
Reactives**

Oxidizers	Organic Peroxides	Water Reactive
Peroxides	Methyl ethyl ketone peroxide Peroxyacetic acid	Calcium carbide
Permangates	Benzoyl peroxide	Metallic sodium
Persulfates	Hydrogen peroxide	
Nitrates	Hydrazine	Metallic potassium
Nitrites	Pyrophoric Materials	
Chlorates	Titanium dichloride	
Chlorites		
Chlorine		
Oxygen		
Nitric acid >70%		
Phosphorous		

7.4 Compressed Gases

A compressed gas refers to a chemical which is typically stored, under pressure, in cylinders.

7.4.1 Physical State

Compressed gases are often shipped and stored as liquids (under pressure at low temperature) or gases (under high pressure).

7.4.2 Classes

Compressed gases can be flammable, corrosive, toxic, or reactive, or they may exhibit various combinations of these traits. Table 6 lists several types of compressed gases.

Table 6
Compressed Gases

Cryogenics (Liquid)	Gases Under Pressure	Liquified Gases
Hydrogen Helium Argon Oxygen Nitrogen Liquified natural gas (LNG)	Carbon dioxide Oxygen Nitrous oxide Air Nitrogen	
Helium Natural gas	Anhydrous ammonia Chlorine LPG (propane, propylene, butane) Vinyl chloride	

7.4.3 BLEVE

A highly dangerous condition that can occur when a closed container is exposed to a fire is known as BLEVE (boiling liquid expanding vapor explosion). BLEVEs occur due to container metal fatigue combined with a tremendous increase in pressure. The container breakup can be explosive, releasing contents in an instant and rocketing the container shell hundreds of feet.

7.5 Chemical Reactions/Compatibility

A chemical reaction is the interaction of two or more substances, resulting in chemical changes.

7.5.1 Types

Chemical reactions usually occur in one of the following ways:

- Combination: $A+B \rightarrow AB$
"Multiplicative" effect
- Decomposition: $AB \rightarrow A+B$
"Breakdown" to either a more hazardous or innocuous substance.
- Single replacement: $A+BC \rightarrow B+AC$
- Double replacement: $AB+CD \rightarrow AD+CB$.

7.5.2 Rate

The rate at which a chemical reaction occurs depends on the following factors:

- Surface area of reactants available at the reaction site - for example, a large chunk of coal is combustible but coal dust can be explosive
- Physical state of reactant - solid, liquid, or gas
- Concentration of reactants
- Temperature
- Pressure
- Presence of a catalyst.

7.5.3 Exothermic Versus Endothermic

Exothermic chemical reactions, which give off heat, can be the most dangerous. A separate source of heat is required to maintain endothermic chemical reactions. Removing the heat source stops the reaction.

7.5.4 Compatibility

Compatibility refers to two or more hazardous materials that remain in contact indefinitely without reaction. However, incompatibility does not necessarily indicate a hazard. For example, dilute acids and bases can mix and neutralize each other to salts and water. On the other hand, a strong acid and base mix can be a hazard because they may react violently to each other. Table 7 presents a list of common hazards which can result from chemical reactions or incompatibilities.

Table 7
Hazards Due to Chemical Reactions (Incompatibilities)

HAZARD	EXAMPLE
Generation of heat	Acid and water
Fire	Hydrogen sulfide and calcium hypochlorite
Explosion	Picric acid and sodium hydroxide
Toxic gas or vapor production	Sulfuric acid and plastic
Flammable gas or vapor production	Acid and metal
Formation of a substance with a greater toxicity than the reactants	Chlorine and ammonia mixed together form the hazardous gas, chloramine
Pressurization of closed vessels	Fire extinguisher
Solubilization of toxic substances	Hydrochloric acid and chromium
Violent polymerization	Ammonia and acrylonitrile, acrolein and water

Compatibility must be considered in the storage of chemicals. General guidelines for the storage of chemicals is contained in Appendix A.

5.7.5.5 Testing/Determination

The identity of unknown reactants must be determined by chemical analysis to establish compatibility. Sometimes it is impossible to ascertain the identity of a waste due to time and money constraints. In this event, simple tests must be performed to determine the nature of the material or mixture. Chemical test strips (SpilFyter), pH paper, and hazard categorization kits (HazCat) can be used to assist in classifying and possibly identifying unknowns. Two varieties of HazCat kits exist: a wet chemistry type and colorimetric detector tube-based.

