ABSTRACT

PROACTIVE TECHNIQUE FOR WORKPLACE CHEMICAL EXPOSURE

by
James Duru

The rapid increase in the number and quantities of chemicals released into the environment has been accompanied by a lack of adequate pre-released testing for advance health outcomes. Chemicals which serve as feed stock to millions of industries all around the world to produce and process food, cosmetics, equipment, and energy to propel industries, automobiles, home heating and electricity have serious adverse health consequences. They are hazardous. These substances can explode, ignite, react and corrode. Adapting the definition of the international program on chemical safety, a "hazard" is a source of danger. This thesis proposes some proactive prevention techniques useful to reduce the risk or potential for harm by chemicals at work place and environment. The methods described in the following paragraphs are traditional, advanced methods and innovative techniques found effective against chemical exposure. Known points of entry into the body through ingestion, inhalation and dermal pathways are discussed, including the mechanism of action of cells under the influence of hazardous chemicals.

It begins with cellular interaction of ligands or chemicals in the body after ingestion, inhalation or dermal exposure. The binding of the ligands and the receptor cells produces reactions that inhibit or activate cells, resulting in abnormal physiological response. To prevent this from occurring, some proactive measures are proposed. Foremost on the list is personal hygiene and good housekeeping, followed by avoidance technique, containment, legislation and guidelines. They form the core of traditional technique. Complementary to that is the advanced methods and innovative techniques which explore new ways of industrial production and hazardous waste disposal that are safe and environmentally friendly. The use and advantages of microwave energy as a safe and most effective method for industrial heating, material processing and organic synthesis over the conventional methods are discussed. The thesis also discusses phytoremediation, the use of species of plants to clean up contaminant as a revolutionary method for safe, efficient and environmentally friendly method for hazardous waste treatment and remediation.

PROACTIVE TECHNIQUE FOR WORKPLACE CHEMICAL EXPOSURE

by
James A. Duru

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for Degree of
Master of Science in Occupational and Safety and Health Engineering

Department of Industrial and Manufacturing Engineering

January 1998

APPROVAL PAGE

PROACTIVE TECHNIQUE FOR WORKPLACE CHEMICAL EXPOSURE

James A. Duru

12/17/97

Dr. One-Jang Jeng, Thesis Advisor — Date
Professor of Industrial and Manufacturing Engineering, NJIT

12/22/97

Dr. Richard Trattner, Committee Member — Date
Associate Chairperson for Environmental Science and Professor of Chemical Engineering, Chemistry and Environmental Science, NJIT.

12/11/97

Dr. Norman J. Van Houten, Committee member — Date
Director of Health and Environmental Safety. NJIT

BIOGRAPHICAL SKETCH

Author: James A. Duru

Degree: Master of Science

Date: January, 1998

Date Of Birth:

Place of Birth:

Undergraduate and Graduate Education:

- Masters of Science in Occupational Safety and Health Engineering, New Jersey Institute of Technology, Newark, NJ, 1998
- Masters of Science in Electrical Engineering, West Coast University Los Angeles, CA, 1984
- Bachelor of Science in Electrical Engineering , Indiana Institute of Technology, Fort Wayne, IN. 1979.

Major: Occupational Safety And Health Engineering.

To My Beloved Family

ACKNOWLEDGEMENT

I would like to express my appreciation to my adviser Dr. One-Jiang Jeng for his dedication and patience. Special thanks to Dr. Howard Cage and Dr. Norman J. Van Houten for their invaluable advise and support. Also special thanks to Dr. Richard Trattner for actively participating in my committee.

I extend my gratitude and thanks to all those who contributed in the typing, and production of this material and to God almighty for making it possible.

TABLE OF CONTENTS

Chapter Page

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Man made toxic substances are present everywhere in modern life. Nearly seventy thousand chemical products have been introduced since World War II and one thousand five hundred new ones are added every year. Total U.S. production of chemicals amount to more than twenty-five million gallons a year for cleaning lawn, food processing, automobile care, home improvement and other purposes. Industries use the rest, more than 90 percent, for manufacturing goods such as cosmetics, clothing, medicines, paper, plastics, food additives and machinery. While thousands of chemicals are potentially hazardous to human health and the environment, less than two percent of those produced have been fully assessed for their toxic effect. Even without complete information on toxicity, we know many of these chemicals have other hazardous properties: they are poisons. These substances can explode, ignite, react and/or corrode.

A poison can be defined as any agent capable of producing a deleterious response in a biological system, seriously interfering function or producing death. This is not, however, a useful working definition for the very simple reason that virtually every known chemical has the potential to produce injury or death if present in a sufficient amount. Paracelsus (1493-1541), phrased this well when he noted “All substances are poisonous, there is none which is not a poison. The right dose differentiates a poison and a remedy”.

Among chemicals there is a wide spectrum of doses needed to produce deleterious effects, serious injury, or death. This is demonstrated in Table 1. It shows the acute lethal LD50 of dosage chemicals needed to produce death in 50 percent of treated

Table 1. Approximate Acute LD50s of Some Representative Chemical Agents

AGENT	LD50 (mg/kg)*
Ethyl Alcohol	10,000
Sodium Chloride	4,000
Ferrous Sulphate	1,500
Morphine Sulphate	900
Phenobarbital Sodium	150
Picrotoxin	5
Strychnine Sulphate	2
Nicotine	1
d-Tubocurarine	0.5
Hemicholinium - 3	0.2
Tetrodotoxin	0.10
Dioxin (TCDD)	0.001
Botulinum Toxin	0.00001

Source: KLASSEN D. CURTIS & EATON L. DAVID. 1993 PRINCIPLES OF TOXICOLOGY.

animals. Some chemicals will produce death in microgram doses and are commonly thought of as being extremely poisonous. Other chemicals may be relatively harmless following doses in excess of several grams. It should be noted, however that measures of acute lethalness such as LD50 may not accurately reflect the full spectrum of toxicity or hazards associated with exposure to a chemical or radiation agent. For example, some chemicals with low acute toxicity may have carcinogenic or teratogenic effects at doses that produce no evidence of acute toxicity. There are several varieties of potentially adverse effects created by chemicals present in our environment. The combination makes for a broad spectrum of specialized areas for analyzing their hazards. According to Klaassen and Eaton, 1993. Toxicologists agreed on three main categories of study for the investigation of the adverse chemical effects on living organisms. The categories are descriptive, mechanistic, and regulatory.

The descriptive toxicologist is concerned directly with toxicity testing which provide necessary information for safety evaluation and regulatory requirements. The appropriate toxicity tests on experimental animals are designed to yield information that can be used to evaluate the risk posed to human and the environment from exposure to specific chemicals. The concern may be limited to effect on human as in the case of drugs or food additives. In the chemical industry such concern should include potentially adverse effect on fishes, birds, wildlife and other factors that might disturb overall the balance of the ecosystem.

The mechanistic toxicologist is involved with tracing/finding the mechanism by which chemicals exert their toxic effects on living organisms. These studies can lead to the development of sensitive and predictive tests useful in risk assessment, design, and production of safer alternative chemicals and rational therapy for chemical poisoning and treatment of disease. It also improves understanding of the mechanism of toxic action to the knowledge of basic physiology, pharmacology, cell biology and biochemistry. For example, studies on the toxicity of fluoro-organic alcohols and acids contribute to the knowledge of basic carbohydrates and lipid metabolism. Knowledge of regulation of ion gradient in nerve and axonal membranes has been gradually aided by studies of natural and synthetic toxins such as tetrodotoxin and dichlorodipheny trichloreethane (DDT).

A regulatory toxicologist has the responsibility of deciding based on the toxicity test and the data provided if drugs or other chemicals pose a sufficiently low risk to be marketed for public consumption. Regulatory toxicologist services are also required by the following government regulatory bodies:

1. The Food and Drug Administration (FDA) is responsible for admitting drugs, cosmetics and food additives onto the market according to the Federal Food Drug and Cosmetic Act (FDCA).

2. The Environmental Protection Agency (EPA) is responsible for regulating most other chemicals according to the Federal Insecticide and Fungicide and Rodenticide Act (FIFRA). The Toxic Substance Control Act (TSCA); the Resource Conservation and Recovery Act (RCRA); the Safe Drinking Water Act (SDWA) and the Clean Air Act. The EPA is also responsible for enforcing the Comprehensive Environmental Response, Compensation and Liability Act. (CERCLA) more commonly call "Superfund". This regulation provides direction and financial support for the clean up of waste sites that contain toxic chemicals and may present a risk to human health or the environment.

3. The Occupational Safety and Health Administration (OSHA) of the Department of Labor was established to ensured that only safe and healthful conditions exist in the workplace.

4. The Consumer Product Safety Commission has the responsibility of protecting consumers from hazardous household substances.

5. The Department of Transportation (DOT) ensures that materials shipped in interstate commerce are labeled and packaged in a manner consistent with the degree of hazard present.

Because of the abundance of man made toxins everywhere in our lives, and the grave consequences of their effects on human, animals and the environment, the government introduced regulatory controls. These regulatory measures help to control the production, distribution and use of these chemicals. Chemical exposure in work place and the consequent fatalities and illnesses in these places led to the establishment of the Occupational Safety and Health Administration (OSHA) by the government. The agency ensures that safe and healthy conditions exit in the workplace. This thesis proposes some preventive techniques that are proactive in design to reduce the risk or potential for harm by chemicals in the work place and the environment. The caption "PROACTIVE TECHNIQUES FOR WORKPLACE CHEMICAL EXPOSURE" is aimed at reinforcing the view that most workplace exposure are preventable.

Proactive technique is defined as a "logical postulate that predicts events and outcome, and introduces adequate corrective measures for the avoidance of harm". Conversely things in nature do not always appear to follow the logical sequence of events. The reason partly is limited knowledge and severally, lack of understanding of the differentiation and combinations of world species. These shortcomings make it more difficult to determine logically thing of nature. Machine design and process control follow logical sequences, therefore proactive techniques can apply to it effectively for the avoidance of harm. The methods to achieve safe exposure to chemicals are detailed in the text. Chapters two through four examine the classification of toxins, route of exposure, and the boitransformation mechanism of toxin in the body. Traditional methods for preventing exposure and some advanced and innovative methods are discussed in chapters five and six. Microwave application for heating, material synthesis and waste remediation described in chapter six is a technology for the future. Because of its low cost, safe to use and environmentally friendly, it will revolutionize the way production is done in industries. Also the innovative method called phytoremediation the use of plant species to remove radionuclides and other radioactive materials reinforces the claim that the twenty first century will be the century for hazardous waste clean up.

Chapter seven discussed all aspect of this thesis. The advantages and disadvantages, and in some case raises other thought on the subject. The thesis ends with a conclusion in chapter 8.

CHAPTER 2

CLASSIFICATION OF TOXINS

Toxic agents are classified in a variety of ways. They can be classified based on:

a) Their chemistry - Aromatic amine, halogenated hydrocarbon, etc.

b) Poisoning potential - Toxic, slightly toxic, very toxic, extremely toxic etc.

c) Physical state - gas, dust, liquid

d) Labeling requirement - explosive, flammable, oxidizes

e) Effects - Cancer, mutation, liver injury, etc.

f) Uses - Pesticides, solvent, food additive, etc.

g) Target organ - liver kidney, homatopoietic system, etc.

Classification may also be based on their biochemical mechanism of action (sulfhydryl inhibitor, methemoglobin producer, etc.) and is usually more informative. Classification could be done in general terms such as irritant, corrosive, air pollutant, acute and/or chronic poison. This approach provides a useful focus for the general public regarding specific problems.

From the foregoing it is clear that no single classification will suffice for the entire spectrum of toxic agents. Classification which takes into account other factors and symptoms with the chemical or biological properties and the exposure characteristics are most useful for control and regulatory purposes. Table 2 shows some chemical agents classified into general groups of sensitizers and irritants that causes skin disorder [Plog, Niland and Quinlan, 1995, pg. 60]. Adverse or toxic effects in human or any biological system, are not produced by a chemical agent unless that agent or its biotransformation products reach appropriate sites in the body at a concentration, and for a length of time

Table 2. Selected Chemical Causes of Skin Disorder

Chemical	*Primary Irritants*	*Sensitizers*	*Selected Skin Manifestations (Some also have important systemic effects on other organs.)*	*Selected Occupations, Trades, or Processes Where Exposure Can Occur*
ACIDS				
Acetic	X	?	Dermatitis and ulceration	Manufacturing acetate rayon, textile printing and dyeing, vinyl plastic makers
Carbolic (phenol)	X		Corrosive action on skin, local anesthetic effect	Carbolic acid makers, disinfectant manufacturing, dye makers, pharmaceutical workers, plastic
Hydrofluoric	X		Severe chemical burn with blisters, erosion, or ulceration	Enamel manufacturing, etchers, hydrofluoric acid makers, flurochemical workers
Lactic	X		Ulceration (if strong solutions are used)	Adhesives, plastics, textiles
ALKALIS				
Ammonia	X		Irritation including airborne dermatitis of face from vapors	Ammonia production, fertilizers, photocopying (blueprint, diazo); gas and liquid forms
Calcium cyanamide	X		Irritation and ulceration	Fertilizer makers, agricultural workers, nitrogen compound makers
Calcium oxide	X		Dermatitis, burns, or ulceration	Lime workers, manufacturing of calcium, salts, glass, and fertilizer
Potassium hydroxide	X		Severe corrosion of skin, deep-seated persistent ulcers, loss of fingernails	Potassium hydroxide makers, electroplaters, paper, soap, and printing ink makers
SALTS OR ELEMENTS				
Antimony and its compounds	X	?	Irritation and lichenoid eruptions of skin	Antimony extractors, glass and rubber mixers, manufacturing of various alloys, fireworks, and aniline colors
Arsenic and its compounds	X	X	Spotty pigmentation of skin, perforation of nasal septum, skin cancer, keratoses especially on palms and soles, dermatitis, pustules	Leather workers, manufacturing insecticides, glass industry, agriculture, pesticides, tanning, taxidermy, alloy, lubricating oils
Barium and its compounds	X		Irritation of skin	Barium carbonate, fireworks, textile dyes, and paint makers
Bromine and its compounds	X		Irritation, vesicles, and ulceration; acne	Bromine extractors, bromine salts makers, dye and drug makers, photographic trades
SOLVENTS				
Acetone	X		Dry (defatted) skin	Spray painters, celluloid industry, artificial silk and leather workers, acetylene workers, lacquer and varnish makers, garage mechanics
Benzene and its homologues (toluene and xylene)	X		Dry (defatted) skin	Chemical and rubber manufacturing

Source: TAYLOR S. JAMES 1995 "THE SKIN AND OCCUPATIONAL DERMATOSES" sufficient to produce the toxic manifestation [Klaassen and Eaton, 1993, pg. 14]. Whether or not a toxic response occurs, therefore, depends on the chemical and physical properties of the agent, the exposure situation and the susceptibility of the individual or biological system. Thus to fully characterize the potential hazard of a specific chemical agent, we need to know not only what type of effect it produces and the dose required to produce that effect but also information about:

I) The agent
II) The exposure
III) Susceptibility of the subject

Also closely following the categories mentioned above, are major factors that influence toxicity as it relates to the exposure situation for a particular chemical. They are:

a) Route of administration
b) Duration of exposure
c) Frequency of exposure

In any environment these factors serve as the gradation steps for evaluation and assessing exposure. As a premise for the furtherance of our discussion, the route duration and frequency of exposure are discussed in detail in the following paragraphs.

2.1 Route of Exposure

The major routes by which toxic agents gain access to the body are through:

1. Ingestion - gastro intestinal tract
2. Inhalation - lungs

3. Skin - topical, percutaneous or dermal
4. Other parental routes (other than intestinal canal) - eyes, ears, etc.

Toxic agents given intravenously elicits the greatest effect and produce the most rapid response. In descending order of effectiveness for the other routes are, inhalation, intraperitotrical, subcutaneous, intramuscular, intradermal oral and dermal. The vehicle used as well as other formulation factors can markedly alter the absorption following ingestion, inhalation or topical exposure. In addition, the route of administration can influence the toxicity of agents. For example, an agent that is detoxified in the liver would be less toxic when given via the portal circulation (oral) than when given via the systemic circulation (inhalation).

Industrial exposure to toxic agents most frequently results from inhalation and dermal exposure. Oral poisoning is effectively controlled by administrative procedures (e.g. prohibiting eating or drinking at work place, etc.), although accidents could still occur through a worker's unintentional oral ingestion. To obtain information concerning the absorption of chemical agents, comparisons are made of the lethal dose of an agent through different routes of exposure - oral, dermal and intravenous. Tests show that the absorption rate is highest intravenously. Lethal doses by the dermal route would be several orders of magnitude higher than oral doses which produce the same effect, because the skin provides an effective barrier to absorption of the agent.

2.1.1 The Skin

Three distinct layers of tissue make up the skin: from the surface downwards they are the epidermis, the dermis and the subcutaneous layer. (See figure 1) It shows the magnified cross section of the skin). The thickness of the skin varies from 0.5 mm on the eyelid (the

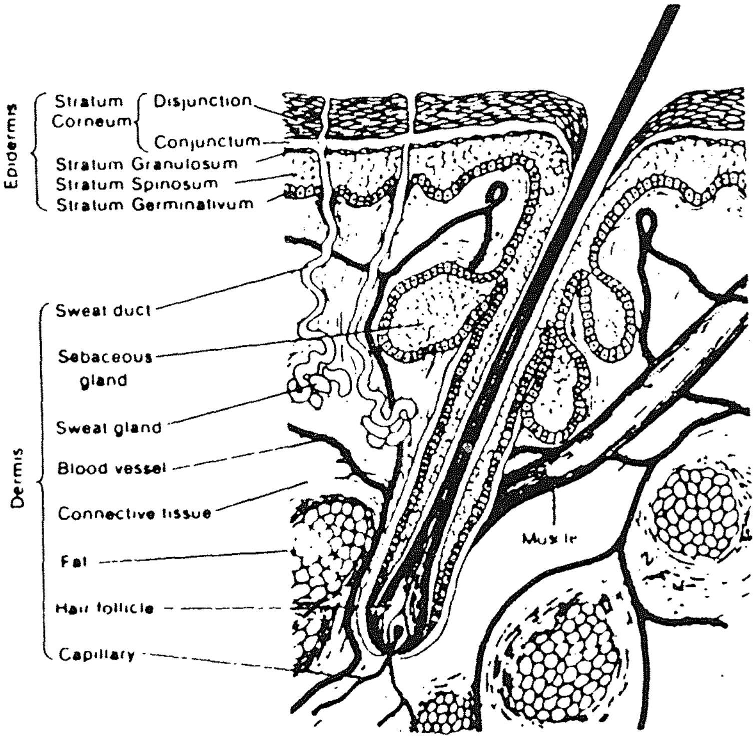


Figure 1. Magnified Cross Section of The Skin

Source: KLASSEN D. CURTIS & EATON L. DAVID. 1993 PRINCIPLES OF TOXICOLOGY.

dermis is thinnest here) to 3-4 mm on the palms of the hand and soles of the feet. (The epidermis is thickest here). Skin is also relatively thin in the skin folds: The axillae (armpits) under the breast, the groins and between the fingers and toes. The variation in the thickness of the skin characterizes the absorption rates.

The top layer of the epidermis is composed of dead cells called the horny or keratin layer, or the stratum corneum. This layer resists chemical attack fairly well, with the notable exception of alkali. It serves as the main-rate limiting barrier against absorption of water and aqueous solution, but offers little protection against lipid soluble materials (such as organic solvents) or gases. The horny layer gradually flakes off, or soaks off when wet. It is constantly being replaced by cells pushed toward the surface as new cell are formed in the deeper, germinative layer of the epidermis. This regenerative and sloughing characteristics serve to some extent as a protection against chemicals and microorganisms.

2.1.2 The Respiratory System

The respiratory system is a quick and direct avenue of entry for toxic materials into the body; because of its intimate association with the circulatory system and the constant need to oxygenate human tissue cells. Humans can survive for weeks without food and for days without water, but only a few minutes without air. Anything affecting the respiratory system, either insufficient oxygen or contaminated air affects the entire human organism. The life-supporting component of air is oxygen, which constitutes a little less than one-fifth of its volume. Each living cell in the body requires a constant supply of oxygen. Some cells however are more vulnerable than others. Cells in the

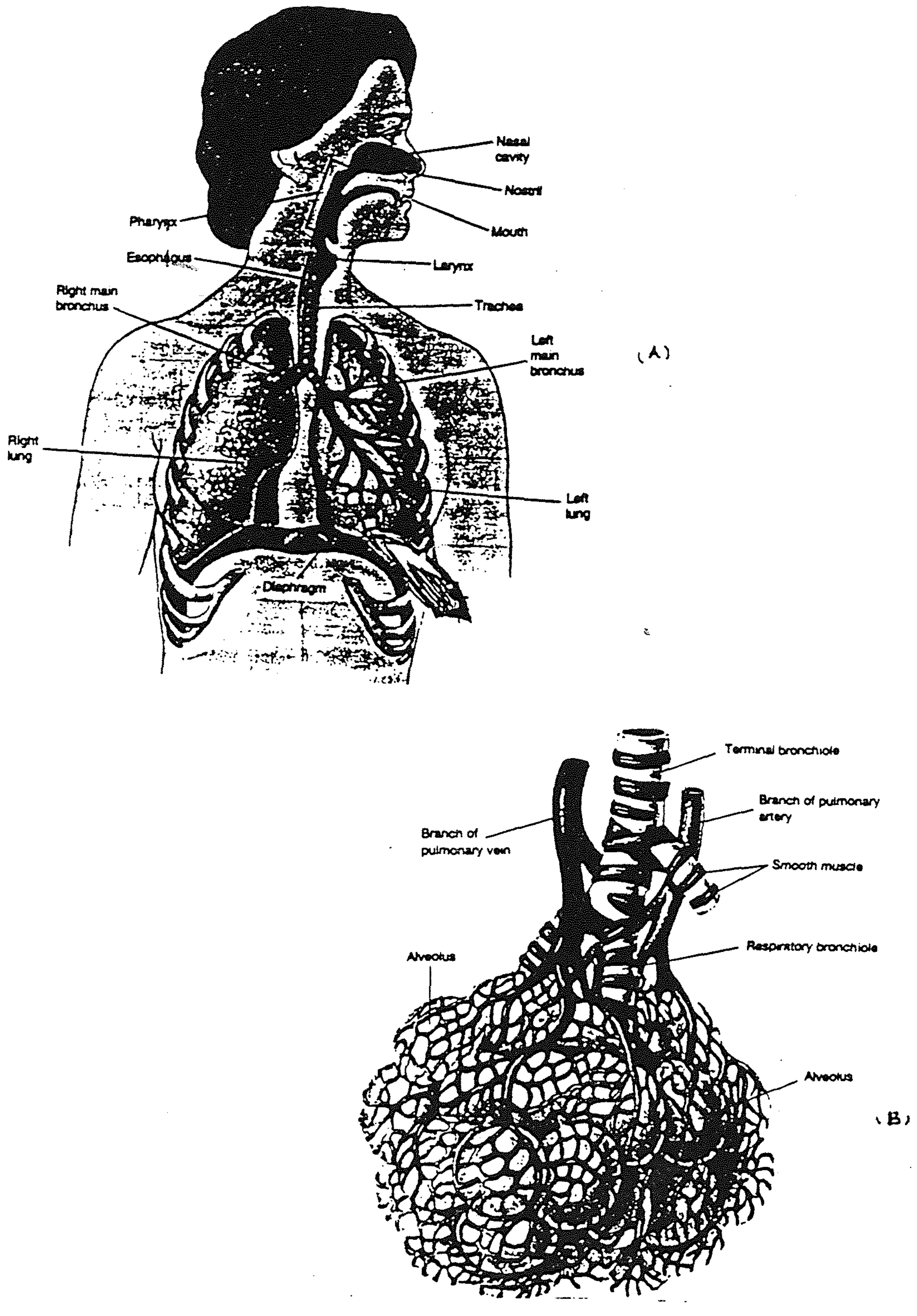


Figure 2 **a.** Organization of the respiratory system.
b. Cross Section of The Left Lung

Source: VANDER A.J., J.H. SHERMAN, D.S. LUCIANO, 1994: Human Physiology.

brain and heart may die after only 4-6 minutes without oxygen. These cells can never be replaced and permanent changes can result from such damage. Other cells in the body are not so critically dependent on an oxygen supply because they are replaceable. Therefore, the respiratory system is a very important function of the body. Oxygen is delivered to the body and carbon dioxide removed through the system [Benjamin, 1996, pg. 35].

As shown in figure 2 [Vander, Sherman, Luciano, 1994, pg. 675 & 677] the respiratory system consist of all organs of the body that contribute to normal respiration or breathing. These include the nose, mouth, upper throat, larynx, trachea, and bronchi (which are called airways or air passages). Also included are the diaphragm and muscles of the chest which permit normal respiratory movements and the lungs, where oxygen is passed into the blood and carbon dioxide is given off. Thus stated, the respiratory system is composed of two main areas: the upper respiratory tract airways (the nose, throat, trachea and major bronchial tubes leading to the lobes of the lungs) and the alveoli, see figure 2, where the actual transfer of gases across the thin cell wall takes place. Only particles smaller than 5 mm in diameter are likely to enter the alveolar sac.

The total amount of toxic compounds absorbed via the respiratory pathway depends on its concentration in the air, the duration of exposure and the pulmonary ventilation volumes which increase with higher work loads. If the toxic substance is present in the form of an aerosol, deposition and absorption can occur in the respiratory tract. Gases and vapors of low water solubility but high fat solubility pass through the alveolar lining into the blood stream and they are distributed to organ sites for which they have special affinity.

As already mentioned, toxic effects by main or other routes of exposure can be influenced by the concentration of the agent in its vehicle, the total volume of the vehicle, the properties of the vehicle to which the biological system is exposed, and the rate at which exposure occurs.

2.1.3 Ear

The ears respond to a vehicular properties of noise whose physical property is pressure. The auditory mechanism that enables us to hear responds in sympathy with the variation of pressure fluctuations or sound waves, which vary in intensity, harmonic content, frequency and direction. These are converted into electrical impulses by the ear and transmitted to the brain. The sensory information received by the brain as electrical impulses is shunted or released from one brain cell to another via electrical and chemical nodes, converted and interpreted at the auditory brain lobe as sound. The outer, middle and inner ear as shown in figure 3 [George and Barry Benjamin, 1996, pg. 89], are the major components of the ear that serve as a vehicle for the conversion process. Sound levels exceeding 60-80 decibels will cause a temporary threshold shift of hearing levels. Prolonged or recurrent exposure will cause a significant permanent threshold shift which in most cases will be irreversible causing permanent damage to the inner ear and loss of hearing.

Effects of noise on humans can be classified in various ways. For example they can be treated as health or medical problems because of their underlying biological basis. Noise induced hearing loss involves damage to the cochlea and medical remedies may be possible. On the other hand, when noise interferes with oral communication or causes

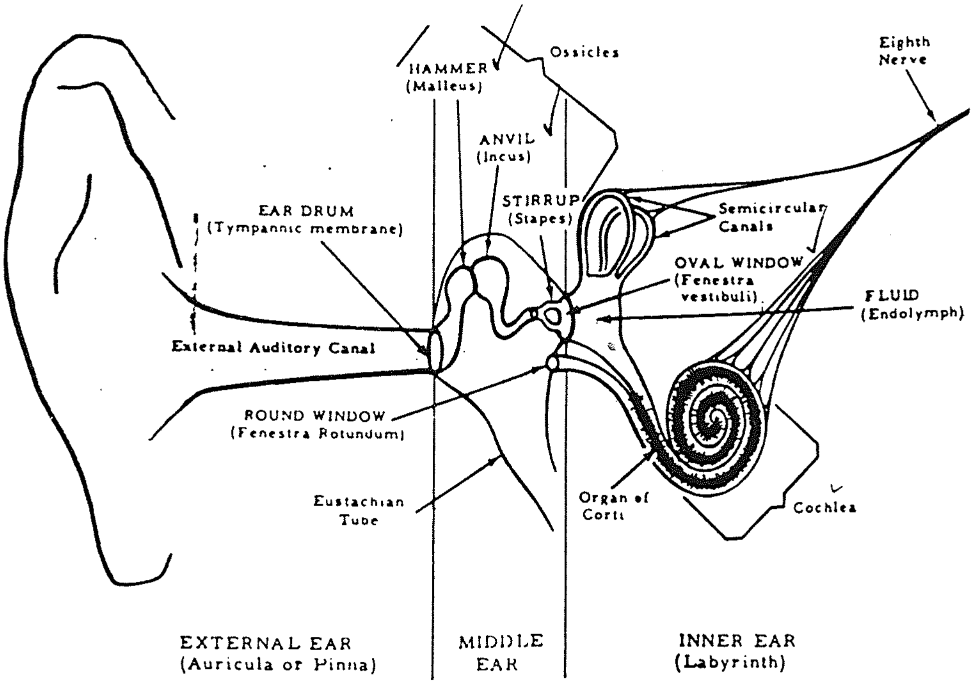


Figure 3. Illustration of the Outer, Middle and Inner Ear

Source: KLAASSEN D. CURTIS & ROZMAN. 1993 PRINCIPLES OF TOXICOLOGY.

stressful annoyance, control options by administrative or engineering should be considered. The vibration of high intensity noise level sets out waves of high frequency into the atmosphere. The physiological damage could be far reaching especially in the body cells. It can cause the cells and some body organs to malfunction. The ear is especially adapted and very responsive to the pressure changes caused by airborne sound or noise. The outer and the middle ear structures are rarely damaged by exposure to intense sound energy. Explosive sounds or blast can rupture the eardrum but more commonly, excessive exposure produces hearing loss by injuring the hair cells of the inner air.

2.1.4 The Eye

The eye, the organ most vulnerable to occupational injuries is other route of exposure to chemical, physical, and biological hazards. Although the eyes have some natural defenses, they do not compare with the healing properties of the skin, the automatic cleansing abilities of the lungs or the recuperative powers of the ear. Hazardous substances can be absorbed into the eyes. Also, foreign objects could be propelled into the eyes if mechanisms for causing traumatic injury exist.

A look at the structure of the human eye and how it can be affected by industrial hazards is necessary in order to engineer proactive protective guards and safety measures for avoidance of this hazard. In addition, a brief discussion of the anatomy of the eyes shall suffice to elucidate the occupational care needed to reduce hazards. Figure 5 shows the schematic drawing of the eye.

It consists of the eyeball housed in a cone of cushioning fatty tissue that insulates it from the skull's bony eye socket. The skull has brow and cheek ridges projecting in

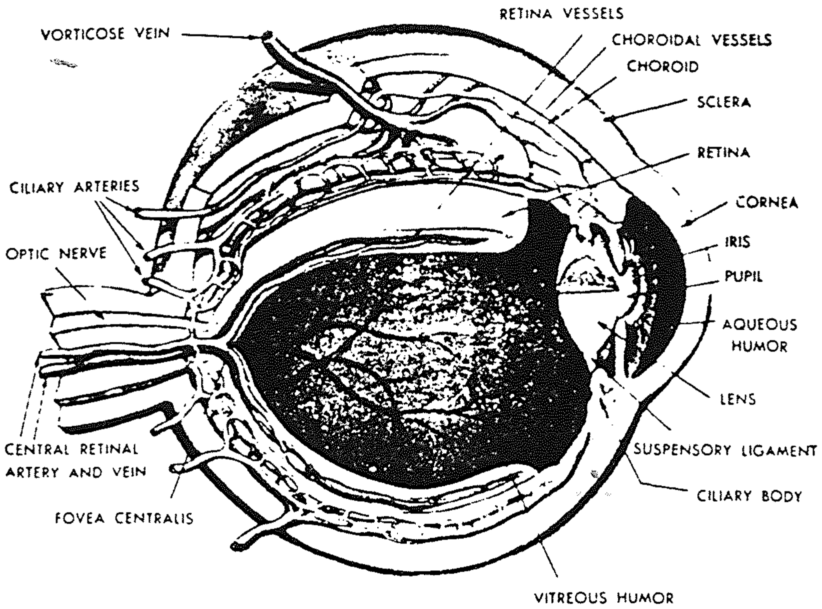


Figure 4. Schematic Drawing of the Eye Showing Anatomic Layers and Vascular Pattern

Source: BENJAMIN G. 1995, Fundamentals of Industrial Hygiene front of the eyeball , which is composed of a specialized tissue that does not react to injury like other body tissue.

The eyeball consists of three coats, or layers of tissue surrounding the transparent internal structures; the external fibrous layer, a middle vascular layer, and an inner layer of nerve tissue. The outermost fibrous layer of the eyeball consists of the sclera and cornea. The sclera or the white of the eye is composed of dense fibrous tissue and is the protective and supporting layer of the eyeball. In front of the lens this layer is modified from a white opaque structure to the transparent cornea. The cornea is composed of a dense fibrous connective tissue and has no blood vessels. The cornea must be transparent to let light through to the receptor in the eyeball.

The middle vascular layer of the eyeball is heavily pigmented and contains many blood vessels that help nourish other tissues. The nerve layer or the retina is the third and innermost layer of the eyeball. Toward the rear, the retina is continuous with the optic nerve and in the front, it ends a short distance behind the ciliary body in a wavy border called the ora serrata. The retina is composed of two parts; the outer part is pigmented and attached to the choroid layer and the inner part consists of nerve tissue. The retina contains the light sensitive cells, called rods and cones. The rods are more sensitive to light than the cones. The cones are sensitive to colors.

The front of the eyeball is protected by a smooth transparent layer of tissue called the conjunctiva. A similar membrane covers the inner surfaces of the eyelids. The eyelid also contains a dozen tiny tarsal glands that secret an oily substance to lubricate the surfaces of the eyeball and eyelids. Further protection is provided by the lacrimal gland located at the outer edge of the eye socket. It secretes tears to clean the protective membrane and keep it moist. The region between the cornea and the lens is filled with a salty, clear fluid known as the aqueous humor. The eyeball behind the lens is filled with a jelly-like substance called a vitreous humor. Light rays enter the transparent cornea and are refracted at the curved interface between air and the fluid bathing the cornea. After passing through the cornea and the clear liquid, the bundle of rays is restricted by a circular variable aperture, the pupil. Its size is changed by action of the iris muscle. The light rays are further refracted by passage through the lens, transferring the clear jelly-like vitreous humor of the posterior chamber so that in a properly focused eye, a sharp image is formed on the retina.

The eye can be contaminated by chemicals, which can cause various effects from minor irritation to complete loss of vision. In addition to accidental splashing, some mists, vapors, and gases can produce either a acute or chronic eye irritation. Many chemicals that do not damage the eyes directly can still cause significant damage through sufficient absorption resulting in systemic poisoning. For example, exposure to irritant chemicals provokes acute inflammation of the cornea with pinpoint vacuoles (holes) of the cornea, which rapidly break down into erosions. Some industrial chemicals irritate the mucous membrane, simulating lacrimation (excessive watering of the eye), discoloration of the conjunctiva, disturbance of vision, double vision, optic atrophy, and temporary or permanent blindness.

Another example are chemical burns from caustics [Benjamin, 1996, pg. 112]. They are much more injurious to the eyes than acids. The medical prognosis of caustic burns is always guarded. An eye might not look too bad on the first day after exposure to a caustic but later may deteriorate markedly. This is in contrast to acid burns in which the initial appearance is a good indication of the ultimate damage. Strong acids tend to precipitate a protein barrier that prevent further penetration into the tissue; the alkalis do not do this. Alkaline continue to soak into the tissue as long as they are allowed to remain in the eye, forming scar tissue on the cornea. Glaucoma may be a condition complicated by chemical Iritis, which penetrates the anterior chamber of the eye.

2.2 Duration and Frequency of Exposure

Chemical exposure hazardous to humans can be studied by exposing animals to various chemicals under laboratory controlled conditions. After exhaustively studying the effects such hazardous chemical may have on the animal, the result can then be extrapolated to humans. The duration, dose and frequency of exposure should follow the laboratory results qualifying exposures into four main categories;

1. Acute
2. Subacute
3. Subchronic
4. Chronic

1) Acute exposure is defined as exposure to chemicals for less than 24 hours, while acute exposure usually refers to a single administration; for an example, intravenous injection. Repeated exposure may be given within a 24 hour period for some slightly toxic or practically nontoxic chemicals. Acute exposure by inhalation refers to continuous exposure for less than 24 hours, most frequently for four hours or less [Klaassen and Eaton, 1993, pg. 14].

2) Subacute, subchronic and chronic are characteristics of repeated exposure. Subacute refers to repeated exposure to a chemical for one month or less, subchronic for one to three months; and chronic for more than three months. For many agents the toxic effects following a single exposure are quite different from those produced by repeated exposure. For example, the primary acute toxic manifestation of benzene is central nervous system depression, but repeated exposure can result in leukemia. Acute exposure to agents that are rapidly absorbed is likely to produce immediate toxic effect. Some can produce delayed toxicity that is different from the effects of chronic exposure.

3) Chronic exposure to a toxic agent may produce some immediate (acute) effects after each administration, in addition to the low-level, long term chronic effect of the agent. In characterizing the toxicity of a specific agent, it is clear that information is needed not only for the single dose (acute) and long term (chronic) effects, but also for exposures of intermediate duration.

4) Frequency of administration is a time related factor for characterization of exposure. A single dose of a chemical that produces severe effects may have no effect if the same total dose is given in several intervals. It is possible that residual cell or tissue damage could be occurring with each dose, even though the chemical itself is not accumulating. The important consideration is whether the interval between doses is sufficient to allow for complete repair of tissue damage.

Studies show that with any type of multiple dose the production of a toxic effect is not only influenced by the frequency of administration, but may in fact be totally dependent on dose rather than duration of exposure. Chronic effects may occur as a result, if the chemical accumulates in the biological system (i.e. when absorption exceeds biotransformation and/or excretion) producing irreversible toxic effects. If there is insufficient time for the system to recover from the toxic, damage will occur within the exposure frequency interval. These referred effects and responses apply when the chemical is monotoxic. Interaction of chemicals could create a spectrum of responses with increasing necessity for consideration of interacting effects of toxicants. These chemical interactions are known to occur in a variety of ways, through a number of mechanisms such as alteration in absorption, protein binding, biotransformation and/or excretion of one or both of the interacting toxicants. In addition, the response of the organism to combinations of toxicants may be increased or decreased because of toxicological responses at the site of action. As an aid to the progression of the hazardous effects of chemical, a brief description of cell biology follows including some of its components, mechanisms of action and related activities.

CHAPTER 3

A COMPOSITE CELL

Cells vary so greatly in size, shape, and function. It is not possible to describe a typical cell. A composite cell will contain parts observed in many kinds of cell.

Commonly a cell consists of two major parts, one within the other and each surrounded by a thin membrane. See figure 5. Showing the structure found in most common cells [Vander Sherman, Luciano, 1994, pg. 43].

I) Cell nucleus (enclosed by nucleus envelop)

ii) Cytoplasm (Mass of fluid the surrounds the nucleus and encircled by cytoplasmic or cell membrane).

Within the cytoplasm are other membranes that separate it into small subdivisions. These are cytoplasmic organelles. These organelles perform specific metabolic functions necessary for cell survival. The nucleus, on the other hand, directs the overall activities of the cell.

The cell membrane is the outermost limit of the cell. It is more than a simple envelope surrounding the cellular contents. It is an actively functioning part of the living material and many important metabolical reactions take place on its surface. In addition to maintaining the wholeness of the cell, the membrane serves to control the entrance and exit of substances. That is, it allows some substances to pass through the membrane and excludes others, thus the name "selectively permeable". A "permeable membrane" on the other hand, is a membrane that allows all materials to pass through.

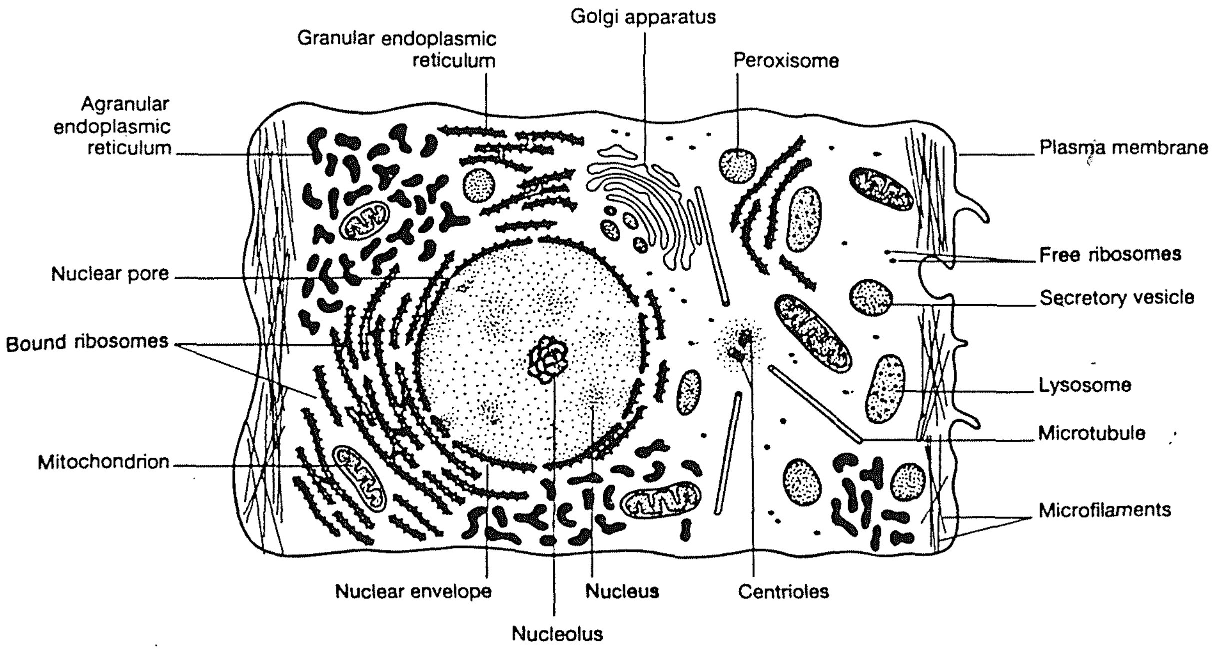


Figure 5. Structures Found in Most Human Cell

Source: VANDER A.J., J.H. SHERMAN, D.S. LUCIANO, 1994: Human Physiology.

Cytoplasm contains networks of membranes and other organelles suspended in a clear liquid (cytosol). It is where food molecules are received, processed, and used. In other words, cytoplasm is a site of metabolic reactions, in which the following cytoplasmic organelles play specific roles.

a) Endoplasmic reticulum

b) Ribosomes

c) Golgi apparatus

d) Mitochondria

e) Lysosomes

f) Peroxisomes

g) Centrosome

h) Cilia and flagella

i) Micro filament and microtubules

A cell nucleus is usually located near the center of the cytoplasm. It is a relatively large spherical structure and functions to direct the activities of the cell. Table 3 Summarizes the structure and function of cellular organelles [Hole, 1987, pg. 83]

The cell membrane provides a surface through which various substances enter and leave the cell. More especially, oxygen and food molecules enter a cell through this membrane while carbon dioxide and other wastes leave through it. These movements can be through physical or physiological mechanism. Physical movement is by means of diffusion, facilitated diffusion, osmosis and filtration. Physiological mechanism involves active transport and entocytosis.

Table 3. Structure and Function of Cellular Organelles

Organelle	Structure	Function
Cell membrane	Membrane composed mainly of protein and lipid molecules	Maintains wholeness of cell and controls passage of materials in and out of cell
Endoplasmic reticulum	Network of interconnected membrane forming sacs and canals	Transports materials within the cell and provides attachment for ribosomes and synthesizes lipids
Ribosomes	Particles composed of protein and RNA molecules	Synthesizes proteins
Golgi apparatus	Group of flattened membranous sacs	Packages proteins molecules for secretion
Mitochondria	Membranous sacs with inner partitions	Release energy from food molecules and transform energy into usable form
Lysosomes	Membranous sacs	Contains enzymes capable of digesting substances that enter cells
Peroxisomes	Membranous vesicles	Contain enzymes called peroxidases
Centrosome	Nonmembranous structure composed of two rodlike centrioles	Helps distribute chromosomes to daughter cells during cell reproduction and initiates formation of cilia
Cilia and flagella	Hairlike projections attached to basal bodies beneath cell membrane	Propels fluids over cellular surface and enables sperm cells to move
Vesicles	Membranous sacs	Contain various substances that recently entered the cell
Microfilaments and microtubles	Thin rods and tubules	Provide support to cytoplasm and help move objects within the cytoplasm
Nuclear envelope	Porous double membrane that separates nuclear contents from cytoplasm	Maintains wholeness of the nucleus and controls passage of materials between nucleus and cytoplasm
Nucleolus	Dense nonmembranous body composed of protein and RNA molecules	Forms ribosomes
Chromatin	Fibers composed of protein and DNA molecules	Contains cellular information for carrying on life processes

Source: HOLE W. JOHN JR. 1987, "THE CELL" Human Anatomy and Physiology.

Diffusion is the process by which molecules or ions become scattered, or are spread from regions where they are in higher concentrations toward regions where they are in lower concentrations. Several factors influence the rate at which diffusion occurs. They include the distance involved, the concentration of the substance, the weight of the molecules, and the temperature. Generally, diffusion occurs more rapidly over a shorter distance. As earlier stated, diffusion increases when the concentration of the diffusing substance is greater, the molecular weight lower and the temperature higher. A typical example of the use of diffusion is in clinical application of dialysis, which is described below [Hole Jr. 1987, pg. 83].

a) Dialysis is the process of separating smaller molecules from larger ones by means of diffusion. It is employed in the artificial kidney, which is often used by patients suffering from kidney dysfunction. When in operation, blood from the patient is passed through a long coiled tubing composed of porous cellophane. The size of the porous allows smaller molecules in blood such as urea to pass out through the cellophane while larger molecules like those of blood proteins, remain inside. The tube is submerged in a tank of wash solution called dialyzing fluid, that contains various concentration of chemicals. The solution is low for instance, in concentrations of substances that should leave the blood and higher in concentration of those should remain in the blood.