8.0 RADIATION HAZARDS

Radiation hazards are typically considered to be physical rather than chemical. However, radioactive materials may exist in combination with hazardous chemicals as "mixed or special waste" in a laboratory, at a facility, or at a hazardous waste site. Therefore, both hazardous characteristics must be considered. A general overview of the hazards of radiation is included here. More information on radiation hazards can be obtained in "Radiation Safety," or from the EPA Radiation Protection Manual.

8.1 Types

Radiation exists in both natural and manmade forms. There are two general categories of radiation:

- Non-ionizing: Radiation that imparts enough energy to remove electrons from one orbital shell to another shell of higher energy (e.g., microwaves, ultraviolet light).
- Ionizing radiation: Radiation that has sufficient energy to remove electrons from an atom.

Table 8 presents a summary of the types of ionizing radiation and their characteristics.

Table 8
Characteristics of Three Types of Ionizing Radiation

Source	Form	Relative Mass	Velocity	Path Length	# of Ionizations/ cm In Air	Biological Hazard
ALPHA	Particle	4 Atomic Mass Units	10% C*	<1 incl	Hundreds of Thousands 100,000's	Internal
BETA	Particle	.000001	29% C	1 Meter	Hundreds	
100's		Internal/ External				
GAMMA X-RAY	Electro- Magnetic Energy	0	C	Several Meters to Kilometers	1	External

*C = Speed of Light

8.2 Radiation Units

The following are the most commonly used units of radiation:

- Curie (Ci) is a special unit for the activity of a substance which is measured in terms of disintegrations per unit time
- Roentgen (R) is a unit for exposure that gives the number of ionizations caused by photons in air;
- REM (Roentgen Equivalent in Man) is the special unit of dose equivalent
- RAD (Radiation Absorbed Dose) is a special unit of absorbed dose.

8.3 Detection and Measurement

Unlike many hazardous substances that possess certain properties which can alert field personnel to over exposures, radiation has no such warning properties. Therefore, it is imperative that properly maintained, calibrated and operational radiation survey meters and dosimeters be utilized whenever radiation is a concern.

8.4 Biological Effects

Ionizing radiation causes primarily nonspecific damage to cells. Radiation passing through living cells will directly ionize or excite atoms and molecules in the cell structure. The total effect on cell processes is a function of the dose of radiation. The cell processes will be affected in varying degrees:

- Some damage to the cell may be repaired
- If the extent of the damage to an organ is quite large, the organ may not be able to repair itself; or
- Cells may also begin to exhibit uncontrolled growth.

8.5 Exposure Control

Continuous monitoring using survey instruments, pocket dosimeters, and other survey equipment are needed to assess external radiation hazards. Because the goal of radiation protection is to reduce exposures to the lowest levels, the following protection factors for external radiation have been established:

- Time: Reducing the amount of time in a radiation field reduces the amount of exposure
- Distance: Increasing the distance between you and a radioactive material decreases the intensity of the hazard.
- Shielding: The greater the mass situated between you and a radioactive material, the less radiation that will penetrate
- As Low As Reasonably Achievable (ALARA): Keeping radiation exposure as low as reasonably achievable can reduce unnecessary occupational exposure.

9.0 MULTIPLE HAZARD CLASS RULE

The multiple hazard concept is one which is extremely important when discussing hazardous materials. Chemicals are typically classified (e.g., DOT) by their principal adverse property (e.g., flammability, corrosivity). This does not mean that chemicals can not exhibit adverse properties other than those associated with their hazard class (e.g., flammable and poisonous). Multiple hazards can also result from the reaction of different chemicals with each and/or with other materials. *Remember, multiple hazards are the rule rather than the exception.* Assume that a hazardous substance will present more than one hazard.

10.0 PRACTICAL CONSIDERATIONS FOR HAZARDOUS CHEMICAL AWARENESS

The following are some practical considerations regarding hazardous reaction awareness:

- Know the chemicals and their properties
- Always consult MSDSs or other reference sources
- Be aware of incompatibilities
- Plan your work procedure
- Be aware of the types of reactions you can expect, especially when other chemicals are introduced to the process
- Know how to respond to an unexpected reaction
 - Stop work in progress
 - Attempt to determine the cause, if safe to do so

- Consult an industrial hygienist or chemist.