Since it is desirable for an artificial kidney to remove blood urea, the dialyzing fluid must have a lower concentration of urea than the blood does; it also desirable to maintain the blood glucose concentration, so the concentration of the glucose in the dialyzing fluid must be kept at least equal to that of the blood. Therefore, by altering the concentration of molecules in the dialyzing fluid it is possible to control those that will diffuse out of the blood and those that will remain in.

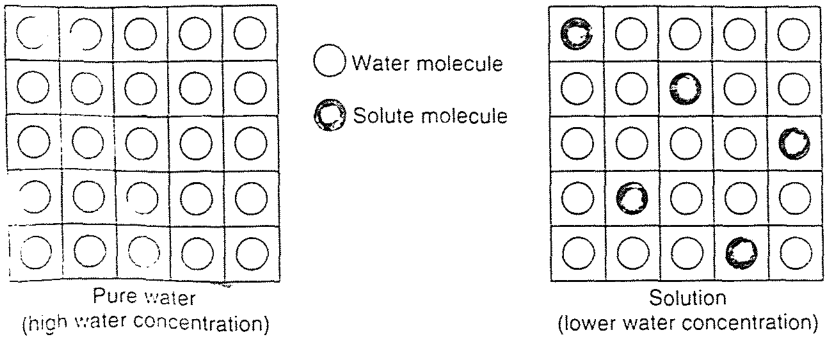
b) Another procedure sometimes used to help patients with kidney problems is called “Peritoneal Dialysis”. In this case, dialyzing fluid is infused into the patient’s abdominal cavity through an artificial opening. This cavity is lined with a thin membrane. As before, the composition of the dialyzing fluid is controlled so that unwanted substances will diffuse from the blood of the vessels in the peritoneum into the dialyzing fluid. After several hours the fluid is drained from the abdominal cavity and is replaced with fresh fluid.

Facilitated diffusion is the process where molecules that cannot diffuse readily at the cell membrane composed largely of lipids are carried into the cell by a special carrier molecule. At the cell membrane, molecules soluble in lipids such as oxygen and carbon dioxide can diffuse readily through it. Other substances that are not soluble in lipids such as water and certain ions cannot diffuse readily through the membrane but may pass through membrane pores. For example, most sugars are insoluble in lipids and they have molecular sizes that prevent them from passing through membrane pores. Some of these such as glucose, can still enter through the lipid portion of the membrane through facilitated diffusion: The glucose combines with a special carrier molecule at the surface of the membrane. The union of glucose and carrier molecules create a compound that is soluble in lipids, and it can diffuse to the other side. There the glucose portion is released, and the carrier molecules return to the opposite side of the membrane and pick up another glucose molecule.

Another special case of diffusion known as Osmosis occurs whenever molecules diffuse from a region of higher water concentration (where the solute concentration is lower) to a region of lower water concentration (where the solute concentration is higher) through a selectively permeable membrane such as the cell membrane. See figures 6. Ordinarily, the concentrations of water molecules are equal on either side of cell membrane. Sometimes, however, the water on one side has more solute dissolved in it than the water on the other side. For example, if there is a greater concentration of glucose (solute) in the water outside the cell, there must be a lesser concentration of water there, because the glucose molecules occupy space that would otherwise contain water molecules. Under such conditions, water molecules diffuse from inside the cell (where they are in higher concentration) toward the outside (where they are in lower concentration). When osmosis occurs, water tends to move toward the region of greater osmotic pressure (higher solute concentration) from a region of lesser osmotic pressure (lower solute concentration). In a cell, the former condition will be called "Hypertonic" (water leaving a cell rather than enter it); and the latter condition "Hypotonic" (water enters the cell rather than leaving it). Depicted in figure 7. A solution that contains the same concentration of solute particle as a cell is said to be isotonic to that cell.

3.1 Filtration

Filtration occur when molecules are forced through a membrane by hydrostatic pressure or blood pressure that is greater on one side of the membrane than the other - unlike diffusion or osmosis, which is due to movements of the molecules of those substances. Filtration is commonly used to separate solids from liquids. In body tissue, fluid is formed when water and dissolved substances are forced out through the thin wall of blood capillaries, while larger particles such as food protein molecules are left inside. The force for this movement comes from blood pressure created largely by heart action which is greater within the vessel than outside. Filtration also takes place in the kidneys, when



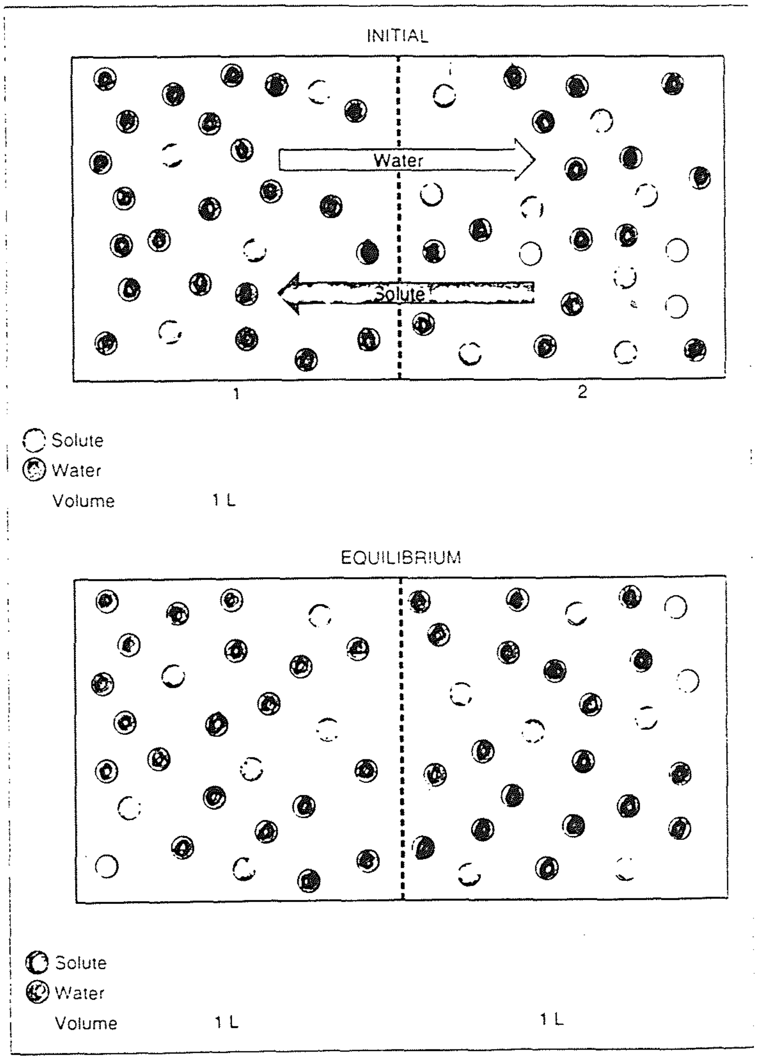


Figure 6. Diffusion of Water and Solute Between Two Compartments

Source: VANDER A.J., J.H. SHERMAN, D.S. LUCIANO, 1994: Human Physiology.

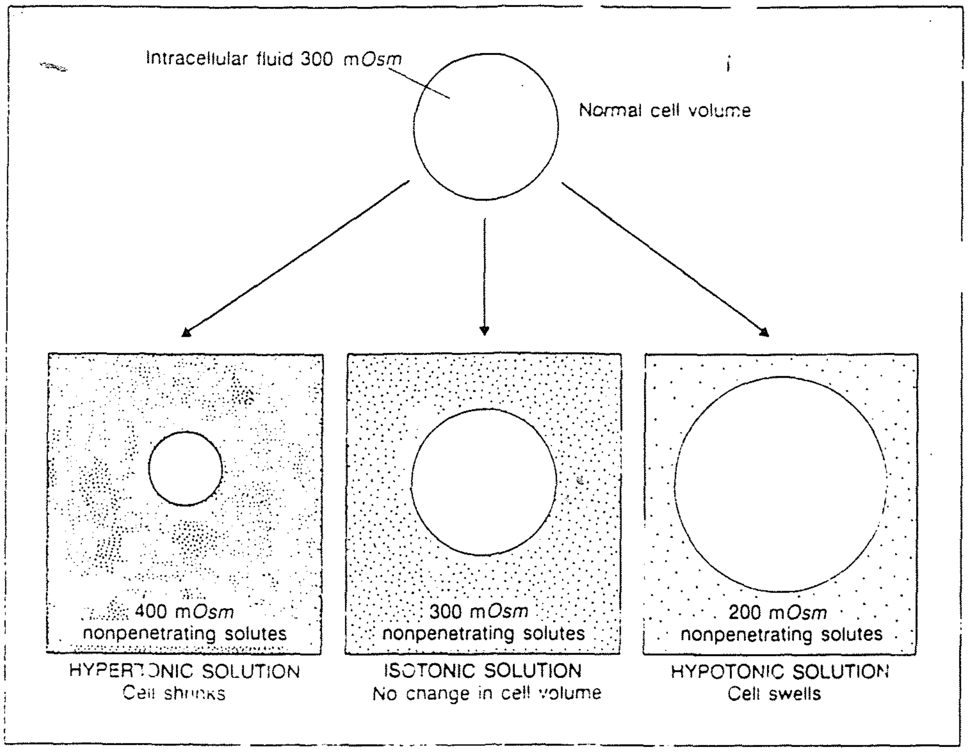


Figure 7. Changes in Cell Volume Produced by Hypertonic, Isotonic and Hypotonic solution's

Source: VANDER A.J., J.H. SHERMAN, D.S. LUCIANO, 1994: Human Physiology.

water and dissolved wastes are forced out of the blood vessels into kidney tubules by blood pressure, leading to the formation of urine.

When molecules or ions pass through cell membranes by diffusion, facilitated diffusion or osmosis, their net movement is from regions of higher concentration to regions of lower concentration. Sometimes, however, the net movement of particles such as ions passing through membranes is in the opposite direction, that is, from a region of lower concentration to one of higher concentration. This is called active transport.

3.2 Mechanism of Active Transport

Although the details are poorly understood, the mechanism of active transport is similar to facilitated diffusion in that it involves specific carrier molecules, probably protein molecules formed within cell membranes. See figures 8 [Vander, Sherman Luciano, 1994]. These carrier molecules have binding sites that combine with the particle being transported at the membrane's surface. Such a union, triggers the release of some cellular energy, and causes the shape of the carrier protein to change. As a result, particles move through the membrane. Once on the other side, the transported particle is released as a result of enzyme action and the carrier molecule can now accept another particle at its binding site.

Particles that are carried across cell membranes by active transport include various amino acids as well as a variety of ions such as sodium, potassium, calcium, and hydrogen. Movements of this type are important for cell survival and are involved with the maintenance of homeostasis.

Another physiological process by which substances may move through cell membranes. In this case, molecules or other particles that are too large to enter a cell by

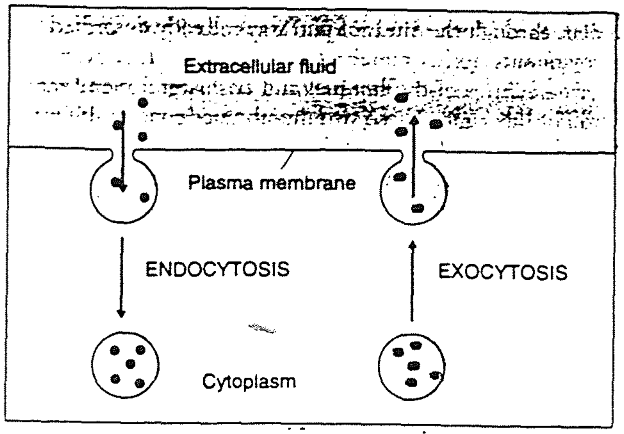
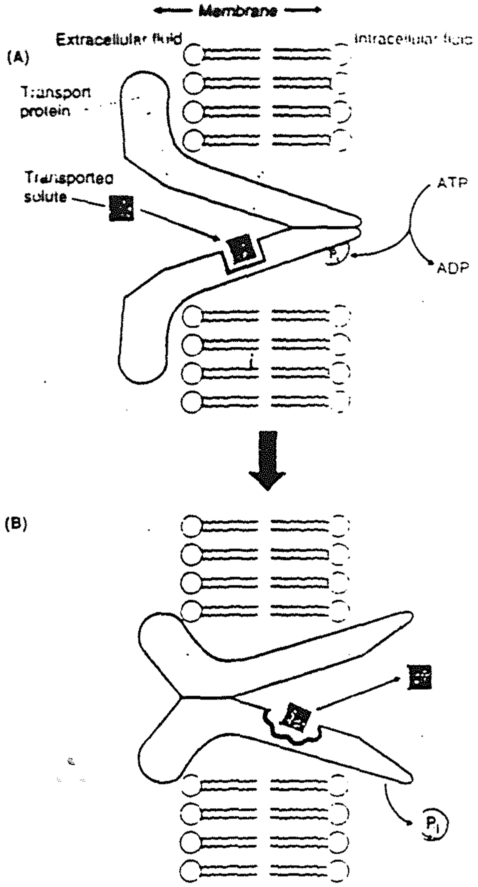
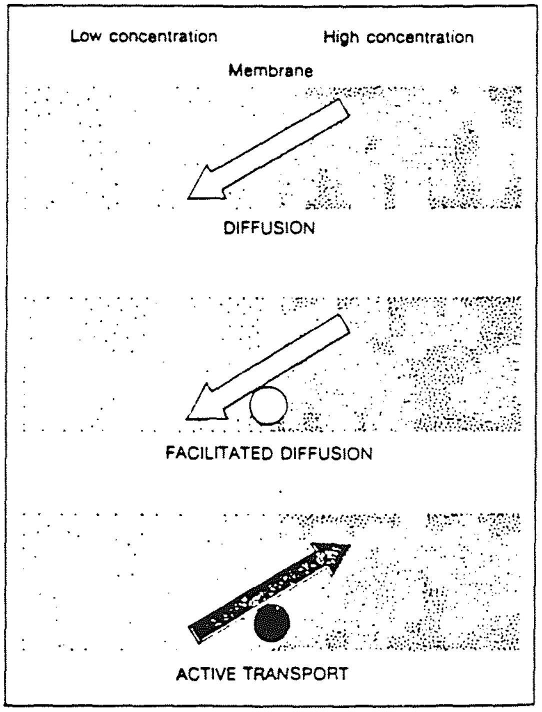


Figure 9. Edocytosis And Exocytosis





(C)

Figure 8a,b. Primary Active Transport

Figure 8c. Direction of Solute Flow Crossing Membrane

- Diffusion – High to Low Concentration
- Facilated diffussion – High to concentration
- Active transport – Low to high concentration

Source: VANDER A.J., J.H. SHERMAN, D.S. LUCIANO, 1994: Human Physiology.

diffusion or active transport may be conveyed within a tiny vesicle formed by a section of the cell membrane. There are three forms of endocytosis - pinocytosis, phagocytosis, and receptor - mediated endocytosis [Hole Jr. 1987, pg. 87].

a) Pinocytosis - cell drinking - refers to the process by which cell take in droplets of liquid from their surrounding. This happens when a small portion of a cell membrane becomes invaginated (indented). The open end of the tubelike part thus formed seals off and forms a small vesicle. This tiny sack becomes detached from the surface and moves into the cytoplasm, where it breaks down and become part of the cytoplasm. Figure 9 shows the process of Edocytosis and Exocytosis [Vander, Sherman Luciano, 1994].
In this way a cell is able to take in water and dissolved particles, such as protein, that otherwise might be unable to enter because of large molecular size.
b) Phagocytosis - cell eating - is a process as that of pinocytosis except that instead of liquid, the material taken into the cell is solid. White blood cells behave in such a manner and are called phagocytes because they can take in tiny solid particles such as bacterial cells.

When a phagocyte first encounters such a particle, the object becomes attached to its cell membrane. This stimulates a portion of the membrane to project outwards, surrounding the object and slowly draws it inside. The part of the cell membrane surrounding the solid detaches from the surface, and a vesicle containing the particle is formed. Commonly a lysosome soon combines with such a vesicle, and lysosome digestive enzymes cause the content to decompose as in figure 10. The products of this decomposition may then diffuse out of the lysosome and into the cell's cytoplasm and may be used as raw material in other metabolic processes. Any remaining residue may be

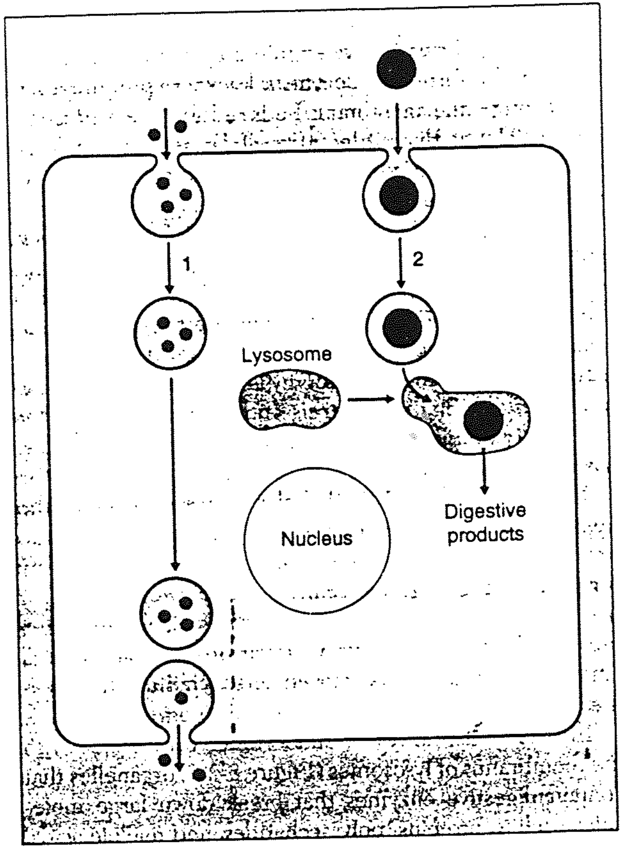


Figure 10. Fate of Edocytosis Vesicle

Source: VANDER A.J., J.H. SHERMAN, D.S. LUCIANO, 1994: Human Physiology.

expelled from the cell (Exocytosis). In this way phagocytic cells can destroy bacteria that might otherwise cause infections, dispose of foreign objects such as dust particles, or remove damaged cells or cell parts that are no longer functional. Phagocytosis as would be seen is an important line of defense against invasion of disease-causing micro-organisms.

Receptor -mediated endocytosis moves very specific kinds of particles through membranes. This process involves the presence of particular protein molecules that extend through the cell membrane and are exposed at its outer surface. These protein serves as receptor sites to which specific substances (ligands) from fluid surroundings of the cell can bind. Thus when molecules that are capable of binding to the receptor sites are present, only those molecules are selected to enter the cell, leaving other kinds of molecules outside of the cell. In this process, selected molecules combine with receptor proteins. The formation of such combinations somehow stimulates the membranes to indent and create a tiny vesicle that contains the selected molecules - an action similar to that discussed above with regard to pinocytosis. Receptor-mediated endocytosis is of particular importance because it allows a cell to remove specific kinds of substances from its surroundings even when these substances are present in very low concentration.

CHAPTER 4

HOW CHEMICALS PRODUCE TOXIC EFFECT

All chemicals produce their toxic effects through alteration in normal cellular biochemistry and physiology. A thorough understanding of the biochemical and molecular sites and modes of actions of specific drugs and chemicals is an essential part of toxicology. Although cell death is one common outcome of chemical induced injury, there are obviously other serious consequences. The extent of tissue damage necessary to elicit a life-threatening response is quite varied depending on both tissue type and the rate at which insult occurs.

Some tissue, most notable, epithelial tissue such as liver, have some capacity to regenerate in response to a loss in tissue mass, whereas other tissues such as neuronal cells cannot regenerate once cells have died. Also, most organs have a capacity for function that exceeds that required for normal homeostasis. For example, it is well known that humans can function quite effectively with only one kidney or part of a lung removed or only half of their normal hemoglobin. This excess function is a critical element in the ability of the body to survive severe toxic insults.

Although many toxic responses are ultimately a result of cell death and loss of critical organ function, other responses may be the result of biochemical and/or pharmacological imbalance in normal physiological process that do not result in cell death. Other chemical effects may result in the expression of toxicity as a result of non - lethal genetic alterations in somatic cells. There are many ways in which chemicals can interfere with normal biochemistry and physiology and a brief overview of some general sites of toxic action is useful for appreciating the diversity of biochemical and cellular processes that underline toxic responses. Several categories such as those discussed below are not exhaustive but illustrate the major mechanisms of action followed by many drugs and chemicals [Klaasen and Eaton 1993, pg. 26].

4.1 Interactions and Steroselective Actions of Chemicals

Receptors are macromolecular components of tissues with which a drug or chemical (ligand) may interact to produce its characteristic biological effect. The binding between a receptor and a ligand is usually reversible. The ligand may be an endogenous substance which interacts with the receptor to produce a normal physiological response or an exogenous substance that may either activate or block the response. Receptor - ligand interactions are generally highly stereospecific and small changes in chemical structure can drastically reduce or eliminate the effect. The importance of stereoseletivity in pharmacological and toxicologic responses cannot be overemphasized. Differences in activity extend not only to structurally distinct chemicals and geometric isomers but to those chemicals that have clinical properties and thus may be present as mixtures of stereo isomers. Thus toxic effects of atropine are largely related to inhibition of the parasympathetic nervous system. In contrast, d-tubocurarine binds to and selectively blocks postsynaptic nicotinic receptors at the neuromuscular function, producing profound paralysis, but has little effect on parasympathetic nervous system function.

4.2 Membrane Functions Interference

To maintain normal physiology, the maintenance and stability of excitable membranes are of paramount importance. Chemicals or radiation can disturb the normal operations of these membranes causing them to malfunction. Klaasen and Eaton in 1993 wrote the general Mechanism of Toxicity, gave the following examples.

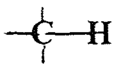
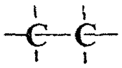
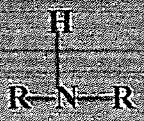
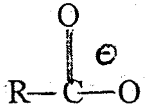
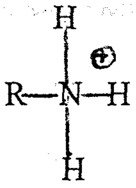
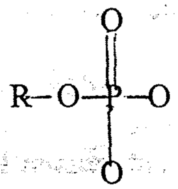
1. The flux of ions across neuronal axons can be blocked by chemicals and radiation causing them ~~to~~ malfunction by acting as ion channel blockers. The marine toxin, saxitoxin, produces its paralyzing effects by blocking sodium channeling in excitable membranes. Tetrodotoxin, derived from the gonads and other organs of the puffer fish, is structurally quite different from saxitoxin, yet acts in essentially the same manner. The insecticide DDT produces its neurotoxic action by interfering with the closing of the sodium channels, thus altering the rate of depolarization of excitable membranes. Organic solvents appear to produce their CNS (Central Nervous System) depressant effects via nonspecific alterations in membrane fluidity, largely as a property of their lipid solubility rather than binding to specific macromolecular receptors. See table 4, example of polar and non polar bonds and ionized chemical group.

2. Many chemicals also interfere with the oxidation of carbohydrates to produce adenosine triphosphate (ATP), the energy the body uses, and therefore must be recycled continuously. This interference can occur by blocking the effective delivery of oxygen to tissues. For example, chemical oxidation of the iron in hemoglobin (methemoglobin) by nitrates also interferes with oxygen delivery because methemoglobin does not effectively bind oxygen. Effective blockade of oxygen to tissues is also a property of cyanide, hydrogen sulfide and azide because of their affinity for cytochrome oxidase.

3. The formation of ATP by oxidation of carbohydrates are blocked at other sites as well. For example, rotenone and antimycin A, interfere with specific enzymes in the electron transport chain; nitrophenols uncouples oxidative phosphorylation; sodium fluroacetate inhibits the tricarboxylic acid (Krebs) cycle. The consequences of ATP depletion are many, including such interference with membrane integrity, ion pumps and protein synthesis which were not mentioned above. Such interference significantly lead to serious energy depletion, giving rise to loss of cell function and perhaps cell death.

4. Many toxic chemicals exert their effects by binding to the active sites of enzymes or proteins that are critical to cellular functions. For example, hydrogen cyanide binds avidly to the ferric iron atom in cytochrome (cytochrome oxidase), which blocks the terminal events in electron transport. This single site of action is responsible for the rapid and often toxic effect of cyanide. Carbon monoxide binds lightly to the reduced form of iron in hemoglobin causing a reduction in the delivery of oxygen to tissues. Many toxic trace metals such as lead, mercury, cadmium, and arsenic bind to proteins with free sulfyhydryl group contributing to their toxicity.

Table 4. Example of nonpolar and polar bonds, and ionized chemical groups.

Non-polar bonds	 $-\overset{\vert}{\underset{\vert}{C}}-H$	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
	Carbon-Hydrogen bond	**Carbon – Carbon bond**
	R—O—H	Hydroxyl group (R–OH)
Polar bonds	R—S—H	Sulfhydryl group (R–SH)
	 $R-\overset{\overset{H}{\vert}}{N}-R$	Nitrogen-hydrogen bond
	 $R-\overset{\overset{O}{\Vert}}{C}-O^{\ominus}$	Carboxyl group (R–COO$^-$)
Ionized groups	 $R-\overset{\overset{H}{\vert}}{\underset{\underset{H}{\vert}}{N^{\oplus}}}-H$	Amino group (R—NH$_3^+$)
	 $R-O-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\vert}}{P}}-O$	Phosphate group (R–PO$_4^{2-}$)

Source Vander, Sherman, Luciano. 1994. " CLASSES OF ORGANIC MOLECULES" Human Physiology 6: 19.

Chemically induced porphyries from lead, mercury, and other metals as well as certain halogenated hydrocarbons (e.g. Hexachlorbenzene) result in part from the inhibition of specific enzymes in the heme-biosynthesis pathway.

As stated earlier, adverse physiological responses will result without the actual death of cells in tissues and organs, (as in case of most receptor-ligand interaction). Other processes, also discussed, eventually lead to loss of organ function and cell death. This is especially true if exposure to toxic substances occurs on a chronic basis where tissue injury can accumulate from repeated chemical exposure. The specific sequence of events leading to cell injury and death is complex and most times defies clear comprehension because of many variables involved in its biomechanism. However, from studies of liver cells, processes leading to chemically induced cell death becomes clearer.

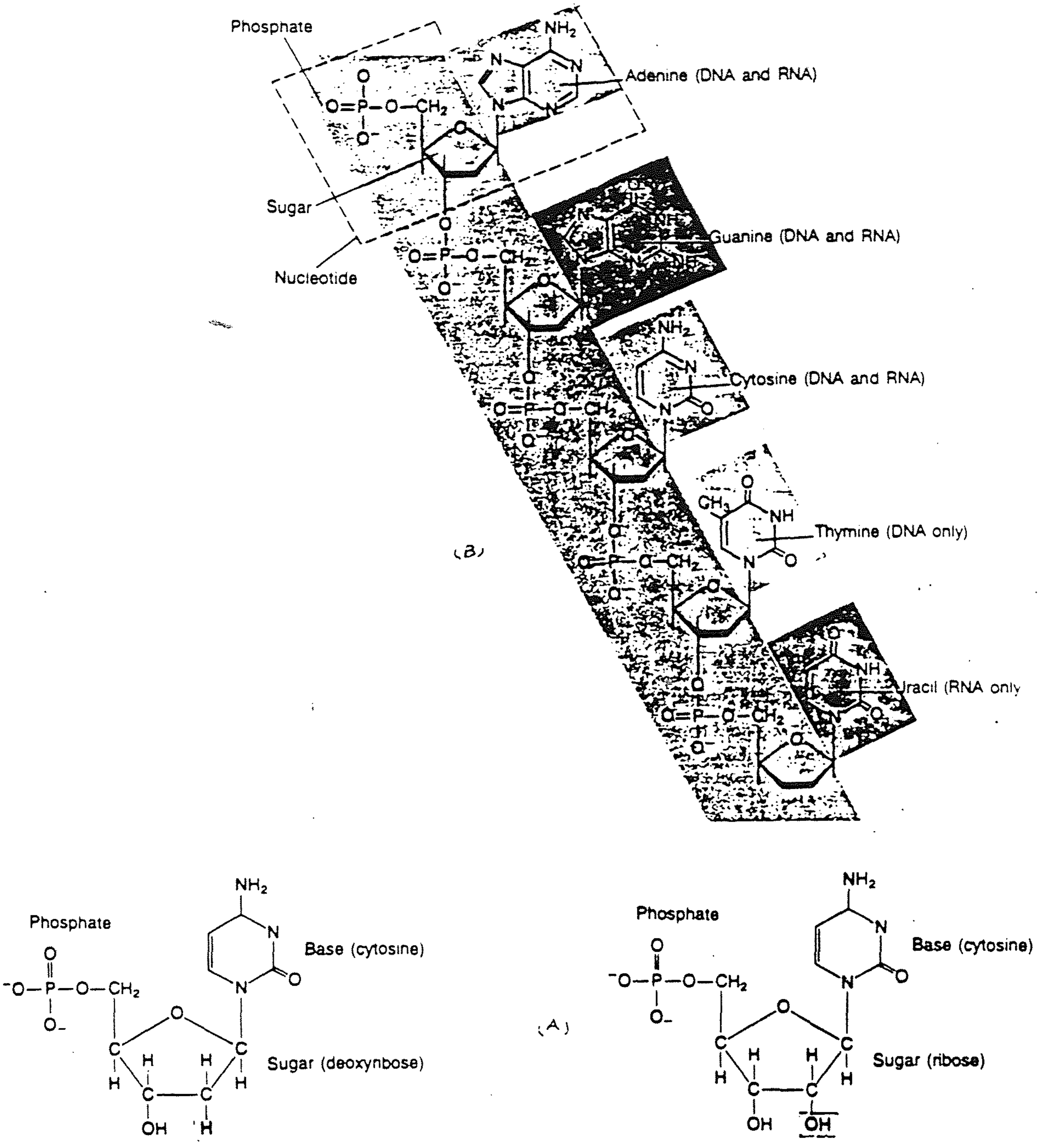
For most chemicals causing tissue necrosis, the initial step appears to be the formation of a reactive, electrophilic intermediate, often a free radical. Formation of free radical may occur via enzyme -mediated one or two electron oxidation, as well as from the autoxidation of small molecules such as a reduced flavine.

Electron transfer from transition metals, such as iron, to oxygen molecules can also initiate, and propagate free radicals reactions. The ignition of lipid per oxidation through interaction of free radical with polyunsaturated fatty acids to form lipid peroxyradicals (ROO) which then produce lipid hydro peroxides (ROOH) and further lipid peroxyradicals has been proposed as one critical step leading to cell injury and death. Peroxidative damage to membrane lipids could then lead to a loss of membrane integrity and rupture of the cell membrane. In any case, lipid peroxidation by itself may not be sufficient to induce cell death, electrophilic intermediates may also covalently interact with other nucleophilic sites in the cell including glutathione (GSH) and thole containing proteins which result in “oxidative stress” to the cell. One group of thole containing enzymes that may play a critical part in cell injury and death as a result of oxidative inactivation (oxidation stress) is the calcium transporting ATPases.

4.3 *Nucleic* Acid

There are numerous nucleophilic sites within DNA that may readily react with electrophilic chemicals. Abduction of DNA with exogenous chemicals may alter the expression of critical gene products necessary for the survival of the cell, and thus binding to DNA will lead to the cell death. Of greater significance is the production of somatic mutations through chemicals - DNA adduct formation that may serve as the initiating event in chemical carcinogenesis. As with DNA ribonucleic acid (RNA) also contains nucleophilic sites and thus critical intracellular functions of RNA, e.g. protein synthesis, may be perturbed by covalent interaction of electrophilic chemicals with RNA (Figure 11). Interference with the normal process responsible for intracellular calcium homeostasis appears to play a critical role in chemical mediated cell injury and death.

Calcium accumulates in tissues following necrotic injury and its accumulation has been associated with cell injury and death. Disruption of intracellular calcium homeostasis can result from enhanced calcium influx, release of calcium from intracellular stores, and inhibition of calcium extrusion at the plasma membrane. A wide variety of cytoxic agents nitrophenols, guinones, peroxides, aldehydes, dioxins, halogenated alkanes and alkanes and some metal ions, have been shown to disrupt calcium homeostasis. Increased intracellular calcium has been associated with the development of membrane abnormalities in isolated cells, which appears to be a general phenomenon associated with toxic and ischemic cell injury and death. Calcium plays a key role as a second messenger in the regulation of many intracellular functions. For example, normal cytoskeletal organization is disturbed when intracellular calcium increases, apparently as a result of a calcium - mediated dissociation of actin micro filaments and an activation of phospholipases and proteases. Under normal



Typical deoxyribonucleotide

Typical ribonucleotide

Figure 11. Nucleotide Submits of DNA and RNA

Note: Thymibic (DNA only); Uracile (RNA only)

(A). Nucleotide Submits of DNA and RNA

(B). Phosphate – Sugar bond Link Nucleotides in Sequence to Form Nucleic Acids

Source: VANDER A.J., J.H. SHERMAN, D.S. LUCIANO, 1994: Human Physiology.

circumstances, activation of phospholipases plays a protective role by removing peroxidized phospholipids from damaged membranes on the other hand phospholipases may enhance membrane phospholipid breakdown which may lead to cell injury and death when activated by nonphysiogic condition that changes the calcium concentration.

Calcium can also activate certain endonucleases, which results in DNA fragmentation and chromatin condensation. Although this process is important in the physiological processes that cause death to occur naturally as a part of tissue growth and differentiation (apoptosis), chemically mediated premature activation of this enzyme system through a perturbation of calcium homeostasis may contribute to the cytologic action of some toxic substances.

Selective cell loss within an organ or tissue may also result in toxicologic effects that are quite specific and in some cases, may mimic other disease processes. For example high doses of manganese causes selective damage to dopamineigic cells in the basal ganglia in the brain, producing a neurological condition nearly indistinguishable from the Parkinson's disease. Some chemicals such as Amitrol (a synthetic drug) and 5 - vinyloxazolidinethione (naturally occurring from the gape-seed plant), stimulate the growth of the thyroid hormone, resulting in a pathological condition similar to goiter. Similarly, the developing embryo is also quite sensitive to many toxic substances. During cell differentiation, loss of even a few cells can have major consequences, leading either to embryonic death or some form of congenital malformation. Also, it was proven that administration of antinausea drug thalidomide to pregnant women at a specific stage of fetal development resulted in the cytologic loss of early limb bud cells with the consequence that children were born with severely underdeveloped or had missing legs and arms.

Table 5 Some General Mechanisms of Toxic Action

Interference with Normal Receptor-Ligand Interactions
Neuroreceptors and neurotransmitters (e.g gastropine, strychnine. LSD. *d*-tubocurarine,
  Organophosphates, antihistamines)
Hormone receptors (DES. TCDD, gottroga)
Enzyme activity (organophosphates, cynande. sodium fluoroacetate)
Transport proteins (carbon monoxide, nitrites)
Interference with Membrane Functions
Excitable membranes
  Ion flux (saxitoxin. tetrodotoxin, DDT)
  Membrane fluidity (organic solvents, ethanol, local anesthetics)
Membranes in organnelles
  Lysosomal membranes (carbon tetrachloride)
  Mitochondrial membranes (organotins)
Interference with Cellular Energy Production
Oxygen delivery to tissues (CO, nitrite)
Uncoupling of oxidative phosphorylation (nitrophenols, organotins)
Inhibition of electron transport (rotenone, antimycin A)
Inhibition of carbohydrate metabolism (fluoroacetate)
Binding to Biomolecules
Interference with enzyme functions
Lipid peroxidation (CCL . paraquat. ozone)
  Free radical generation
  Formation of lipid hydroperoxides
Oxidative stress
  Depletion of GSH (acetaminophen)
  Oxidation of protein thiols
Nucleic Acids
  DNA
  RNA
Perturbation in Calcium Homeostasis
Cytoskeletal alterations
Activation of phospholipases
Activation of proteases
Activation of endonucleases
Toxicity from Selective Cell Loss
Hormonal and physiological imbalances (e.g. loss of dopaminergic neurons: thyroid insufficiency)
Birth defects
Nonlethal Genetic Alterations in Somatic Cells
Cancer
  Initiation
  Promotion
Birth defects and transplacental carcinogens

Source: KLASSEN D. CURTIS & EATON L. DAVID. 1993 Principles of Toxicology.

As noted earlier, the covalent interaction of xenobiotics (foreign compounds) with DNA can directly lead to the death of the cell but may also result in the initiation of a complex series of events that may ultimately result in cancer. The vast majority of chemically induced lesions in DNA are repaired by the body's defenses, but some may escape leading to the introduction of a mutilated gene that is inherited. If the mutation occurs in a somatic cell, then the genetic lesion cannot be passed onto future generations, but could serve as a precursor for the eventual development of cancer.

4.4 Chemical Barrier and Biotransformation of Toxicants

The skin, lungs, and alimentary canal are the main barriers separating higher organisms from an environment that contains a large number of chemicals. Toxicants need to cross one or several of these incomplete barriers to exert deleterious effects at one or several sites of the body, with the exception of caustic and corrosive agents, which act topically. A chemical absorbed through any of these three barriers into the bloodstream is distributed to some extent throughout the body.

The site where chemicals produce damage is often called target organ or target tissue. A chemical may have one or several target organs. For example, benzene affects the hematopoietic system, and carbon tetrachloride the liver. Lead and mercury both damage the central nervous system, and kidney. It is self-evident that in order to produce a direct toxic effect in an organ, a chemical must reach that organ. However, indirect toxic responses may be precipitated at distant sites if a toxicant alters regulatory functions. For example, cholestyramine, a non absorbable resin may trap certain acidic vitamins in the intestinal lumen and cause systemic toxicity in the form of various vitamin deficiency syndromes. Several factors other than concentration influence the susceptibility of organs to toxicants. Therefore the organ or tissue with the highest concentration of a toxicant is not necessarily the site where toxicity is exerted. A good example is chlorinated hydrocarbon insecticide leg dichlorodiphenyltrichloroethane (DDT) which attains the highest concentrations in fatty deposits of the body, but produce no known toxic effects in this tissue. A toxicant may also exert its adverse effects directly on the blood stream as in the case with arsine gas which causes hemolysis (the liberation of the hemoglobin).

Toxicants are removed from the circulation system by biotransformation, excretion and storage at various sites of the body. The relative contribution of these processes to total elimination depends on the physical and chemical properties of the chemical. The kidney plays a major role in the elimination of most toxicants but other organs may be of critical importance for some toxic agents. The elimination of a volatile agent such as carbon monoxide by the lungs or that of lead in the bile are examples of this effect. Although liver is the most active organ in the biotransformation of toxicants, other organs or tissues (enzymes in plasma, kidney, lungs, gastrointestinal track, etc.) may also contribute to overall biotransformation. Biotransformation often is a prerequisite for renal excretion because many toxicants are lipid soluble and are therefore reabsorbed from the renal tubule after glomerular filtration.

After a toxicant is biotransformed its metabolites may be excreted preferentially into bile, as are the metabolites of DDT or they may be excreted into urine as are the metabolites of organophosphate insecticides. It should be noted that the degree of ionization and lipid solubility of chemicals are very important for oral and percutaneous exposures, whereas water solubility, tissue reactivity and blood - to - gas phase partition coefficients, are important after exposure to certain gases and vapors.

CHAPTER 5

PREVENTIVE TECHNIQUE

There are many ways or techniques for the prevention of chemical exposure. The most common is the traditional technique, known as personal hygiene and good housekeeping. Progressively over the years, new techniques were added, such as "avoidance" and "containment of hazardous chemicals," by government legislations and guidelines. These techniques called group 1 complement the advanced methods and innovation techniques group 2 discussed in Chapter 6. They provide far reaching solutions to the problems of workplace and environment pollution.

5.1 Traditional Techniques (Group 1)

The traditional technique used to limit or prevent chemical exposure at work places and the environment are in four categories.

1. Personal hygiene and housekeeping
2. Avoidance of hazardous chemicals
3. Containment of hazardous chemicals
4. Legislation and guidelines

5.1.1 Personal Hygiene and Good Housekeeping

Commonly, most individuals learned the good habit of personal hygiene for the prevention of disease and illness early in their formative years such as washing and taking a bath. However not many of these individuals formed the habit of maintaining this good attribute at adulthood. The reason can be attributed to lifestyle and sometimes laziness, which in most cases result to harm. In an environment where there is a probability of chemical exposure, eating and drinking at task area should be prohibited. Proper hand wash before lunch and during coffee breaks is a barrier against ingestion exposure. Wearing of proper work clothes, hair covering and hand gloves are necessary for the prevention of dermal exposure. Unfortunately some workers become recontaminated after hand wash or body wash. For example workers inadvertently put on their work cloths after body wash before going to the locker room for a change of clothing, a practice that defeats the idea of taking a clean bath. Chemical dusts or fumes that collect on work clothes may not be seen thus exposing one to the danger of recontamination if such work clothes are not separated. Work boots, gloves and other personal protection equipment shall always be decontaminated and stored separate from workmen fresh clothing, after each shift to prevent the risk of exposure. Also space limitation, improper work flow, bad position of equipment, work benches, tables and storage for materials are factors that contribute to poor housekeeping. They cause congestion and expose workers to the risk of physical injuries, such as tripping falls and laceration. They can also trigger chemical spill, sparks and fire hazards with the attendant environmental consequences. Uncontrolled inventory for raw materials coupled with over production reduce working space and cause over crowding. Therefore proper care must be taken to plan out space areas ideally, during design stages to reduce accident. Work flow shall be unrestricted and task areas shall be clearly visible for prompt response in case of accident. The aisles shall be wide enough to permit free flow of workers and equipment within the plant.

Workers shall remove racks and stock trucks from production areas and return them to stock room as soon as the items are emptied. Extension cables and connectors shall not be allowed to be loose on the floor or hang about from the roof or ceiling. They shall be properly installed and connected in electrical conduct to prevent tripping hazard and electrocution. Sweeping and cleaning of the floor shall be done with cleansing agents that reduce dust level to a minimum. Chemical dust is a serious health hazard, because of its characteristic nature to become airborne. Poor housekeeping accounts for one-third of physical injuries according to statistics, for that reason each worker needs to realize that it is part of his or her responsibility to keep the work area clean. Any unsafe condition should be reported promptly, such as spills, exposed cable, obstructive equipment and chemical leaks. Spills and chemical leaks should be barricaded until the hazard can be removed. A special warning sign can be used to prevent workers from walking into the exposed area.

5.1.2 Avoidance of Hazardous Chemical

Chemical exposure hazards can be controlled or limited by using the Avoidance of Hazardous Chemical Technique. The importance of this technique is predicted by the enforcement of the Hazard Communication standard- 29 CFR 1910. 1200-which include manufacturing and non-manufacturing sectors of the economy. The intent of the hazard communication standard is to provide employees with information about the potential health hazards from exposure to workplace chemicals. Numerous state and local governments have promulgated similar legislation also known as the right- to- know laws. This law differs in some respect with the hazard communication standard and has a further additions to the burden of compliance to the employer. It carries complex record keeping and reporting requirements and stiff penalties for noncompliance. The law requires the employer to train and provide the employees with enough information about the hazardous substance used at work place to allow them to make more knowledgeable decisions with respect to the risks of their work. It also impresses on them the need for safe work practices. Not only must workers be kept informed of hazardous substances being used in the workplace but the community as well has a right to the information.

As the awareness of workplace hazard grew, employees through training, began to develop safe work practices; like using the proper personal protective devices; cleaning up chemical spills properly to avoid evaporation and becoming airborne; evolving new processing technique that will reduce agitation of gaseous substances; and developing new ways of doing work. In the manufacturing sector, the hazardous chemical avoidance technique results in new research and development to discover chemically compatible elements. Such chemicals can be used to produce the same products without pollution hazard. The abundance of botanic species in nature offers good promise for such discoveries. In February 10, 1997 issue of Chemical and Engineering News, it was reported that Research and development spending increased in 1997 by 3.7% from last year 1996. The combined spending by 26 companies led by Dupont is 3.9 billion dollars. With this amount it is hoped that new breakthroughs in chemical with less toxic effect and environmentally safe will save the future of the industry.

5.1.3 Containment

Another method used to limit chemical exposure is to *contain the effects of hazardous exposure.* This is basically an engineering solution. The engineer must address this solution with fail-safe, error free knowledge afforded by his discipline. In addition he must be fully educated on the chemical nature of the materials used as feedstock, i.e. corrosivity, reactivity, inflammability, etc., and all process stages (especially areas of hazardous releases) safety minima and other environmental conditions. Regulatory requirements of both state and local authorities, including other chemical safety plans must be used to resolve past, present, and future safety requirements of the plant.

Conformance with design codes and standards and other safety regulatory measures required by the state or local governments should be considered a minimum requirement for a comprehensive fail-safe error free design. Care must be taken to effect proper supervision of construction work after the design and regulatory approval. Cutting ends to save cost is often an unwise investment. Of great importance is the ventilation and heating system. Good hood design for effective capture as well as reduction of pollutants in the work zones should be an important consideration.

Other safety attributes include good concrete structure, high quality pipelines, vessels and instrumentation shall be able to withstand static and dynamic forces occurring within and outside the system. The margin of safety comparable to the maximum dismembering force, empirically quantified and obtained should always be used. However, hurricanes, earthquakes, floods, and other natural disasters can wreck the best designs and structures. Until humans are capable of averting such natural disasters (which is impossible), engineers must design and construct plants with minimal probability of failure.

5.1.4 Legislation and Guidelines

OSHA Rule 29 CFR 1910.119 (1) and 29CFR 1910.1450 respectively contain requirements for preventing or minimizing the consequences of hazardous exposure in process management of highly hazardous chemicals in both industrial and laboratory environment. The requirements contained in 29CFR 1910.119 (1) for preventing hazardous exposure shall serve as a minimum for the prevention, exposure, containment and removal of hazardous materials, substances and wastes from work places and the environment. In addition, adequate training in hazard recognition, evaluation and control is essential for the formulation of comprehensive health and safety plan. 29CFR 1910.119(1)subpart-H and subpart, entitled *Hazardous Material* (see appendix I) addresses toxic, reactive, flammable or explosive chemicals, that may result in toxic, fire or explosive hazards. OSHA law is far reaching but cannot be completely exhaustive given the unpredictable nature of human behavior and the continually changing environment in response to changing technology. To overcome the constraint mitigating against safe hazard exposure, proactive safety measure should be incorporated during the planning and construction phases of all chemical process plant. During the planning and design phases, all problems of incompatibility between equipment and operator, equipment and equipment, equipment and environment must be resolved progressively [Gage, 1993, pg. 81]. For example, equipment from different manufacturers behave differently under similar input conditions even when they are identical. Some electronic equipment with identical operational amplifier could exhibit different operational modes under similar bias characteristic. These problems need to be monitored for optimum bias efficiency to give the right response. Also, the man - machine interface should be optimized through the design and construction phases. The engineer designing the plant should be thoroughly familiar with the operator's respective abilities and limitations: what humans can do well, what they can only do marginally and what they can't do at all.