11.0 HAZARD CONTROL PRACTICES

The following safe work practices should always be used in hazard control:

- Handle materials so as to prevent direct contamination
- Limit exposure levels and time as much as possible
- Enforce good hygiene practices
- Take appropriate fire prevention and control measures
- Use appropriate personal protective equipment
- Use equipment and tools not affected by the chemical being handled
- Ensure that a chemical is not mixed with other chemicals or substances which may result in adverse reactions
- Use engineering controls
- Use good common sense.

In general, the key to hazard control is a combination of competent risk conversion and a technical system of "Information without Intervention" which builds on the basics of awareness training (occupancy, location, container shape and size, placards, labels and markings, and senses) and continues to emphasize this information gathering and evaluation throughout all field activities.

12.0 SUMMARY

This module has presented information on the various chemical hazards and reactions that may be encountered during field activities. EPA personnel must be aware of the warning properties, physical properties, toxicity, and hazardous characteristics associated with the chemicals present in the field. In addition, personnel must be able to determine appropriate control measures (e.g., engineering controls, PPE) and implement emergency procedures as necessary.

Key concepts presented in this module are:

- The degree of hazard posed by a chemical depends on its physical properties, toxicity, use, and environment
- The physical and chemical characteristics of chemicals include solubility, specific gravity, vapor density, vapor pressure, boiling/melting point, flashpoint, autoignition temperature, and explosive limits
- Warning properties, such as odor, color, eye/nose/throat irritation and taste, may alert you to the presence of a chemical. However, these qualitative measures should never be relied on exclusively
- Temperature, humidity, wind, and precipitation may have an impact on the potential hazards encountered in the field
- Chemicals may present a number of different hazards including:

- Fire and explosion
- Combustion and fire
- Explosives
- Corrosives
- Oxidizers
- Organic peroxides
- Water reactives
- Pyrophoric materials
- Multiple hazards are the rule rather than the exception.

Measures you can take to minimize the risks associated with chemical hazards and reactions include:

- Recognize chemical hazards, depending on physical properties, toxicity, use and the environmental conditions present.
- Know the various hazard classes.
- Familiarize yourself with the chemical and physical characteristics and the warning properties of chemical hazards you may encounter during the course of your work.
- Be aware of the effect environmental factors may have on potential hazards.
- Know hazard control and evaluation methods for the potential hazards.
- Always consult MSDSs or other reference sources for more information about chemical substances.
- Understand the multiple hazard rule.

EXERCISE

Choose the best answer for the following:

1. _____ The following is true regarding the physical classification of chemicals as solids:
 - A. All forms of a chemical pose a health hazard
 - B. A chemical may be hazardous even in solid form
 - C. No solids are hazardous alone
 - D. None of the above

2. _____ The following is true regarding the physical classification of chemicals as liquids:
 - A. The degree of hazard depends on its characteristics and the way it is used
 - B. Many liquids are hazardous by contact with the skin
 - C. Liquids can create a splash and slipping hazard
 - D. All of the above

3. _____ The following is true regarding the physical classification of chemicals as aerosols:
 - A. An aerosol is a fine particulate suspended in air

- B. Knowing how aerosols are generated can help you to anticipate hazards
 - C. Aerosols are not a hazard to the skin
 - D. Both A and B
4. _____ The following are physical and chemical characteristics of chemicals, except:
- A. Solubility
 - B. Vapor density, vapor pressure
 - C. Boiling point, melting point, flashpoint
 - D. Odor threshold
5. _____ The four components required to produce fire include all but which of the following:
- A. Fuel
 - B. Light
 - C. Heat
 - D. Chemical reaction
6. _____ Explosives undergo a rapid chemical transformation to produce:
- A. Heat
 - B. Gases
 - C. Shockwave
 - D. All of the above
7. _____ When there is a possibility of unexploded ordnance at a site, specially trained personnel and support shall:
- A. Locate and identify UXO
 - B. Recover, remove, dispose and consolidate UXO
 - C. Attend site orientation
 - D. All of the above
8. _____ Static electricity is generated by all but the following:
- A. Walking across the floor
 - B. Breathing
 - C. Particulates moving through a stack
 - D. Pouring nonconducting liquids
9. _____ Upon contact, a corrosive material may destroy:
- A. Body tissues
 - B. Metals
 - C. Plastics
 - D. All of the above