In many chemical plants, unique conditions exist due to constant changes in production processes. The atmosphere is constantly charged with chemical pollutants. These highly hazardous areas must be clearly identified, marked and defined. They should be analyzed to understand how all aspects of the interface impacts other operations. It is also necessary to synthesizing various aspects of performance in the system in operation and during trial run phases.

Construction costs and operational costs most times cause designers and engineers to trade off local design parameters, which can sometimes compromise safety. This is especially true where original technical information no longer exists, or when a new technology supersedes the existing one, or when the local or state inspectors are still grappling with local or state laws and guidelines. To develop such information, a new process hazard analysis should be developed, even if not detailed enough. A computer simulation of the process combined with the process hazard analysis will only approximate actual activities in the process. Simulation based primarily on deterministic input can produce predictable and faithfully reproduced output. But in the actual process many probabilistic input may come into play. One such input is the human operator which can be one serious source of error.

Sources of error traced to human operators are very difficult to control. People are individuals and their performance is to some extent unpredictable. Each of us has a unique genetic make-up and educational and social background, no matter how carefully selected, well trained or highly motivated we are still liable to make mistakes, at any time and for no apparent reason whatsoever. However, human flexibility is indispensable and cannot be matched or substituted by any equipment or machinery. It is invaluable in all operations despite its probabilistic nature which can never be totally error free [Gage, 1993, pg. 127].

On the other hand, machines are consistent and predictable if properly set up or programmed. They should perform over and over again until their source of power is shut out, or a malfunction occurs. All that is needed are the data describing the equipment's operating characteristics. Many tasks that cannot be performed by humans are transferred to machines, which are remotely monitored by human by direct readout, visual readout loudspeakers and other forms of output. The invention of machines replaced human involvement in monitoring explosive and volatile environments – such as in a reactor vessel. It provides safe and conducive data recording and interpreting centers without which grave consequences could result. The objective therefore, is to maximize total performance, of man and machine while minimizing opportunities for errors. Most accident reports attribute cause to "human error", a phrase generally used by system designers to describe an action that violates some tolerance limits of a system. In real terms it ought to suggest system incompatibility rather than an operator's shortcomings.

The complementary aspects of human and machinery/equipment must always be optimized to achieve system reliability. Although the evaluation process on failure for humans and machines are different, the self correction capability of humans should be taken full advantage of. Standards must be clearly detailed; operational nodes and cues quantified and learned thoroughly for skill enhancement. Examples of applicable methods for quantifying human error is found in the Human Reliability Assessment Technique (HRS). This technique is used to improve worker's productivity and reduces accident. It comprises of ten steps for carrying out typical human reliability measurement examining;

1. Problem definition: Identifies the goal and any deviations therefrom
2. Task analysis: Examines system variables which can impact human performance (especially at the machine - man interface)

3. Human Error Analysis:	Sources of error which could effect safe operation of the system. It also predicts correction and recovery periods.
4. Representation:	Model and simulation of human error paths in a logical manner to assess their impact on system operations. "Fault-tree" or "Event tree" are examples of analytical techniques that could be used.
5. Screening:	Set boundary conditions to limit non active incidental errors from significant human error due to man machine interactions.
6. Impact Assessment:	Examines human reliability from the perspective of its impact on system reliability, equipment modification and design changes.
7. Quantification:	Applies probabilities associated with human errors and recoveries to define the likelihood that the system will meet its operating goals.
8. Error reduction:	Identifies error reduction sources and mechanisms along with their respective probabilities and impacts - modifying hardware/software designs, making the system more error tolerant and increased ability for system error recovery.
9. Quality Assurance:	Ensures that standards are maintained in a dynamic setting. System configuration remains stable with age.
10. Documentation:	Records all information needed for others to comprehend, audit, or reproduce for similar application. Also a database may be established in order to compare predicted

developments against actual performance results. Such data may also serve as valuable inputs in the design of future systems.

Human Reliability Assessment (HRS) employ techniques such as SLIM (Success Likelihood Index Method), HERT (Human Error Assessment Reduction Technique) or THERP (Technique For Human Error Rate Prediction). These are all procedures designed to improve worker productivity, predict errors and reduce the risk of accident. Also, OSHA's Construction safety and health standards promulgated in 1971 for concrete, concrete forms and shoring and revised in 1988, did not completely eliminate accident in concrete and masonry construction. Before the revised standard "Subpart Q, Concrete and Masonry Construction Safety Standard" 29CFR 1926.700 of June 16, 1988, form-work failure and the collapse of masonry wall were regular occurrences. For example, at Willow Island, West Virginia, fifty one deaths were reported. Also at the Skyline Tower Plaza Construction in Fairfax County, Virginia the death toll was fourteen.

The ambiguities and gaps in the OSHA Standard plus some requirement that did not allow the use of current technologies, gave vent to construction lapses which resulted in fatal accidents. For these reasons, the OSHA requirement shall be considered as a minimum safety requirement in the construction of chemical plants. Release of hazardous chemicals caused by structural failures can be very acute and lethal. Therefore protection of workers from accidents and injuries must be a priority at all times. Solidly braced masonry walls, fail-safe support of precast panels and well guarded reinforced steel are some of the pro-active solutions needed for accident reduction. The materials used are also very critical elements that form the framework and the physical part of all constructions. A firm's procurement department must be familiar with the various aspects and attributes of these construction materials.

In a highly corrosive process, (i.e. the ability of the material to increase the hydrogen ion concentration of another material, it may have the ability to transfer electron pairs to or from itself of another substance) it is essential that the reactor vessels are made of low carbon stainless steel. As already mentioned, a corrosive agent is a reactive compound or element that can produce destructive chemical changes in a material upon which it is acting. Example of such materials are acetic acid, hydrofluoric acid, nitric acid, and sulfuric acid to mention a few.

Fasteners and connectors such as bolts, screws, nails, etc. forming the connecting points in all construction are items of serious safety concerns. Shear due to stress and strains caused by loading (static or dynamic) or "acts of God" (earthquakes, hurricane, etc) act on these supports producing constant changes of moment of forces. This is a nightmare which designers and planners always gaple with to avoid structural failure. With available technology, one can predict static load and in some cases dynamic loads on a structure or equipment within constrained limits with fairly good accuracy. But earthquakes and hurricanes are elements that defy science and our ability to predict both magnitude and direction of force vectors they may create. However, uniform stability of structures and equipment is highly limited but can be maintained even under serious stress and strain when the connecting points do not fail. For example, one of the worst air disasters was caused when a bolt connecting the flap on the wing of the airplane failed. Air pressure below the airplane was greater than that above. Consequently landing became difficult, resulting in a crash.

Steel structures must rest on well piled soil, and the foundation must be thoroughly tested to avoid structural failure due to ecological conditions. Ecological effects on structure must be computer stimulated and tested. The geology of the area must be defined on past, present, and future topography and uses in order to assess safety condition, and concerns to the users. Design codes and standards must conform with accepted standards applicable in the region or with local government areas. Continuous monitoring of the air during and after construction, and at the plant during startup or trial periods, may often be necessary.

All instruments and monitoring or measuring devices must meet not only production requirements but also field requirements for different altitudes and temperatures. Most common test equipment for air monitoring and combustible gases are of the unbalanced Wheaston Bridge type, which are temperature and pressure sensitive. Therefore, they must be calibrated on site to eliminate systematic errors. Other monitoring equipment, which rely for their operation on electromagnetic induction are indeed sensitive to extraneous magnetic fields as well as temperature. They must be screened from magnetic influences and protected from a highly humid environment, to guarantee accuracy. The best approach, therefore is to use equipment and devices with built in error compensating mechanisms for fail-safe operation in all chemical processing outfit.

5.1.5 Continuous Exposure Monitoring

The greatest risk to workers at a chemical process plant is air borne contaminants. Risk is a function of hazard. If hazard levels are high and there is a significant exposure, then harm will be done. For all exposures, the dose concentration of chemicals as well as the duration of exposure determine the amount of harm that can be done to a person. Other environmental stressors such as physical hazards (noise, thermal and radiation) and ergonomic hazards (repetitive motions, poorly designed work tables and tools) can be controlled by engineering and administrative methods or by the use of personal protective equipment (PPE). For example, noise reduction could be achieved by the installation of one or more noise damper devices at the source of noise, or by erecting a noise barrier between workers and noise energy source. But airborne contaminants are difficult to control even with the use of personal protection equipment (PPE).

Because site activities and weather conditions change, an ongoing air monitoring program should be implemented after site characterization has determined that the site is safe for the commencement of operations. Monitoring also includes continual evaluation of any changes in site conditions or work activities that could affect worker safety. The monitoring of atmospheric chemical hazards should be conducted using a combination of stationary sampling equipment, personnel monitoring devices and periodic area monitoring with direct reading instruments. The direct reading air monitoring instrument is used to provide an integral portion of the information necessary to determine the potential for real danger of chemical exposure from the environment; immediate and long term risk to workers; appropriate personnel protection and respiratory equipment to be used on site and actions to mitigate the hazard safely and effectively.

Air monitoring establish the where, what, when, and how, for remedial action. It also establishes work zones, identifies changes in concentration and migration of contaminants with which to establish a background value and characterizes exposure appropriately to prevent Immediate Danger to Life and Health (IDLH). Flammable gas, toxic materials and radioactive radiation are substances classified as (IDLH). Plant construction should aim to provide proper ventilation to remove airborne chemical fumes and gases from work zones and provide fresh air for workers through forced or natural ventilation.

The body requires oxygen to live. If the oxygen concentration decreases the body reacts. The atmosphere contains 78% nitrogen, 21% oxygen, 0.9% inert gas, and 0.04% carbon dioxide by volume at normal atmospheric temperature and pressure. The potential physiological effects of oxygen deficiency is tabulated in table 6. These values are approximate and vary with the individual's state of health and physical activity. Physiological affects of oxygen deficiency are not apparent until the concentration decreases to 16%. In a chemical exposure environment, less than 19.5 % oxygen is considered alarming, necessitating the use of a respirator.

Removal of oxygen by combustion, reduction reactions or displacement by gases or vapor is a hazard not easily detectable by personnel unless they are wearing appropriate monitoring device. When a significant change occurs, the hazards should be reassessed. Some indicators of the need for measurement are:

- Commencement of a new work phase
- Change in job task during work phase
- Change in season
- Change in weather
- Change in ambient level of contaminants

Once the presence and concentration of chemicals has been established, and the hazard associated with each chemical determined, then safety measures must be enacted or put in place to reduce the risk to humans. This is done by referring to standard reference source for data and guidelines on permissible levels of exposure, flammability, corrosivity, etc. such as the Threshold limit value (TLV's), Permissible Exposure Limit (PEL) and Recommended Exposure Limit (REL).

Table 6. Physiological Effects of Oxygen Deficiency

Oxygen Content	**Effects and Symptoms**
(% by volume)	(At atmospheric pressure)
19.5%	Minimum permissible oxygen level Nothing abnormal
15-19%	Decreased ability to do work strenuously. May impair condition and may induce early symptoms in persons coronary, pulmonary or circulatory problems.
12-14%	Respiration increases in exertion, pulse up, impaired coordination, perception and judgement.
10-12%	Respiration further increases in rate and dept, poor judgement, lips blue
8-10%	Mental failure, fainting, unconsciousness, ashen face, blueness of lips, nausea and vomiting
6-8%	8 minutes - 100% fatal 6 minutes 50% fatal 4-5 minutes - recovery with treatment
4-6%	Coma in 60 seconds, convulsions, respiration ceases, death

Sources: Site investigation and characteristic EOHIS handbook, 1996 Section III pg. 23

Threshold Limit Value (TLV) can be used as a guideline for determining the appropriate level of worker's protection. Theses values have been derived for many substances and can be found in the threshold limit value for chemical substances and physical agents which is published annually by the American Conference of Governmental Industrial Hygienists (ACGIH). The ACGIH defines three categories of TLVs:

i) Time Weighted Average (TWA)

ii) Short Term Exposure Limit (STEL)

iii) Ceiling (C)

All three categories may be useful in selecting appropriate levels of protection at any hazardous location. Threshold limit values (TLVs) refer to airborne concentration of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects. Because of wide variations in individual susceptibility, a small percentage of workers may experience discomfort from some substances at concentrations at or below the threshold limit. A smaller percentage may be affected more seriously by aggravation of pre-existing conditions or by development of an occupational illness. Smoking of tobacco is harmful for several reasons. Smoking may act to enhance the biological effects of chemicals encountered in the workplace and may reduce the body's defense mechanism against toxic substances.

****Time Weighted Average*** (TLV-TWA) - is defined as the time weighted average concentration for a normal, eight hour workday and a forty hour work week, to which nearly all workers may be repeatedly exposed day after day without adverse effect.

Short Term Exposure Limit (TLV-STEL) - is the concentration to which workers can be exposed continuously for short period of time without:

a) Irritation

b) Chronic or irreversible tissue damage or

c) Narcosis of sufficient degree to increase the likelihood of accidental injury, impair self rescue or materially reduce work efficiency, and provided that the daily TLV-TWA is not exceeded.

It is not a separate independent exposure limit, rather it supplements the Time Weighted Average (TWA) limit where there are recognized acute effect from a substance whose toxic effects are primarily of a chronic nature. STELs are recommended only where toxic effects have been reported from high short-term exposures in either human or animals.

A STEL is defined as a 15 minute TWA exposure which should not be exceeded at anytime during a workday even if the eight hour TWA is within the TLV-TWA. Exposures above the TLV-TWA up to the STEL should not be longer than 15 minutes and should not occur more than four times a day. There should be at least 60 minutes between successive exposure in this range. An average period other than 15 minutes may be recommended when this is warranted by observed biological effects.

Threshold Limit-Ceiling (TLV-C) - The concentration that should not be exceeded during any part of the working exposure. If instantaneous monitoring is not feasible then the TLV-C can be assessed by sampling over 15 minute period except for those substances that may cause immediate irritations when exposures are short.

The TLV committee believes that certain chemical substances based on physical irritations should be considered no less binding than those based on physical impairment. There is increasing evidence that physical irritation may initiate, promote, or accelerate physical impairment through interaction with other chemical or biological agents.

Permissible Exposure Limit (PEL) are enforceable standards promulgated by OSHA. In many cases they are derived from TLVs published in 1968. The PEL for a substance is the eight hour time weighted average or ceiling concentration above which worker may not be exposed. Although personal protective equipment may not be required for exposure below the PEL, its use may be advisable where there is potential for over exposure.

Recommended Exposure Limit (REL)- A NIOSH recommended exposure limit (REL) is the workplace exposure concentration recommended by NIOSH for promulgation by OSHA as PEL, but it is not enforceable as in OSHA PEL. In some cases NIOSH has described TWA concentrations in terms of 10-hour rather that 8-hour averages.

Immediate Danger to Life and Health (IDLH) Concentrations have been established by the NIOSH/OSHA standards completion program (SCP) as a guideline for electing receptors for some chemicals. The definition of IDLH varies depending on the source. For example, Mine Safety and Health Administration Standard (MSHA), [30 CFR Part 11.3 (t)], defines IDLH condition, as those that poses an immediate threat to life and health, or that poses immediate threat of severe exposure to contaminants such as radioactive materials, that are likely to have adverse cumulative or delayed effects on health. The NIOSH pocket guide to chemical hazards defines IDLH as stipulated in the NOISH respiratory decision logic (DHHS) [NOISH] publication, as a condition "that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such environment. Regardless of their exact definition, all IDLH values indicate those concentrations of toxic substances from which escape is possible without irreversible harm should a worker respiratory equipment fail.

For example, during air monitoring of an unknown chemical, a reading of 19.5 % of oxygen concentration by volume was observed. This translates to (21-19.5%) of unknown gas i.e. 1.5 % or 15000 PPM present in the environment. If the unknown gas is Xylene having IDLH 10,000 PPM (NIOSH), the worker would have been overexposed by 5000 PPM which would be acute even before the expiration of the 30 minutes escape period. The worker would have suffered an irreversible health effect which perhaps could be fatal. Therefore a rational approach should guide all operations regarding unknown chemical hazard monitors. Prescription and regulations are at best minimal as mentioned earlier.

CHAPTER 6

ADVANCED METHODS AND INNOVATIVE TECHNIQUES (GROUP II)

Methods that are proactive for preventing and limiting hazardous exposure were unveiled at the world first conference on microwave processing held at Lake Burma Vista Florida. At that conference more than 330 scientists, engineers and other researchers from twenty three countries met and discussed new ways to use microwave for organic synthesis, materials processing and waste remediation that is safe and environmentally friendly. Microwave energy is "cold" producing heat only when it is absorbed by a sample. In contrast, majority of the heat producing sources used in industries for food processing, synthesis and chemical reaction, etc. burn one type of fossil fuel or another. The byproducts of these fossil fuel units contain carbon monoxide, carbon dioxide and other dangerous hydrocarbons that pollute the atmosphere. The use of microwave will reduce the burning of fossil fuel by conserving energy which will reduce the amount of pollutants in the air.[Ron Dagoni, 1997, pg. 27].

Factors that made the use of microwave energy an efficient, safe and environmentally friendly alternative for heating and heat-based applications in industries are many. Some of these factors are

1. Conservation of energy (no by-products)
2. Reduction of polluting chemicals and reagents.
3. Cleaner and efficient reactions
4. Safe and environmentally friendly.

The application of microwave energy to hazardous waste remediation was another spring board that provoked serious discussion on the commercialization of the technique.

At the conference Professor Van Loock of the University of Ghant Belgium noted that few groups have demonstrated successful application of microwave energy in areas such as radioactive waste, soil decontamination incineration and treatment of sludge. One of such group is Imperial Petroleum Recovery Corp based in Stratford Texas. The company used microwave energy for the treatment of oil sludge. Ron Dagoni described the application of microwave energy for material synthesis, processing and waste remediation in the article titled "Molecular Magic", published in the science and technical journal of February 10, 1997. This article is paraphrased and produced below in three subheadings, Organic synthesis, material processing, and waste remediation. From our earlier definition of proactive technique, it shows that logical postulate exist based on events and outcome for the use of microwave energy over the current methods.

6.1 Organic Synthesis

The use of microwaves for heating and cooking is a common knowledge now in most homes world wide. The principle behind it is simple yet bewildering. Microwave causes dipolar molecules to rotate and ions to migrate, and the energy absorbed is dissipated as heat.

In a conventional gas or electric oven, an object is warmed gradually as heat penetrates from the outside in. Microwave energy, by contrast, is "cold" producing heat only when it is absorbed by a sample. The easy penetration of microwave in materials (except metals) cause the sample to absorb it uniformly over its entire volume, thus heating up evenly and rapidly. This capability makes it possible for organic synthesis without using solvent which would have prolonged reactions and contribute to pollution and chemical hazard. For example, to synthesize a reaction that required heating in an oil bath for four days, was done in four hours with a computer controlled microwave oven, and was able to maintain a constant reaction temperature with a relatively small amount of degradation according to scientists at Wyeth - Ayerst Research of Pearl River, NY. [Ron Dagoni, 1997 pg. 26]. Another example given by researchers at Wyeth Ayerst is the reaction of peptide hydrolysis. Using conventional heating, this reaction typically has been run overnight in a sealed tube containing hydrochloric acid. The advent of microwave heating shortened the reaction time to fifteen minutes, in an open tube and without the harsh reagent. They find that they can completely hydrolyze di-tri and tetrapeptides in three to fifteen minutes using a saturated barium hydroxide solution in an open flask inside a microwave oven. Still another example is the use of microwave heating to simplify the reaction for peptide structure determination. In this reaction hydrazine is used to chop off the last segment from the carboxyl end of a polypeptide to yield a free amino acid that is easily identified. Traditionally this cleavage is carried out over 12 hours in a sealed tube at approximately 120 degrees Celsius using a hot oil bath or electrically heated oven. But in a microwave oven, the reaction can be completed in a few minutes in an open vessel - without the use of a solvent. Simply put, the peptide and hydrazine in a flask and irradiate it.

6.2 Material Processing

At Sam Houston State University in Huntsville, Texas and Houston Advanced Research Center in the Woodlands Texas, scientists performed organic transformations rapidly using catalysts under solvent free or "dry" conditions. The catalysts (or doped supports) could be alumina, silica gel, clay, or zeolite. The organic reagents absorb to the surface of these inorganic oxides and absorb microwaves. The solid support neither absorbs nor restricts the transmissions of the microwaves. Pure products are produced in high yields and the catalysts and supports are recyclable [Ron Dagoni 1997 pg. 30].

At IBM's Thomas J. Watson Research Center in Yorktown Height NY., scientists have found new ways of processing/manufacturing a key precursor of circuit boards - pre-impregnated glass cloth (Prepreg, as it is usually called). This board is used extensively in both the composite and electronic industries. The current method of manufacturing involves dipping a loosely woven glass cloth (typically about 50 mm thick) into a solution of resin, usually an epoxy dissolved in methyl ethyl ketone (MEK). The wet cloth is then moved through a drying tower, where hot air is used to drive off the solvent and partially cure the resin. These early processing steps are critical because if it is not done properly, the electrical properties of the circuit board will be compromised. Subsequently the prepreg is laminated with copper foils under pressure and the resin is fully cured to yield a rigid circuit board.

The hazardous properties of MEK - a strong oxidizer, and highly reactive substance irritates the eyes and can cause skin and respiratory system problems. It is known to cause cancer in animal, target organs including the liver and kidney. The use of these agents violated regulatory requirement of the state and federal agencies. Replacing MEK with a non hazardous substance became inevitable. For these and other reasons, a water based system was devised for making Prepreg. But therein lies the major challenge because water is harder to evaporate than MEK. The problem was overcome by using microwave irradiation, that has the potential to dry water soaked cloth more quickly than hot air drying tower. In test of the prototype system with water based resins, microwave irradiation provided very fast heating rates, according to IBM engineers.

Another example of process change in manufacturing which is proactive for the safety and health of the workers is the use of microwaves for making porous parts by sintering polymers. Porous components produced from polymers have diverse uses in industry, including filters for gases and liquids, baffles, mufflers for absorbing sound, roller coasters, and dispensers. The former process of manufacturing that involves pouring ultrahigh molecular weight polyethylene powder into a metal mold and sintering it for several hours with a high speed blower is not cost effective. It is inefficient and can cause serious health hazard. With the microwave process method, the sintering time which originally took several hours was reduced to minutes. At the same time the homogeneity of the part is improved thus increasing efficiency and decreasing production cost in addition to being less hazardous to health and environment.