10. _____ The rate at which a chemical reaction occurs depends on:
- A. Surface area
 - B. Temperature
 - C. Pressure
 - D. All of the above
11. _____ Exposure control practices for external radiation include all but the following:
- A. Distance
 - B. Dosimetry
 - C. Shielding
 - D. ALARA
12. _____ Chemical hazard control practices include the following:
- A. Limit exposure time
 - B. Use good hygiene
 - C. Prevent contamination
 - D. All of the above

EXERCISE KEY

Choose the best answer for the following:

1. _____ The following is true regarding the physical classification of chemicals as solids:
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 - D. ALARA
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- A. Limit exposure time
 - B. Use good hygiene
 - C. Prevent contamination
 - D. All of the above**

APPENDIX A: CHEMICAL COMPATIBILITY CHART

 Chemical Compatibility Chart

REACTIVITY GROUPS

GROUP 1 - INORGANIC ACIDS

chlorosulfonic acid
hydrochloric acid (aqueous)
hydrofluoric acid (aqueous)
hydrogen chloride (anhydrous)
hydrogen fluoride (anhydrous)
nitric acid
oleum
phosphoric acid
sulfuric acid

GROUP 2 - ORGANIC ACIDS

acetic acid
butyric acid (n-)
formic acid
propionic acid
rosin oil
tall oil

GROUP 3 - CAUSTICS

caustic potash solution
caustic soda solution

GROUP 4 - AMINES AND ALKANOLAMINES

aminoethylethanolamine
aniline
diethanolamine
diethylamine
diethylenetriamine
diisopropanolamine
dimethylamine
ethylenediamine
hexamethylenediamine
hexamethylenetetramine
2-methyl 5-ethyl pyridine
monoethanolamine
monoisopropanolamine
morpholine
pyridine
triethanolamine

dextrose solution
diacetone alcohol
diethylene glycol
diethylene glycol dimethyl ether

triethylamine
triethylenetetramine
trimethylamine

GROUP 5 - HALOGENATED COMPOUNDS

allyl chloride
carbon tetrachloride
chlorobenzene
chloroform
chlorohydrins, crude
dichlorobenzene (o-)
dichlorobenzene (p-)
dichlorodifluoromethane
dichloroethyl ether
dichloropropane
dichloropropene
ethyl chloride
ethylene dibromide
ethylene dichloride
methyl bromide
methyl chloride
methylene chloride
monochlorodifluoromethane
perchloroethylene
propylene dichloride
1,2,4 trichlorobenzene
1,1,1 trichloroethane
trichloroethylene
trichlorofluoromethane

GROUP 6 - ALCHOLS, GLYCOLS AND GLYCOL ETHERS

allyl alcohol
amyl alcohol
1,4 butanediol
butyl alcohol (iso, n, sec, tert)
butylene glycol
corn syrup
cyclohexyl alcohol
decyl alcohols (n, iso)

diethylene glycol monobutyl ether
diethylene glycol monoethyl ether
diethylene glycol monomethyl ether
diisobutyl carbinol

* Not presently included in CHRIS system.

REACTIVITY GROUPS

dipropylene glycol
dodecanol
ethoxylated dodecanol
ethoxylated pentadecanol
ethoxylated tetradecanol
ethoxylated tridecanol
ethoxytriglycol
ethyl alcohol
ethyl butanol
2-ethylbutyl alcohol
2-ethylhexyl alcohol
ethylene glycol
ethylene glycol monobutyl ether
ethylene glycol monoethyl ether
ethylene glycol monomethyl ether
furfuryl alcohol*
glycerine
heptanol
hexanol
hexylene glycol
isoamyl alcohol
isooctyl alcohol
methoxytriglycol*
methyl alcohol
methylamyl alcohol
molasses, all
nonanol
octanol
pentadecanol
polypropylene glycol methyl ether
propyl alcohols (n, iso)
propylene glycol
sorbitol
tetradecanol
tetraethylene glycol
tridecyl alcohol
triethylene glycol

isobutane
liquefied natural gas
liquefied petroleum gas
methane
nonane
n-paraffins
paraffin wax
pentane (n, iso)

undecanol

GROUP 7 - ALDEHYDES

acetaldehyde
acrolein (inhibited)
butyraldehyde (n, iso)
crotonaldehyde
decaldehyde (n, iso)
2-ethyl-3-propylacrolein
formaldehyde solution
furfural
hexamethylenetetramine
isooctyl aldehyde
methyl butyraldehyde
methyl formal*
paraformaldehyde
propionaldehyde
valeraldehyde

GROUP 8 - KETONES

acetone
acetophenone
camphor oil
cyclohexanone
diisobutylketone
isophorone*
mesityl oxide*
methyl ethyl ketone
methyl isobutyl ketone

GROUP 9 - SATURATED HYDROCARBONS

butane
cyclohexane
ethane
heptane (n-)
hexane (n, iso)

petrolatum
petroleum ether
petroleum naphtha
polybutene
propane
propylene butylene polymer

* Not presently included in CHRIS system.