Microwaves also are showing great promise in the area of ceramic synthesis. Professor Rustum Roy of Pennsylvania State University stated that even though researchers have created very few new solid - state phases using microwaves, they have charted new pathways to known phases. Three improved pathways to technologically important ceramic powder were discovered in Roy's lab. The most dramatic result obtained involved the synthesis of barium titanate ($BaTiO_3$) a very important dielectric used in capacitors and other electronic devices. The conventional synthesis of this ceramic involves heating a mixture of barium carbonate ($BaCo_3$) and titanium dioxide (TiO_2) powder at a temperature of 1000 to 1300 degrees Celsius for several hours. But with microwave heating the two phase formation - the kinetic phase, (hexagonal $BaTiO_3$) and the thermodynamically stable phase (tetragonal $BaTiO_3$) were completed at 700 degrees Celsius. The diffusion of atoms occurs so quickly from cold start to finish that it took less than eight minutes to complete a process which was performed in several hours by the conventional method. This shows that microwave heating completely changes the reaction pathway - a great technological improvement for ceramic synthesis allowing a gross reduction in exposure hazards from barium carbonate ($BaCo_3$) and titanium dioxide (TiO_2) [Ron Dagoni, 1997. Pg. 31].

The use of microwave energy under solvent free conditions will lead to new methods for conducting cleaner and efficient chemical reactions when fully commercialized. It will be adopted into industrial processes, and will reduce the usage of energy polluting chemicals, reagents, and solvents and minimize the generation of byproducts of waste streams.

In the area of hazardous waste treatment and processing, microwave heating methods hold the promise for the future. Hazardous waste treatment and processing has become a serious problem all over the world. According to the Environmental Protection Agency (EPA), it is estimated that there are approximately 30,000 candidate sites for hazardous waste treatment services in the United States, including industrial sites containing water and solid waste contaminated with toxic metals. The current cost for the clean up of contaminated soils and ground water, and the routine disposal of industrial and municipal wastes is estimated at $400 billion world wide. Toxic metals comprise a particularly difficult component of this clean up and waste treatment challenge with no efficient and cost effective approach presently available. For example, incineration and land filling are two of the oldest and most widely used methods of soil remediation. They are not very efficient in eliminating contaminants from the environment and are relatively expensive. They also are not proactive in process and design.

Another example is the systemic use of micro-organisms for environmental contaminant treatment called bio remediation; a developing technique that is currently used though on a small scale to clean some sites of halogenated and nonhalogentaed volatile and semi-volatile organic compounds and petroleum hydrocarbons. The contaminants are degraded by naturally occurring microbes that are stimulated by introducing nutrients and oxygen to the soil or water. This method is highly site specific and requires extensive laboratory testing. In mixed exposure (hazardous sites) it is difficult and time consuming to apply the bioremdiation method. There is also the likelihood of hazardous exposure for the field workers during taking of field sample and laboratory testing. Again it is not a proactive method. Some of the technologies that could potentially have a huge impact in hazardous wastes processing and remediation are the microwaves heating method and Phytoremediation (the use of plants for environmental contaminant treatment technique discussed in section 6.4). Both methods are proactive both in designs and processes.

6.3 Waste Remediation

The use of microwaves heating for processing hazardous wastes has received considerable attention. Professor M. Van Loock of the Department of Information Technology at the University of Ghent, Belgium noted that few groups have demonstrated successful applications of microwaves in areas such as radioactive waste, soil decontamination, incineration and treatment of sludge. An example of the use of microwave for the treatment of sludge was demonstrated by scientists at the Imperial Petroleum Recovery Corp based in Stratford, Texas [Ron Dagoni, 1997. Pg. 28]..

When oil is pumped out of the ground it typically consists of an emulsion from which most of the crude oil can be separated. As much as 5% of the pumped material, however, consists of such a stubbornly stable emulsion that is usually discarded in excavated pits creating black marsh like lakes. Thousands of these sludge pits - containing mixtures of oil, water, salt, sand, clay, dead animals and vegetation - exist around the world, some the size of a football field. Their growing numbers present an ever worsening health hazard and remediation problem. The Imperial Petroleum Company Microwave System breaks up such recalcitrant sludges, stated a chemical engineer Edward R. Peterson of Imperial. He explained the three factors that lead to the breaking up of the sludge. First, because water consists of polar molecules and oil does not, water absorbs much more microwave energy and heats up more. This differential heating causes a temperature gradient that reduces the stability of the surface tension that holds the oil and water interface together.

A second factor Peterson explained involves the natural surfactant molecules that bind oil to water in these sludges. Because surfactant molecules have both a dipolar end and nonpolar end, they interact with microwaves unevenly on the molecular scale. The dipolar end, which is receptive to microwaves "is wrenched back and forth in sympathy" with their rapid changing electric field oscillations. This differential interaction stresses the surfactant molecules disrupting their close association and weakening their ability to preserve the oil/water interface.

The third factor is the movement of ions. Since microwaves cause ions to move, they likely also jiggle the emulsion's soil particles which tend to have positive charge on their surface. The jiggling of the particles within their surrounding sheath of water molecules and negative ions causes a "shear stress" at the soil/water interface helping the particles separate from water. These three types of selective energetic effect cannot be achieved using conventional heating. After the separation is achieved it is centrifuged in a continuos process. In test of this first generation system carried out in 1996, on a water rich sludge considered "unbreakable". The system was able to separate about 75 gallons of emulsion per minute into "pipeline quality oil, low solids water and a pasty solid". Oil recovery was 98%. The solid residue can then be disposed of in a landfill.

The microwave process is simple, cleaner and more efficient to operate. It reduces waste volume by more than 50%. The final vitrified product made without any additives, immobilizes hazardous component well enough to meet environmental standards.

6.4 Phytoremediation

In an effort to overcome the shortcomings of conventional bio remediation and waste removal strategies (e.g. site specificity, excavation, elaborate field test, transportation, exposures, landfills, etc.), scientists have demonstrated that certain green plants are effective in removing large amounts of toxic metals from soil and water. This approach termed Phytoremediation offers a proactive cost effective, efficient and environmentally compatible means of addressing heavy metal contamination. Plants that accumulate toxic metals from contaminated soil and water can be grown and harvested economically leaving soil and water in place with only residual levels of pollutants. The feasibility of Phytoremediation at the laboratory scale has been extensively investigated with considerable success and confirmed on a larger scale with field results. Such investigation and exploration of the use of plants for environmental clean up has led to the development of three distinct approaches to Phytoremediation of toxic metals and radionuclides:

i) Phytoextration: The use of metal accumulating plant that transport and concentrate metals from soil in the roots and above ground shoot.

ii) Rhizofiltration: The use of plants to absorb, concentrate and precipitate toxic metal form aqueous streams.

iii) Phytostabilization: The use of plant to eliminate the availability of toxic metal in soil.

(i) *Phytoextraction* uses plant to absorb contaminants such as heavy metals from soil into roots and harvestable parts such as stems and leaves. Heavy metals are present in soil as natural components or as a result of human activity. Metal- rich mine tailings, metal smelting, electroplating, gas exhausts, energy and fuel production, down wash from power lines, intensive agriculture, and sludge dumping are the most important human activities that contaminate soils with large quantities of toxic metals. In addition to sites contaminated by human activity natural mineral deposits containing particularly large quantities of heavy metals are present in many regions of the globe. These areas often support characteristic plant species that thrive in these metal enriched environments. Some of these species can accumulate unusually high concentrations of toxic metals to level which far exceed the soil level. As a result many of metallophyte plants (as they are known) are used in prospecting for mineral deposits. Only recently has the value of metal- accumulating plants for environmental remediation has been fully utilized[Kumar, Dushenkov, Motto, and Raskin. 1995].

The process of phytoextraction generally requires the translocation of heavy metals to the easily harvestable shoots. In some cases, roots can be harvested as well. Current research and development conducted by IILYA Rasking and group at Phytotech Inc. NJ in collaboration with the Agbiotech Center and Department of Environmental Science, Rutgers University, Cook College NJ identified several cultivators of Indian Mustard (Brassica Juncea) a high biomass crop plant that efficiently accumulate lead (Pb) and other heavy metals such as chromium, nickel and zinc in the roots and shoots. The use of lead in most of the initial studies is because of its importance as an environmental pollutant. In addition lead is tightly bound in most soils, a property which makes it a particularly challenging metal for phytoextraction. To increase the uptake of toxic metals to shoots of plant, an approach was devised which required adding a chelating agent, EDTA (ethylenedenitrilotetraacetic acid) and citric acid to the soil, which solubilizes the soil and increased lead uptake and translocation to the shoots by more than 60%.

There are many advantages in using metal accumulation plants for the removal of metals from contaminated soils: lower costs, generation of a recyclable metal-rich plant residue, applicability to a range of toxic metals and radionuclide, minimal environmental disturbance, elimination of secondary air or water- borne wastes and public acceptance.

(ii) *Rhizofultration* is perhaps the most developed and widely used phytoremechation application. Artificial marshes (wetland), a rhizofiltration technology have been constructed to help treat waste water from municipal sewage treatment facilities and several industrial processing operations. In Magnolia Arkansas, the Albemarle corporation's bromine production facilities, constructed two such artificial marshes for the treatment of rain water run off and noncontact process water from the factory. Each marsh consists of thousands of plants like bullrush, maiden cane and cattails. The marshes are less expensive to create and have a considerable lower operating cost than a mechanical waste water treatment system, in addition they meet the regulatory demand of "Clean Water Act".

Another artificial marsh (wetland) located in Richmond, California was constructed by Chevron crude oil refinery to reduce selenuim waste from crude oil refining. In high doses, selenuim can be toxic to fish and wildlife. It is also a health hazard to human with symptoms of eye, nose and skin irritation when inhaled, ingested or in contact with the skin. Bulrush and cattails which consist the wetland, result in the reduction of solenium. The wetland can periodically be dried and the vegetation harvested for proper disposal. Recent research sponsored by Chevron at the university of California Beckley indicates that a portion of the selenium removed by the wetland plant is volatilized in a less toxic form. Successful rhizofiltration techniques require identification of species of plants that have the ability to process large quantities of water. An example of such plants is a special strain of sunflower that when grown hydroponically on rafts has removed radionuclides from water. A company known as Phytotech Inc. located in New Jersey developed and patented such system. The sunflower rhizofiltration system successfully reduce uranium, strontium and cesium levels in water to below clean-up standards set by the U.S. Environmental Production Agency (EPA). The field test at the Chernobyl nuclear power plant in Ukraine as well as Department Of Energy site in Ohio attest to this fact. At the Chernobyl site, scientists were able to demonstrate a dramatic reduction in the level of cesium (Cs-137) and strontium (Sr-90) contamination in the ground water over a four to eight week period. Similarly, at the US Energy Department facility in Ashtabula Ohio Site, uranium contaminated water with concentrations as high as 350 ppb was reduced by 95% within the first 24 hours. The uranium concentration in the outlet water never exceeded 5ppb and in most cases was 1 ppb or less, well below the EPA ground water standard of 20 ppb.

Pythotech estimates the cost to remove radionuclides from water would be between two- dollars and five- dollars per 1,000 gallons including disposal cost. A standard treatment of microfiltration and precipitation would cost nearly eighty dollars per 1,000 gallons according to Department Of Energy estimate. A savings that supercedes all estimates. If approved by EPA regulators and site owners
the process could commercialized within one year. Accumulation of uranium occurs primarily in the roots, whereas strontium and cesium accumulate throughout the plant. The harvested plants are reduced to ash or ventrified and disposed of in a safe place.

(iii) *Phytostabilization* uses plants that are tolerant of a contaminant in soil such as heavy metals to reduce the contaminants mobility and prevent further environmental contamination, such as leaching into ground water or becoming airborne by wind erosion. An example of such plant is Brassica. Brassica roots take up and immobilize lead in soil. Also some species of trees are currently being used to remediate organic pollutants. Poplar trees for example are used as buffers and caps to prevent pollutants- for instance from landfills- from reaching waterways and ground water. They have been used to remove chemicals at Urea fertilizer spills, old herbicide- equipment rinsing areas, and buffers as a final filler for surface and ground water.

Poplar tree research is continuing at the university of Iowa, EPA Laboratory in Athens, Georgia, and The National Salinity laboratory in Riverside California to mention just a few.

Though phytoremechation technologies are still primarily in research and development phases various applications have shown potential for success. Each of these applications aforementioned provides a novel approach to hazardous material clean up. Materials in Appendix 2 is a technical summary written by the following authors on this subject, for further reading. Vasuder, Tracey Ledder, Slavick Dushenkov, Amona Epstein, Nanda Kumar Yoram Kapulnick, and Burt Ensley of Phytotech Inc. NJ and Illya Raskin of AgBiotech Center, Cook College, Rutgers University, New Brunswick, NJ.

CHAPTER 7

DISCUSSION

Good hygiene is the separation between health and illness. Exposure to chemicals can be avoided if one took basic precautionary measures such as simple hygiene to stay healthy. Ingestion exposure, dermal and inhalation exposure can be prevented or minimized by simple personal hygiene and good housekeeping. However for many of the world population, it is not as simple as it seems. A casual look at some of the cottage work places, (garages, gas stations, restaurants, social centers, etc.) show the failure of the population to maintain simple hygiene and good housekeeping. Motor repair garage shops for example are saturated with hydrocarbons, spill on the floor, hands and clothing of the operators are common sight. Exposure risk to these hydrocarbons are common. They make one ill and cause death. Some conditions exist in motor body shops where inhaling chemical dust are also a common phenomena. The emphasis therefore is to create awareness of these danger by training in order to change behavior of the general public towards cleanliness. Other intervention methods for safe exposure like the use of personal protection equipment (PPE) should be enforced at work places to reduce or prevent incidents of hazardous exposure.

As earlier stated in chapter one, toxins are poisons, depending on the dose and frequency of use. They can adversely affect human, animals and other ecological system. Chemicals and solvents used for manufacturing and other purposes need to be handled with care. They can corrode explode ignite, and can cause serious ecological damage if not handled properly. When ingested, inhaled or touched, they can cause burns, cancer, skin and eye irritation and cell damage. The knowledge of how these chemicals interact with cells in our body when absorbed through skin eyes mouth and respiratory system provided insight to the prevention technique that is efficient in limiting exposure. One of such technique explained earlier is the "Proactive technique". This technique takes an a priory posture. As defined in Chapter one. It is a logical postulate that predicts events and outcome and introduce measures for the avoidance of harm. Simple hygiene and good house keeping supports this premise.

In industries where new technologies and innovation are replacing old methods, care must be taken not to introduce other forms of hazards. Studies show the numerous finding that ceramic, polymers and other materials can be processed more quickly with microwaves radiation than with conventional heating system. But is this simply due to the faster, more uniform heating that microwaves energy provide or is there a unique "microwave effects?" Would there be future health concern from the use of this technology that is yet undiscovered? These questions can be answered based on events and outcome evident by the introduction of microwave energy as shown below.

Table 7 Comparison Between Two Events.

Event	**Outcome**
Microwave energy	"Cold" producing heat when absorbed by the object
Conventional heating	Gradual warm-up objects from outside in.
(gas and electric)	

Comment

In conventional gas and electric heating system an object is warmed up gradually as heat penetrates from the outside in. A condition which consumes more energy and longer heating time. If the medium is a chemical solution it will reach its boiling point temperature before the object. The result is the production of chemical fumes with exposure hazards. Microwave in contrast transfer energy passing through the material. A "cold" process producing heat only when it is absorbed by the object. Microwave energy penetrates easily in materials and cause the sample to absorb heat easily over its entire volume. The result is a quick, clean and exposure free reaction.

The advantage of microwave energy for all processes requiring heat or heat inducing reaction over conventional method are overwhelming. A common feature of the heat induced reactions is present in chemical industries, refineries, petrochemical industries, pharmaceuticals industries, foundries, waste treatment plants, incinerators, and others. The effect is far reaching and surely will change the way things are done in these industries. It will entail "re-engineering" which most company executives fear because of costs. It is one of the factors that will conspire and hold back the commercialization of this technique.

Other factors like reluctance to change, cost-benefit, regulatory controls and standardization are concerns which most company executives would like to address before they can accept these technologies. For example it is possible to go out and buy a turnkey furnace for most heating requirements and tasks. The same cannot be true for microwaves equipment. It must be custom made to adapt to space, functions and general flow of work. There is no "one solution fits all." To overcome these obstacle won't be easy. Also the negative effect of the microwave energy on the environment has not been fully assessed. Microwave energy systems use industrial, scientific band and frequency nomenclature (i.e. ISM band). Its construction consists of power supplied by a magnetron tube, to the cooking chamber via a wave guide. The radiation leaving the wave guide passes over a rotor set in motion by moving air. When there is radiation leak (amplitude modulated) from the chamber where energy is being transferred to the object, it could be picked up by cardiac pacemaker. The pacemaker could amplify the leaking radiation with serious consequences to the user [Miller, 1996. Pg. 295]. However the radiation leak can be controlled by shielding and electrostatic screening. These preventive measures keep away extraneous field and prevent environmental hazard.

Therefore the task ahead of researchers and developers are adaptability, acceptability, health and safety, in addition to product efficiency. It must be cost effective when compared with other emerging technologies and innovations. For example in the area of hazardous waste treatment and remediation, Phytoremediation is conceivable the most cost effective and safer alternative than these other technologies and innovation. Commercial use of phytoremediation is currently very limited. Metals in the soil environment exist as components of several different fractions. Some components are amended to enhance their plant uptake. Manipulation of the soil to enhance the availability of metal for plant for plant uptake is critical for effective phytoremediation.

Chelating agents have been used as soil extractant, a source of micronutrient fertilizer which increases metal solubility and plant uptake. Unfortunately high level of chelating agent will increase mobilization of contaminants and pose serious threat to ground water. Also wild animals and birds that feed on the contaminated plant such as sunflower seeds are likely to acquire high doses of heavy metals in their system which will endanger them. Therefore adherence to strict agricultural practices must follow phytoremediation techniques to protect wild life and other species. This perhaps is difficult to achieve.

Though phythoremediation technologies are still primarily in research and development phases various applications have shown potential for success. In an attempt to develop Phytoremediation into a commercially viable industry some key technical hurdles must be overcome to enhance the growth of the industry. These are:

- Identifying more species of plant that have remediative abilities
- Optimizing phythoremediation process such as appropriate plant selection and agronomic practices
- Understanding more about how plant uptake, translocate and metabolize contaminants
- Identifying genes responsible for uptake and/or degradation for transfer to appropriate high-biomass plants
- Decreasing the amount of time needed for phythoremediation to work
- Devising appropriate methods for contaminated biomass disposal, particularly for heavy metals, and radionuclides that do not degrade to harmless substance
- Compliance with state and federal regulation on agricultural activities.

CHAPTER 8

CONCLUSION

Exposure to chemicals that are safety and health hazards to human could result in a series of undesirable effects on the body. It could cause premature excitation of the membrane; accelerated or decelerated firing of the neurons and nerve centers, uncontrolled motor reflexes, asphyxiation and cell death. Such exposures could be avoided by employing precautionary measures both rudimentary and high tech. They may serve as reduction intervention methods which are proactive in design for the avoidance of harm caused by the hazardous chemicals. The precautionary measure in the line of the first defense is: *Good personal hygiene and avoidance of the use of hazardous chemicals.*

To restate the fact, all botanic life forms common in nature contain poisons. Depending on their concentration, uses and application they contain chemicals which can react, explode, inflame or corrode. The skin, lungs and alimentary canal are the main barriers which prevent deleterious effects at one or several sites of the body, with the exception of caustic and corrosive agents, which act topically. A chemical absorbed through any of these three barriers into the bloodstream is distributed to some extent throughout the body. The site where the chemical produces damage is often called the target organ or target tissue. A chemical may have one or several target organs. For example, benzene affects the hematopoietic system, and carbon tetrachloride the liver. Lead and mercury both damage the central nervous system and kidney. It is self evident that in order to produce a direct toxic effect in an organ, a chemical must reach that organ. However, indirect toxic responses may be precipitated at distant sites if a toxicant alters regulatory functions. For example, cholestyramine, a non absorbable resin may trap certain acidic vitamins in the intestinal lumen and cause systemic toxicity in the form of various vitamin deficiency syndromes. Several factors other than concentration, influence the susceptibility of organs to toxicants. Therefore, the organ or tissue with the highest concentration of a toxicant is not necessarily the site where toxicity is exerted. A good example is chlorinated hydrocarbon insecticide leg dichlorodiphenyltrichloroethane (DDT) which attains the highest concentrations in fatty deposits of the body, but produce no known effects in this tissue. A toxicant may also exert its adverse effects directly on the blood stream as in the case with arsine gas which causes hemolysis. However good personal hygiene and house keeping including measures to avoid inhalation, ingestion or physical contact with hazardous chemical will reduce the risk of exposure. Also the abundance of botanic species available in nature offer a good promise to the future discoveries of chemically compatible elements that could be substituted in industrial processes and produce the desired end product without polluting the environment.

Yet another proactive reduction method is the use of *advanced method and some naturally occurring botanic life forms* to reduce or limit hazardous wastes. Microwave energy has been harnessed by scientists for material processing, organic synthesis, and waste remediation. Its potential will in due time cause changes in the current use of solvents and high heating energy in chemical process plants for a solvent-free, energy efficient, cleaner chemical reactions. The generation of by-products of waste stream will be relatively a thing of the past and our environment will be hazard free while life forms will be able to survive for much longer periods of time. The experiments by scientists in USA, Germany, Holland, and Japan on microwave energy systems have already proven that such chemical process plants are now available and will be soon commercially viable. The enormous advantages and flexibility microwave energy system have over conventional systems presently used, will enhance their acceptability in all aspects of industries sooner than first predicted.

Also certain species of green plants can remove heavy metals from contaminated soil and ground water - a process known as Phytoremediation - a proactive way of cleaning radioactive, heavy metal contamination from soil, as well as providing non-contaminated fresh water for the population. Of the three process mentioned i.e. phytoextraction, rhizofiltration, and Phytostabilization - the use of rhizofiltration for cleaning up ground water contaminated by radionuclides such as uranium, tritium, cesium, strontium, plutonium, and technetium is a very welcome approach. Traditionally these contaminants have posed a serious challenge for clean up. Approaches using techniques such as ion exchange chromatography, reverse osmosis, microfiltration, or flocculation are often difficult to implement and prohibitively expensive when applied to large water volumes of dilute concentrations and where clean up standards are strict.

The use of such plants to treat these sites offers an economical and cost effective alternative for radioactive clean up. Scientists estimate the cost of rhizofiltration using plants at a mere $2 to $6 per thousand gallons of water treated including capital and waste disposal. Such methods as precipitation and microfiltration can cost anywhere from $35 to $80 per thousand gallons of water. Aside from the cost advantage, Phytoremediation improves the appearance of sites, adding aesthetic pleasure by bringing green leaves to desolate and very toxic sites.

Also the disposal technique of this method is simple and very proactive compared to other remedial methods. The species of plants absorb heavy metals from soil or water leaving the soil and water in place with only residual amount of pollutants remaining.

The harvested plants are reduced to ash or ventrified and disposed of in a safe place. Often non-radioactive metals can be recovered from the ash and recycled.

Finally, *training as a proactive reduction technique* for chemical exposure can not be overemphasized. Training helps workers demonstrate a satisfactory understanding of the job, and the proper use of PPE. The health and safety professional should identify the needs of the organization. Accident and injury records together with specific investigation reports can reveal areas of weakness and failures in training - a proactive approach aimed at preventing similar incidents or occurrences. According to Heinrich's theory, past events forecast the possibility of future and potentially more severe accidents. Workplace surveys (safety audits) human factors consideration during the design and construction stages, ergonomically design work stations and tools, regularly scheduled inspections and employee opinion surveys are all pro-active reduction techniques that would prevent unsafe practices and errors that could cause accidents. Reports have strongly suggested that the majority of accidents are caused by workers' poor judgment and unsafe work practices, rather than by equipment failure or poor engineering. At least in part, training can change undesired behavior and/or reinforce the desired behaviors. The focus on safety training should include both the workers and supervisors. Supportive training for management staff should also be included. A well-planned training program should form part of the policy statement of the organization to help reinforce the principle that safety training is good business and can actually improve production. When management staff is guided by a policy statement, the training program becomes part of the company's overall operational standards, which improves communication at all levels, provides higher efficiency and an improved accident record and greater productivity for the entire organization.

From the foregoing it is almost certain that threat to human lives and ecological system will continue as long as we keep harnessing nature. The many combinations and differentiation in nature makes it impossible to harness nature without offsetting the balance and introduce harm. A proactive technique ensures the avoidance of harm and occupational exposure by using logical postulate (a priori evaluation of situation, circumstances- past, present and future) to predict events and outcomes (tests, simulation, identifying common variables) and introduce measures (controls, barricades, avoidance, substitution, change of process) for the avoidance of harm.

This proactive technique is not exhaustive. It shall be improved upon as changes in technologies, human knowledge and intellectual awareness increases. It is hoped that it will serve a useful purpose as supplement to the regulatory guideline of OSHA and other regulatory agencies in US and the world at large.

APPENDIX 1

LEGISLATION AND GUIDELINES

pp. 1 - 10

1910.119(1)

Title	**Process safety management of highly hazardous chemicals.**
Subpart	**H**
Subpart Title	**Hazardous Materials**

Purpose. This section contains requirements for preventing or minimizing the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. These releases may result in toxic, fire or explosion hazards.

(a)(2) Application. (1) This section applies to the following:

(i)(3) A process which involves a chemical at or above the specified threshold quantities listed in Appendix A to this section;

(ii)(4) A process which involves a flammable liquid or gas (as defined in 1910.1200(c) of this part) on site in one location, in a quantity of 10,000 pounds (4535.9 kg) or more except for:

(A)(5) Hydrocarbon fuels used solely for workplace consumption as a fuel (e.g., propane used for comfort heating, gasoline for vehicle refueling), if such fuels are not a part of a process containing another highly hazardous chemical covered by this standard;

(B)(6) Flammable liquids stored in atmospheric tanks or transferred which are kept below their normal boiling point without benefit of chilling or refrigeration.

(2) This section does not apply to:

(i)(7) Retail facilities;

(ii)(8) Oil or gas well drilling or servicing operations; or,

(iii)(9) Normally unoccupied remote facilities.

(b)(10) Definitions.

"Atmospheric tank" means a storage tank which has been designed to operate at pressures from atmospheric through 0.5 p.s.i.g. (pounds per square inch gauge, 3.45 Kpa).

* "Boiling point" means the boiling point of a liquid at a pressure of 14.7 pounds per square inch absolute (p.s.i.a.) (760 mm.). For the purposes of this section, where an accurate boiling point is unavailable for the material in question, or for mixtures which do not have a constant boiling point, the 10 percent point of a distillation performed in accordance with the Standard Method of Test for Distillation of Petroleum Products, ASTM D-86-62, which is incorporated by reference as specified in Sec. 1910.6, may be used as the boiling point of the liquid.

"Catastrophic release" means a major uncontrolled emission, fire, or explosion, involving one or more highly hazardous chemicals, that presents serious danger to employees in the workplace. "Facility" means the buildings, containers or equipment which contain a process.

"Highly hazardous chemical" means a substance possessing toxic, reactive, flammable, or explosive properties and specified by paragraph (a)(1) of this section.

"Hot work" means work involving electric or gas welding, cutting, brazing, or similar flame or spark-producing operations.

"Normally unoccupied remote facility" means a facility which is operated, maintained or serviced by employees who visit the facility only periodically to check its operation and to perform necessary operating or maintenance tasks. No employees are permanently stationed at the facility. Facilities meeting this definition are not contiguous with, and must be geographically remote from all other buildings, processes or persons.

"Process" means any activity involving a highly hazardous chemical including any use, storage, manufacturing, handling, or the on-site movement of such chemicals, or combination of these activities. For purposes of this definition, any group of vessels which are interconnected and separate vessels which are located such that a highly hazardous chemical could be involved in a potential release shall be considered a single process.

"Replacement in kind" means a replacement which satisfies the design specification.

"Trade secret" means any confidential formula, pattern, process, device, information or compilation of information that is used in an employer's business, and that gives the employer an opportunity to obtain an advantage over competitors who do not know or use it. Appendix D contained in 1910.1200 sets out the criteria to be used in evaluating trade secrets.

(c)(11) Employee participation. (1) Employers shall develop a written plan of action regarding the implementation of the employee participation required by this paragraph.

(2)(12) Employers shall consult with employees and their representatives on the conduct and development of process hazards analyses and on the development of the other elements of process safety management in this standard.

(3)(13) Employers shall provide to employees and their representatives access to process hazard analyses and to all other information required to be developed under this standard.

(d)(14) Process safety information. In accordance with the schedule set forth in paragraph (e)(1) of this section, the employer shall complete a compilation of written process safety information before conducting any process hazard analysis required by the standard. The compilation of written process safety information is to enable the employer and the employees involved in operating the process to identify and understand the hazards posed by those processes involving highly hazardous chemicals. This process safety information shall include information pertaining to the hazards of the highly hazardous chemicals used or produced by the process, information pertaining to the technology of the process, and information pertaining to the equipment in the process.

(1)(15) Information pertaining to the hazards of the highly hazardous chemicals in the process. This information shall consist of at least the following:

(i)(16) Toxicity information;

(ii)(17) Permissible exposure limits;

(iii)(18) Physical data;

(iv)(19) Reactivity data:

(v)(20) Corrosivity data;

(vi)(21) Thermal and chemical stability data; and

(vii)(22) Hazardous effects of inadvertent mixing of different materials that could foreseeably occur.

Note: Material Safety Data Sheets meeting the requirements of 29 CFR 1910.1200(g) may be used to comply with this requirement to the extent they contain the information required by this subparagraph.

(2) Information pertaining to the technology of the process.

(i)(23) Information concerning the technology of the process shall include at least the following:

(A)(24) A block flow diagram or simplified process flow diagram (see Appendix B to this section);

(B)(25) Process chemistry;

(C)(26) Maximum intended inventory;

(D)(27) Safe upper and lower limits for such items as temperatures, pressures, flows or compositions; and,

(E)(28) An evaluation of the consequences of deviations, including those affecting the safety and health of employees.

(ii) Where the original technical information no longer exists, such information may be developed in conjunction with the process hazard analysis in sufficient detail to support the analysis.

(3) Information pertaining to the equipment in the process.

(i)(29) Information pertaining to the equipment in the process shall include:

(A)(30) Materials of construction;

(B)(31) Piping and instrument diagrams (P&ID's);

(C)(32) Electrical classification;

(D)(33) Relief system design and design basis;

(E)(34) Ventilation system design;

(F)(35) Design codes and standards employed;

(G)(36) Material and energy balances for processes built after May 26, 1992; and,

(H)(37) Safety systems (e.g. interlocks, detection or suppression systems).

(ii)(38) The employer shall document that equipment complies with recognized and generally accepted good engineering practices.

(iii)(39) For existing equipment designed and constructed in accordance with codes, standards, or practices that are no longer in general use, the employer shall determine and document that the equipment is designed, maintained, inspected, tested, and operating in a safe manner.

(e)(40) Process hazard analysis. (1) The employer shall perform an initial process hazard analysis (hazard evaluation) on processes covered by this standard. The process hazard analysis shall be appropriate to the complexity of the process and shall identify, evaluate, and control the hazards involved in the process. Employers shall determine and document the priority order for conducting process hazard analyses based on a rationale which includes such considerations as extent of the process hazards, number of potentially affected employees, age of the process, and operating history of the process. The process hazard analysis shall be conducted as soon as possible, but not later than the following schedule:

(i) No less than 25 percent of the initial process hazards analyses shall be completed by May 26, 1994;

(ii) No less than 50 percent of the initial process hazards analyses shall be completed by May 26, 1995;

(iii) No less than 75 percent of the initial process hazards analyses shall be completed by May 26, 1996;

(iv) All initial process hazards analyses shall be completed by May 26, 1997.

(v) Process hazards analyses completed after May 26, 1987 which meet the requirements of this paragraph are acceptable as initial process hazards analyses. These process hazard analyses shall be updated and revalidated, based on their completion date, in accordance with paragraph (e)(6) of this standard.

(2)(41) The employer shall use one or more of the following methodologies that are appropriate to determine and evaluate the hazards of the process being analyzed.

(i) What-If;

(ii) Checklist;

(iii) What-If/Checklist;

(iv) Hazard and Operability Study (HAZOP);

(v) Failure Mode and Effects Analysis (FMEA);

(vi) Fault Tree Analysis; or

(vii) An appropriate equivalent methodology.

(3) The process hazard analysis shall address:

(i)(42) The hazards of the process;

(ii)(43) The identification of any previous incident which had a likely potential for catastrophic consequences in the workplace;

(iii)(44) Engineering and administrative controls applicable to the hazards and their interrelationships such as appropriate application of detection methodologies to provide early warning of releases. (Acceptable detection methods might include process monitoring and control instrumentation with alarms, and detection hardware such as hydrocarbon sensors.);

(iv)(45) Consequences of failure of engineering and administrative controls;

(v)(46) Facility siting;

(vi)(47) Human factors; and

(vii)(48) A qualitative evaluation of a range of the possible safety and health effects of failure of controls on employees in the workplace.

(4)(49) The process hazard analysis shall be performed by a team with expertise in engineering and process operations, and the team shall include at least one employee who has experience and knowledge specific to the process being evaluated. Also, one member of the team must be knowledgeable in the specific process hazard analysis methodology being used.

(5)(50) The employer shall establish a system to promptly address the team's findings and recommendations; assure that the recommendations are resolved in a timely manner and that the resolution is documented; document what actions are to be taken; complete actions as soon as possible; develop a written schedule of when these actions are to be completed; communicate the actions to operating, maintenance and other employees whose work assignments are in the process and who may be affected by the recommendations or actions.

(6)(51) At least every five (5) years after the completion of the initial process hazard analysis, the process hazard analysis shall be updated and revalidated by a team meeting the requirements in paragraph (e)(4) of this section, to assure that the process hazard analysis is consistent with the current process.

(7)(52) Employers shall retain process hazards analyses and updates or revalidations for each process covered by this section, as well as the documented resolution of recommendations described in paragraph (e)(5) of this section for the life of the process.

(f)(53) Operating procedures. (1) The employer shall develop and implement written operating procedures that provide clear instructions for safely conducting activities involved in each covered process consistent with the process safety information and shall address at least the following elements.

(i) Steps for each operating phase:

(A)(54) Initial startup;

(B)(55) Normal operations;

(C)(56) Temporary operations;

(D)(57) Emergency shutdown including the conditions under which emergency shutdown is required, and the assignment of shutdown responsibility to qualified operators to ensure that emergency shutdown is executed in a safe and timely manner.

(E)(58) Emergency Operations;

(F)(59) Normal shutdown; and,

(G)(60) Startup following a turnaround, or after an emergency shutdown.

(ii)(61) Operating limits:

(A)(62) Consequences of deviation; and

(B)(63) Steps required to correct or avoid deviation.

(iii)(64) Safety and health considerations:

(A)(65) Properties of, and hazards presented by, the chemicals used in the process;

(B)(66) Precautions necessary to prevent exposure, including engineering controls, administrative controls, and personal protective equipment;

(C)(67) Control measures to be taken if physical contact or airborne exposure occurs;

(D)(68) Quality control for raw materials and control of hazardous chemical inventory levels; and,

(E)(69) Any special or unique hazards.

(iv)(70) Safety systems and their functions.

(2)(71) Operating procedures shall be readily accessible to employees who work in or maintain a process.

(3)(72) The operating procedures shall be reviewed as often as necessary to assure that they reflect current operating practice, including changes that result from changes in process chemicals, technology, and equipment, and changes to facilities. The employer shall certify annually that these operating procedures are current and accurate.

(4)(73) The employer shall develop and implement safe work practices to provide for the control of hazards during operations such as lockout/tagout; confined space entry; opening process equipment or piping; and control over entrance into a facility by maintenance, contractor, laboratory, or other support personnel. These safe work practices shall apply to employees and contractor employees.

(g)(74) Training. (1) Initial training. (i) Each employee presently involved in operating a process, and each employee before being involved in operating a newly assigned process, shall be trained in an overview of the process and in the operating procedures as specified in paragraph (f) of this section. The training shall include emphasis on the specific safety and health hazards, emergency operations including shutdown, and safe work practices applicable to the employee's job tasks.

(ii)(75) In lieu of initial training for those employees already involved in operating a process on May 26, 1992, an employer may certify in writing that the employee has the required knowledge, skills, and abilities to safely carry out the duties and responsibilities as specified in the operating procedures.

(2)(76) Refresher training. Refresher training shall be provided at least every three years, and more often if necessary, to each employee involved in operating a process to assure that the employee understands and adheres to the current operating procedures of the process. The employer, in consultation with the employees involved in operating the process, shall determine the appropriate frequency of refresher training.

(3)(77) Training documentation. The employer shall ascertain that each employee involved in operating a process has received and understood the training required by this paragraph. The employer shall prepare a record which contains the identity of the employee, the date of training, and the means used to verify that the employee understood the training.

(h) Contractors. (1) Application. This paragraph applies to contractors performing maintenance or repair, turnaround, major renovation, or specialty work on or adjacent to a covered process. It does not apply to contractors providing incidental services which do not influence process safety, such as janitorial work, food and drink services, laundry, delivery or other supply services.

(2)(78) Employer responsibilities. (i) The employer, when selecting a contractor, shall obtain and evaluate information regarding the contract employer's safety performance and programs.

(ii)(79) The employer shall inform contract employers of the known potential fire, explosion, or toxic release hazards related to the contractor's work and the process.

(iii)(80) The employer shall explain to contract employers the applicable provisions of the emergency action plan required by paragraph (n) of this section.

(iv)(81) The employer shall develop and implement safe work practices consistent with paragraph (f)(4) of this section, to control the entrance, presence and exit of contract employers and contract employees in covered process areas.

(v)(82) The employer shall periodically evaluate the performance of contract employers in fulfilling their obligations as specified in paragraph (h)(3) of this section.

(vi)(83) The employer shall maintain a contract employee injury and illness log related to the contractor's work in process areas.

(3)(84) Contract employer responsibilities. (i) The contract employer shall assure that each contract employee is trained in the work practices necessary to safely perform his/her job.

(ii)(85) The contract employer shall assure that each contract employee is instructed in the known potential fire, explosion, or toxic release hazards related to his/her job and the process, and the applicable provisions of the emergency action plan.

(iii)(86) The contract employer shall document that each contract employee has received and understood the training required by this paragraph. The contract employer shall prepare a record which contains the identity of the contract employee, the date of training, and the means used to verify that the employee understood the training.

(iv)(87) The contract employer shall assure that each contract employee follows the safety rules of the facility including the safe work practices required by paragraph (f)(4) of this section.

(v)(88) The contract employer shall advise the employer of any unique hazards presented by the contract employer's work, or of any hazards found by the contract employer's work.

(i)(89) Pre-startup safety review. (1) The employer shall perform a pre-startup safety review for new facilities and for modified facilities when the modification is significant enough to require a change in the process safety information.

(2) The pre-startup safety review shall confirm that prior to the introduction of highly hazardous chemicals to a process:

(i)(90) Construction and equipment is in accordance with design specifications;

(ii)(91) Safety, operating, maintenance, and emergency procedures are in place and are adequate;

(iii)(92) For new facilities, a process hazard analysis has been performed and recommendations have been resolved or implemented before startup; and modified facilities meet the requirements contained in management of change, paragraph (l).

(iv)(93) Training of each employee involved in operating a process has been completed.

(j) Mechanical integrity. (1) Application. Paragraphs (j)(2) through (j)(6) of this section apply to the following process equipment:

(i) Pressure vessels and storage tanks;

(ii) Piping systems (including piping components such as valves);

(iii) Relief and vent systems and devices;

(iv) Emergency shutdown systems;

(v) Controls (including monitoring devices and sensors, alarms, and interlocks) and,

(vi) Pumps.

(2)(94) Written procedures. The employer shall establish and implement written procedures to maintain the on-going integrity of process equipment.

(3)(95) Training for process maintenance activities. The employer shall train each employee involved in maintaining the on-going integrity of process equipment in an overview of that process and its hazards and in the procedures applicable to the employee's job tasks to assure that the employee can perform the job tasks in a safe manner.

(4)(96) Inspection and testing. (i) Inspections and tests shall be performed on process equipment.

(ii)(97) Inspection and testing procedures shall follow recognized and generally accepted good engineering practices.

(iii)(98) The frequency of inspections and tests of process equipment shall be consistent with applicable manufacturers' recommendations and good engineering practices, and more frequently if determined to be necessary by prior operating experience.

(iv)(99) The employer shall document each inspection and test that has been performed on process equipment. The documentation shall identify the date of the inspection or test, the name of the person who performed the inspection or test, the serial number or other identifier of the equipment on which the inspection or test was performed, a description of the inspection or test performed, and the results of the inspection or test.

(5)(100) Equipment deficiencies. The employer shall correct deficiencies in equipment that are outside acceptable limits (defined by the process safety information in paragraph (d) of this section) before further use or in a safe and timely manner when necessary means are taken to assure safe operation.

(6)(101) Quality assurance. **(i)** In the construction of new plants and equipment, the employer shall assure that equipment as it is fabricated is suitable for the process application for which they will be used.

(ii)(102) Appropriate checks and inspections shall be performed to assure that equipment is installed properly and consistent with design specifications and the manufacturer's instructions.

(iii)(103) The employer shall assure that maintenance materials, spare parts and equipment are suitable for the process application for which they will be used.

(k)(104) Hot work permit. **(1)** The employer shall issue a hot work permit for hot work operations conducted on or near a covered process.

(2)(105) The permit shall document that the fire prevention and protection requirements in 29 CFR 1910.252(a) have been implemented prior to beginning the hot work operations; it shall indicate the date(s) authorized for hot work; and identify the object on which hot work is to be performed. The permit shall be kept on file until completion of the hot work operations.

(l)(106) Management of change. **(1)** The employer shall establish and implement written procedures to manage changes (except for "replacements in kind") to process chemicals, technology, equipment, and procedures; and, changes to facilities that affect a covered process.

(2) The procedures shall assure that the following considerations are addressed prior to any change:

(i)(107) The technical basis for the proposed change;

(ii)(108) Impact of change on safety and health;

(iii)(109) Modifications to operating procedures;

(iv)(110) Necessary time period for the change; and,

(v)(111) Authorization requirements for the proposed change.

(3)(112) Employees involved in operating a process and maintenance and contract employees whose job tasks will be affected by a change in the process shall be informed of, and trained in, the change prior to start-up of the process or affected part of the process.

(4)(113) If a change covered by this paragraph results in a change in the process safety information required by paragraph (d) of this section, such information shall be updated accordingly.

(5)(114) If a change covered by this paragraph results in a change in the operating procedures or practices required by paragraph (f) of this section, such procedures or practices shall be updated accordingly.

(m)(115) Incident investigation. **(1)** The employer shall investigate each incident which resulted in, or could reasonably have resulted in a catastrophic release of highly hazardous chemical in the workplace.

(2)(116) An incident investigation shall be initiated as promptly as possible, but not later than 48 hours following the incident.

(3)(117) An incident investigation team shall be established and consist of at least one person knowledgeable in the process involved, including a contract employee if the incident involved work of the contractor, and other persons with appropriate knowledge and experience to thoroughly investigate and analyze the incident.

(4)(118) A report shall be prepared at the conclusion of the investigation which includes at a minimum:

(i)(119) Date of incident;

(ii)(120) Date investigation began;

(iii)(121) A description of the incident;

(iv)(122) The factors that contributed to the incident; and,

(v)(123) Any recommendations resulting from the investigation.

(5)(124) The employer shall establish a system to promptly address and resolve the incident report findings and recommendations. Resolutions and corrective actions shall be documented.

(6)(125) The report shall be reviewed with all affected personnel whose job tasks are relevant to the incident findings including contract employees where applicable.

(7)(126) Incident investigation reports shall be retained for five years.

(n)(127) Emergency planning and response. The employer shall establish and implement an emergency action plan for the entire plant in accordance with the provisions of 29 CFR 1910.38(a). In addition, the emergency action plan shall include procedures for handling small releases. Employers covered under this standard may also be subject to the hazardous waste and emergency response provisions contained in 29 CFR 1910.120(a), (p) and (q).

(o)(128) Compliance Audits. (1) Employers shall certify that they have evaluated compliance with the provisions of this section at least every three years to verify that the procedures and practices developed under the standard are adequate and are being followed.

(2)(129) The compliance audit shall be conducted by at least one person knowledgeable in the process.

(3)(130) A report of the findings of the audit shall be developed.

(4)(131) The employer shall promptly determine and document an appropriate response to each of the findings of the compliance audit, and document that deficiencies have been corrected.

(5)(132) Employers shall retain the two (2) most recent compliance audit reports.

(p)(1) Trade secrets. **(1)** Employers shall make all information necessary to comply with the section available to those persons responsible for compiling the process safety information (required by paragraph (d) of this section), those assisting in the development of the process hazard analysis (required by paragraph (e) of this section), those responsible for developing the operating procedures (required by paragraph (f) of this section), and those involved in incident investigations (required by paragraph (m) of this section), emergency planning and response (paragraph (n) of this section) and compliance audits (paragraph (o) of this section) without regard to possible trade secret status of such information.

(2) Nothing in this paragraph shall preclude the employer from requiring the persons to whom the information is made available under paragraph (p)(1) of this section to enter into confidentiality agreements not to disclose the information as set forth in 29 CFR 1910.1200.

(3)(2) Subject to the rules and procedures set forth in 29 CFR 1910.1200(i)(1) through 1910.1200(i)(12), employees and their designated representatives shall have access to trade secret information contained within the process hazard analysis and other documents required to be developed by this standard.

* [57 FR 23060, June 1, 1992; 61 FR 9227, March 7, 1996]

APPENDIX 2

TECHNICAL SUMMARY PHYTOREMEDIATION

pp. 1 - 9

PHYTOREMEDIATION
TECHNICAL SUMMARY

Toxic metal-contaminated soils, aqueous waste streams and groundwaters pose a major environmental and human health problem. Bioremediation, i.e. the use of living organisms to treat contaminants, is increasingly favored by both the public and the private sectors as a method for waste treatment because of its low costs and minimal environmental impact. Current bioremediation methods cannot economically treat toxic metals, thus making many sites suitable only for conventional and very costly "removal and burial" technology. Phytoremediation technology has been developed to overcome the shortcomings of classical bioremediation and waste removal methods. Plants that accumulate toxic metals from contaminated soil and water can be grown and harvested economically, leaving soil or water with only residual levels of pollutants.