REACTIVITY GROUPS

GROUP 10 - AROMATIC HYDROCARBONS

benzene
cumene
p-cymene*
coal tar oil
diethylbenzene
dodecyl benzene*
Dowtherm
ethyl benzene
naphtha, coal tar
naphthalene (includes molten)
tetrahydronaphthalene
toluene
triethyl benzene
xylene (m-, o-, p-)

GROUP 11 - OLEFINS

butylene
1-decene
dicyclopentadiene
diisobutylene
dipentene*
dodecene
1-dodecene
ethylene
liquefied petroleum gas
1-heptene
1-hexene
isobutylene
nonene
1-octene
1-pentene
polybutene

No. 1-D
No. 2
No. 2-D
No. 4
No. 5
No. 6

lubricating oil
mineral oil
mineral seal oil
motor oil
penetrating oil

propylene
propylene butylene polymer
propylene tetramer (dodecene)
1-tetradecene
1-tridecene
turpentine
1-undecene

GROUP 12 - PETROLEUM OILS

asphalt
gasolines
 casinghead
 automotive
 aviation
jet fuels
 JP-1 (kerosene)
 JP-3
 JP-4
 JP-5 (kerosene, heavy)
kerosene
mineral spirits
naphtha (non-aromatic)
naphtha
 solvent
 Stoddard solvent
 VM&P
oils
 absorption oil
 clarified oil
 crude oil
 diesel oil
 fuel oils
 No. 1 (kerosene)
range oil
road oil
spindle oil
spray oil
transformer oil
turbine oil*

GROUP 13 - ESTERS

amyl acetate
amyl tallate
butyl acetates (n, iso, sec)

* Not presently included in CHRIS system.

REACTIVITY GROUPS

butyl benzyl phthalate
castor oil
cottonseed oil
croton oil*
dibutyl phthalate
diethyl carbonate
dimethyl sulfate
dioctyl adipate
dioctyl phthalate
epoxidized vegetable oils
ethyl acetate
ethyl diacetate
ethylene glycol monoethyl ether acetate
ethylhexyl tallate
fish oil
glycol diacetate
methyl acetate
methyl aml acetate
neatsfoot oil
Olive oil
peanut oil
propyl acetates (n, iso)
resin oil
soya bean oil
sperm oil
tallow
tanner's oil
vegetable oil
wax, carnauba

GROUP 17 - CYANOHYDRINS

acetone cyanohydrin
ethylene cyanohydrin

GROUP 18 - NITRILES

acetonitrile
adiponitrile

GROUP 19 - AMMONIA

ammonium hydroxide

GROUP 20 - HALOGENS

bromine
chlorine

GROUP 14 - MONOMERS AND POLYMERIZABLE ESTERS

acrylic acid (inhibited)
acrylonitrile
butadiene (inhibited)
butyl acrylate (n, iso)
ethyl acrylate (inhibited)
2-ethylhexyl acrylate (inhibited)
isodecyl acrylate (inhibited) *
isoprene (inhibited)
methyl acrylate (inhibited)
methyl methacrylate (inhibited)
beta-propiolactone *
styrene (inhibited)
vinyl acetate (inhibited)
vinyl chloride (inhibited)
vinylidene chloride (inhibited)
vinyl olvene

GROUP 15 - PHENOLS

carbolic oil
creosote, coal, tar *
cresols
nonylphenol
phenol

GROUP 16 ALKYLENE OXIDE

ethylene oxide
propylene oxide

GROUP 21 - ETHERS

diethylether (ethylether)
1, 4-dioxane
isopropyl ether
tetrahydrofuran

GROUP 22 - PHOSPHORUS, ELEMENTAL

GROUP 23 - SULPHUR, MOLTEN

GROUP 24 - ACID ANHYDRIDE

acetic anhydride
propionic anhydride

* Not presently included in CHRIS system.

REACTIVITY GROUPS

* Not presently included in CHRIS system.