The ability of certain selected plants to effectively remove large amounts of toxic metals from soils and waters can provide novel, economically efficient and environmentally friendly approaches to reduce toxic metals in the environment. The demonstrated feasibility of this approach at the laboratory scale has led to the development of three distinct approaches to phytoremediation :

- **Phytoextraction:** the use of metal-accumulating plants, which can transport and concentrate metals from the soil in the roots and aboveground shoots.
- **Rhizofiltration:** the use of plant roots to absorb, concentrate and precipitate toxic metals from polluted aqueous streams.
- **Phytostabilization:** the use of plants to eliminate the bioavailability of toxic metals in soils.

A. Approaches To Treatment

Several approaches are currently used for treating soils contaminated with toxic metals:

- **Fixation:** the chemical processing of soils to immobilize the metals, is usually followed by treatment of the soil surface to eliminate penetration by water.
- **Landfilling :** the excavation, transport and deposit of contaminated soil in a permitted hazardous waste landfill.
- **Leaching:** using acid solutions or proprietary leachants can be very effective in removing certain metals from soil and permits the return of clean soil to the site.

Phytoextraction may be a cost-effective alternative to these approaches. We estimate that using phytoextraction to clean up of one acre of sandy loam soil to a depth of 50 cm will cost $60,000-100,000 compared to at least $400,000 for excavation and storage alone using traditional soil removal methods. Phytoremediation applications will involve costs related to treatment of hazardous materials, extensive metal analysis during and after the treatment, and handling and disposing of metal-containing plant residues. Growing several sequential crops of metal-accumulating plants will still be up to an order of magnitude cheaper than soil removal methods. Furthermore, this method is ecologically preferable, since it reclaims soil at the site, recycling it in a biologically safe state rather than permanently disposing of it by removal to a storage site.

Cost Advantage Of Phytoextraction

Type of Treatment	Cost/m^3 ($)	Time Required (months)	Additional factors/expense	Safety Issues
Fixation	90-200	6-9	Transport/excavation Long-term monitoring	Leaching
Landfilling	100-400	6-9	Long-term monitoring	Leaching
Soil extraction, leaching	250-500	8-12	5,000 m^3 minimum Chemical recycle	Residue disposal
Phytoextraction	15-40	18-60	Time/land commitment	Residue disposal

Current approaches to treating heavy metal contamination in water include:

i. **Precipitation or flocculation**, followed by sedimentation and disposal of the resulting sludge. For many water streams, treatment is relatively simple and inexpensive, but the special characteristics of some toxic metals in water make these streams much more difficult and expensive to treat. For example, the treatment of chelated copper in electroplating rinse water can cost up to $40 per pound of copper removed; rhizofiltration cost estimates range from $1-5 per pound.

ii. **Ion exchange** processes are used to treat waters containing a variety of cationic metals at moderate to high concentrations. A recently developed ion-exchange process for treating chelated copper, which assumes that the copper can be electrochemically recovered from the residue to eliminate disposal, reduces treatment costs to $15 per pound of copper removed.

iii. **Reverse Osmosis** is a sophisticated treatment technology widely used to purify saline water for drinking in arid countries. This approach is effective in removing contaminants to below discharge standards, but generates a residual brine and is relatively expensive.

iv. **Microfiltration** is used to "polish" certain highly toxic metals after conventional treatment to meet discharge standards. An important example is radionuclide waste. Precipitation and microfiltration to recover radionuclides from water has projected site-related costs of over $1 million to treat a relatively small flow of 2 gallons per minute, primarily due to the cost of radioactive sludge disposal.

Rhizofiltration offers a major cost advantage in water treatment because of the ability of plants to remove up to 60% of their dry weight as toxic metals, thus markedly reducing the generation and disposal cost of the hazardous or radioactive residue. Rhizofiltration will also be a cost-competitive technology in the treatment of surface or ground water containing low but significant concentrations of toxic metals such as chromium, lead and zinc.

B. *Results of Work to Date*

i. **Phytoextraction:** Extensive screening and selection procedures have identified promising metal-accumulating lines of fast-growing plants which can effectively remove toxic metals from soils. These plants concentrate metals in their roots and transport metals to the above-ground shoots which can be easily harvested.

Phytoextraction technology has been advanced by intentionally avoiding known non-crop metal-accumulating species because of their low biomass production, handling difficulties, genetic variability and lack of established cultivation practices. Instead, screening efforts have focused on crop and crop-related species because of their ability to accumulate metals and their good agronomic characteristics. Of 16 species studied, *Brassica* was the best accumulator of lead in shoots. In addition to having the highest metal-accumulating ability, it showed low levels of lead toxicity. It is also a high biomass producer (average yield of 18 tons/hectare) - meaning that it can extract and store more contaminants from the soil. The ease of cultivation and predictable field performance led to the choice of *Brassica* as the best metal-accumulating species for phytoextraction.

Identification of *Brassicas* as the best metal-accumulator was followed by screening of 120 cultivars to utilize existing genetic variability and find the best phytoextracting line(s). Fig. 1 demonstrates the ability of the ten best lead-accumulating cultivars identified in the screen to concentrate lead in shoots (A) and roots (B). Cultivar 426308, the best metal-accumulator identified to date, contained almost 3.5% of lead by weight in the dried shoots. In a number of experiments, roots of cultivar number 426308 were able to concentrate lead 173-fold over the lead levels in the growing medium. The highest root accumulation was observed in lines 211000, 478326 and 478336. All lead accumulating cultivars are vigorous plants with high above-ground biomass.

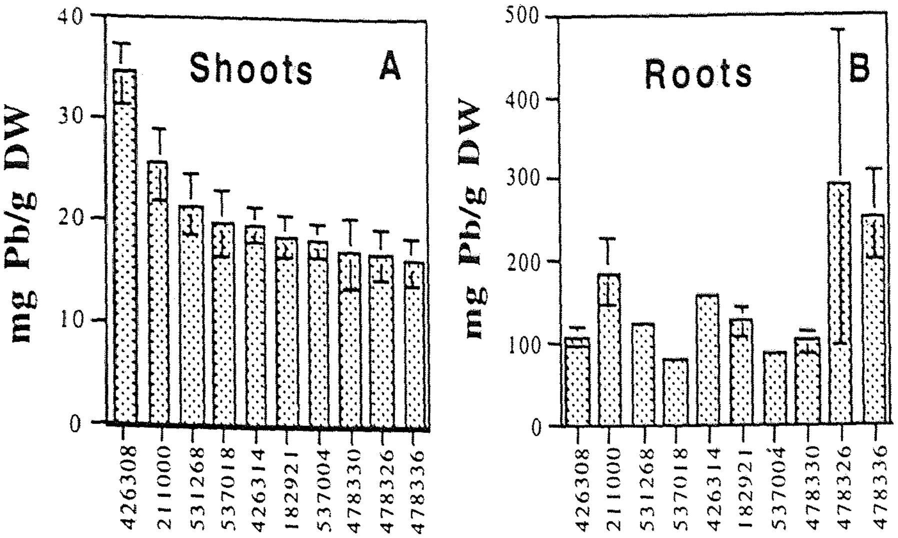


Figure 1. Lead content of shoots (A) and roots (B) of *B. juncea* cultivars grown in sand/Perlite mixture containing 625 µg Pb/g DW for 14 days. Vertical bars denote S.E. (n=4).

Chromium is another major environmental contaminant of soils and waters. Preliminary results indicate that these plants are also extremely good accumulators of chromium. The phytoextractability of copper, cadmium, zinc, nickel, lead, and both trivalent and hexavalent chromium by *Brassica* cultivars was tested and is shown in Figure 2.

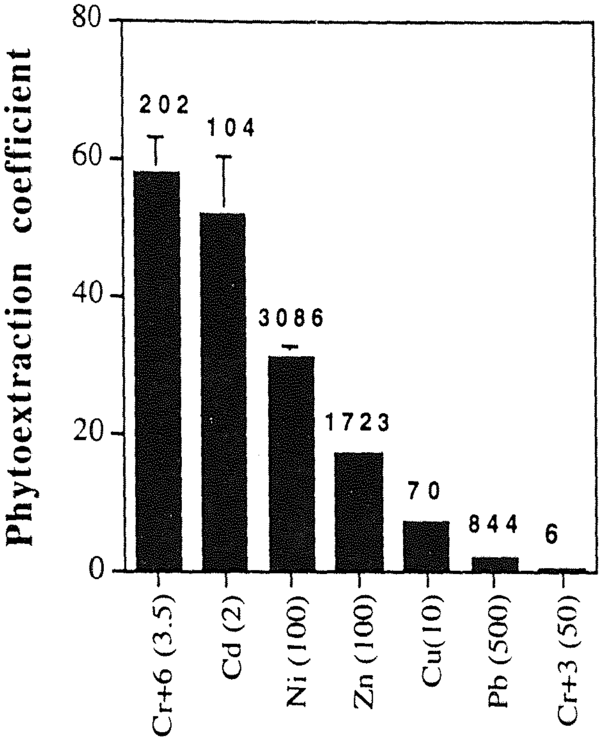


Figure 2. Phytoextraction Coefficient of different heavy metals in shoots of *B. juncea* cultivar 182921 grown for 14 days in a fertilized sand/Perlite mixture supplemented with a heavy metal. The values in parenthesis indicate the µg metal/g DW soil. The values above the columns indicate µg metal/g DW shoot tissue. Phytoextraction coefficients are the ratios between µg metal/g DW shoot and µg metal/g DW soil. Vertical bars denote S.E. (n=4).

ii. Rhizofiltration: The roots of living plants can absorb remarkably large quantities of lead and chromium from contaminated soil. Rhizofiltration technology exploits the ability of plant roots to treat aqueous streams. Fig. 3 shows a flow-through pilot system in which water containing toxic metals is passed through a trough packed with plant roots. An intermittent-action system has also been developed. The batch system performed similarly to the flow-through system in all trials. In addition to concentrating metals in root tissue, rhizofiltrating plants can precipitate large amounts of metal with compounds exuded from the roots (see below). The suspended particles containing metals precipitated by root exudates are filtered and collected at the outlet to produce clean water. Various plants can be used in a rhizofiltration system. Metal-enriched roots are harvested after the remediation cycle. Shoots can be discarded or allowed to regenerate new roots depending on the species used. New plants can be added to the system to maintain the continuity of the operation.

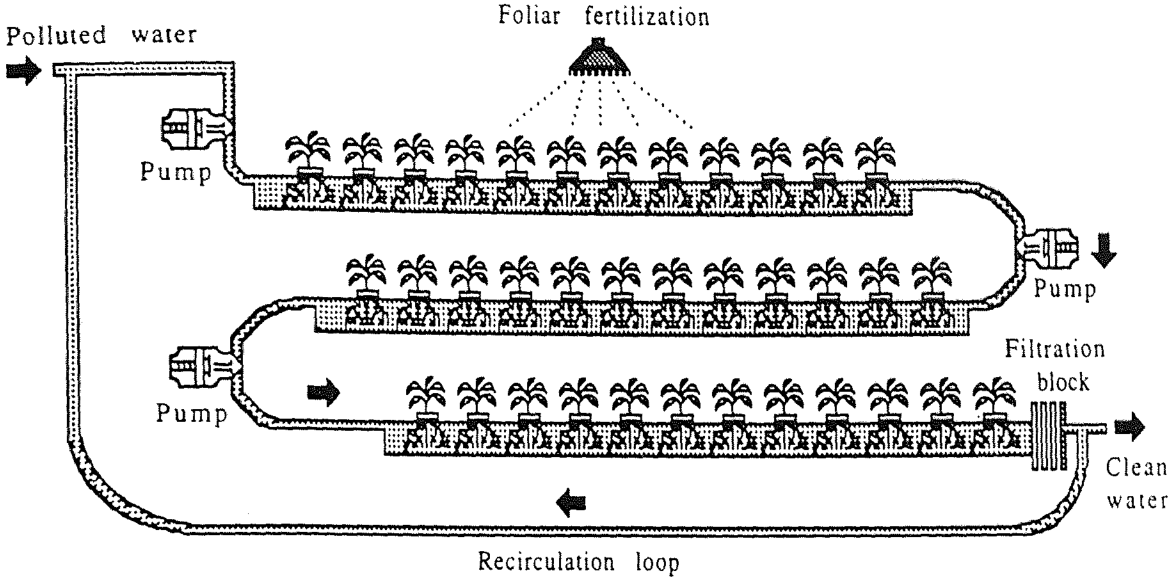


Figure 3. Flow-through rhizofiltration system

The ability to absorb different metal ions is a common property of all plant roots but varies widely between plant species. Brassicas efficiently and rapidly remove a variety of heavy metals from water. This was demonstrated by immersing roots of hydroponically grown*B. juncea* plants in 400 ml of deionized water containing Cd^{+2} (2 mg/L), Ni^{+2}(10 mg/L), Cu^{+2}(6 mg/L), Zn^{+2}(100 mg/L), Cr^{+6}(4 mg/L), or Pb^{+2} (2 mg/L) (Figure 4). These concentrations exceeded NJ ground water quality criteria by 500, 400, 100, 40, 20 and 6 fold, respectively. Experimental plants did not show visible phytotoxicity for the duration of the experiment. In 8 hours roots dramatically reduced the content of all tested metals in solution. Bioaccumulation coefficients, the ratio of metal concentration in root tissue (µg/g DW) to initial metal concentration in solution (mg/L), determined after 24 h of metal treatment varied significantly for different metals.

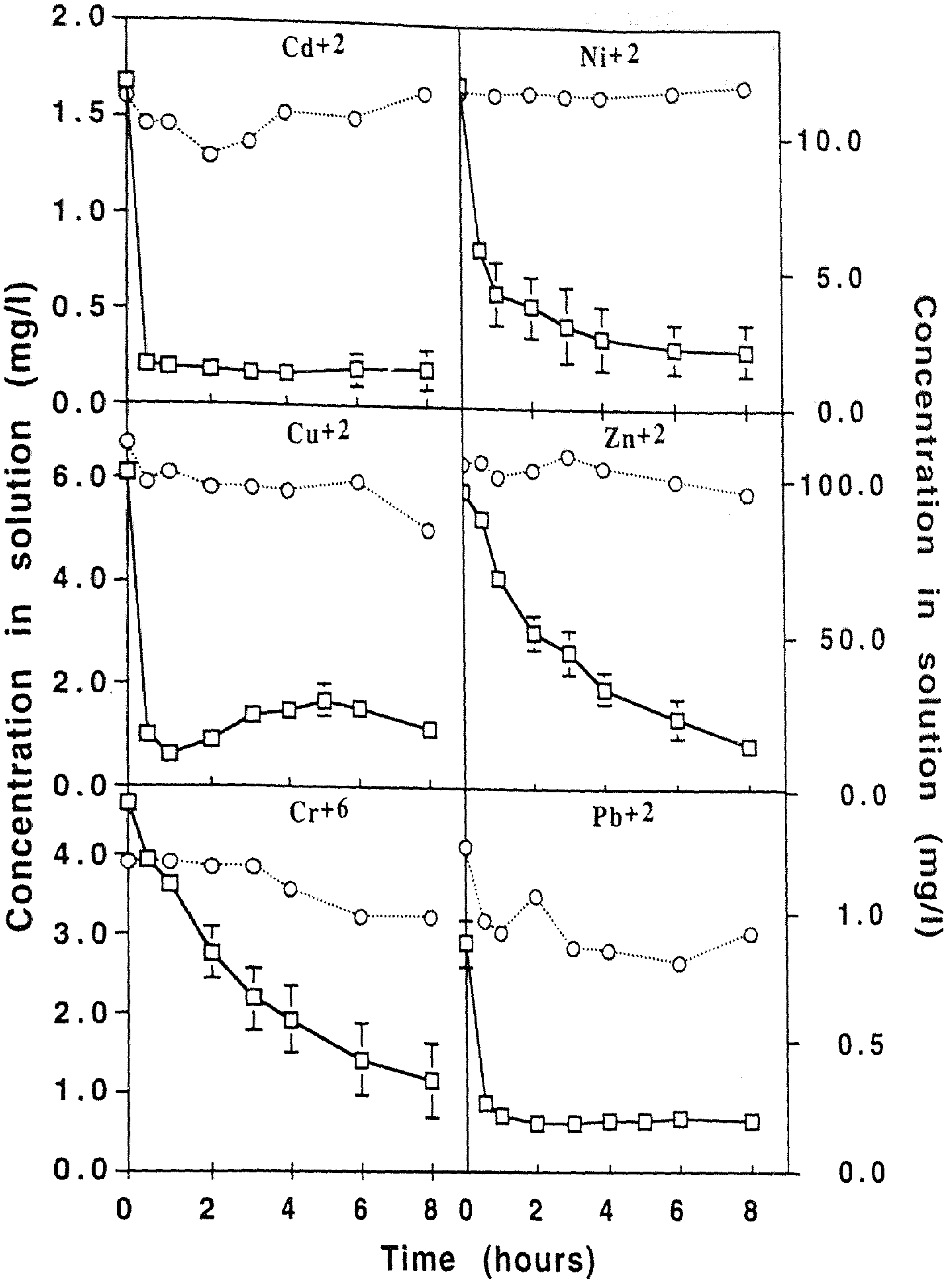


Figure 4. Removal of different metals from aqueous solutions by *B. juncea* roots ( ). Metal ions are indicated on the top of each panel. Control treatments (O) did not contain roots. Vertical bars denote S.E. (n=4). Vertical axis scales are metal concentrations in mg/L (ppm).

iii. Phytostabilization: The ability of plant roots to absorb and precipitate large quantities of toxic metals can be utilized to reduce the bioavailability of toxic metals in soils and to prevent their entry into ground water and food chains; therefore, a technology which will render toxic metals not bioavailable will greatly reduce human exposure to them. Figure 5 demonstrates the ability of Brassica roots to take up and immobilize lead in the soil. Seedlings were grown in sand-Perlite mixtures, and when the plants were 3 weeks old, a lead solution was administered to pots with and without plants to obtain a final lead concentration of 625 ppm. On the sixth day after lead treatment, solution leached from each pot was collected to determine the available lead by atomic absorption spectroscopy. Leachate from pots containing plants had almost no lead; however, leachate from pots with no plants contained large amounts of lead.

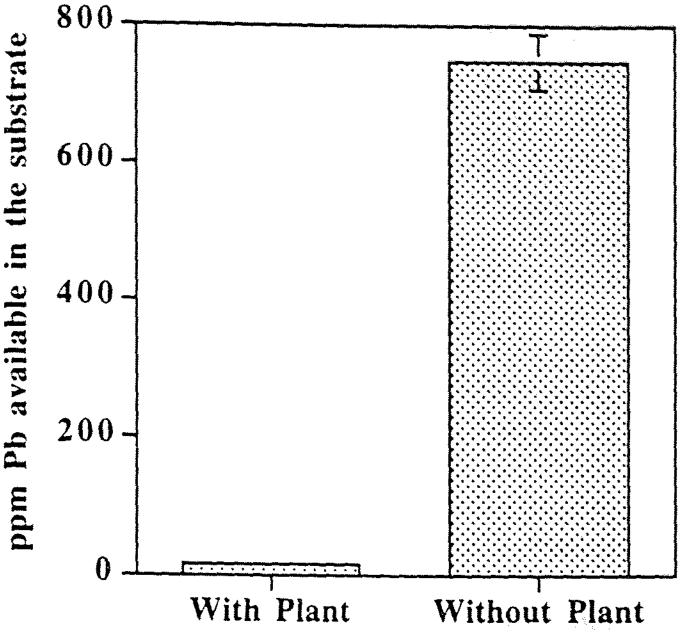


Figure 5. Effect of plant roots on the leachability of lead in soil (ppm = parts per million)

This study demonstrates that roots of plants can effectively immobilize lead in soil, thereby making it much more harmless to the environment. The ability of various plants to phytostabilize other toxic metals is currently under investigation. Phytostabilization research is directed towards development of plant varieties which can develop a substantial root biomass capable of binding and retaining toxic metals in the contaminated soils without transporting metal to the shoots. Reduced shoot transport will eliminate the necessity of treating harvested shoot residue as hazardous waste.

C. Applications

The low cost of phytoextraction will allow on-site remediation of many locations that are not being cleaned up because of the prohibitively high cost of currently available methods. The amount of hazardous materials generated as a result of the cleanup will be dramatically reduced. Top soil will be preserved. The environmentally friendly nature of phytoremediation should be attractive to the public, government and regulatory agencies.

Rhizofiltration may have as broad an application as phytoextraction and phytostabilization. It can be used to remove certain metals from groundwaters, industrial waste streams, sewage sludges, downwashes from powerlines, mining operations and construction sites, effluents from water treatment plants, agricultural run-offs, and output from other activities which generate toxic metals. Rhizofiltration and phytoextraction offer efficiency and low cost.

i. Phytoextraction: Based on available information, the rate of lead removal from contaminated soils can be estimated: Total aboveground biomass production is 18 tons/hectare with up to 2.5% lead accumulation in plant shoots, and approximately 8 tons/hectare production of root mass with 20% lead. One planting of the best lead accumulating lines can remove as much as 2000 kg lead/hectare when grown in soil containing lead. In most of the areas of the US at least three sequential crops can be grown each year. An optimistic scenario would suggest that the best metal-accumulating lines can extract approximately 6000 kg lead/hectare/year. At those sites where only the aboveground biomass can be harvested, plants can still remove 1.9 tons of lead/hectare/year. Dried biomass, if combusted, will produce ash containing up to 25 % lead which may then be used to reclaim and recycle the metal, precluding landfill disposal.

ii. Rhizofiltration: Roots of the best rhizofiltrating plants identified in screens contain 15% lead in dry biomass, which is equivalent to 65 % in ash. By combining absorption and precipitation the roots of the most efficient rhizofiltrating plants remove lead equal to 60% of their dry weight. This high concentration also makes reclaiming metals from ash a potentially viable alternative to ash burial.

iii. Phytostabilization: Phytostabilization can be particularly useful in situations where there is a need for a rapid immobilization of metal in soils in order to prevent its movement into ground and/or surface waters. It may be also used on large sites which have marginally elevated levels of toxic metals. In addition, phytostabilization can be used as a follow-up treatment to phytoextraction or conventional removal and burial methods.

The application of phytoremediation will be driven by its technical and economic advantages over alternative approaches:

- **Lower costs for soil, groundwater and end-of-pipe treatment**
- **Generation of a recyclable metal-rich plant residue**
- **Applicability to a range of toxic metals and radionuclides**
- **Minimal environmental disturbance**
- **Elimination of secondary air or water-borne wastes**
- **Public acceptance.**

REGULATORY APPROVALS

Successful phytoremediation must meet cleanup standards in order to be approved by regulatory agencies. Preliminary results indicate that, in situations where phytoremediation is appropriate, cleanup standards will be met. In addition, the commercialization of the technology can only increase the ability to match standards. This is true in large part because the broader technology of bioremediation, of which phytoremediation is a novel and distinctive subset, is currently clearing the path to government approvals. For example, EPA's Bioremediation Action Committee, in conjunction with EPA's Office of Engineering and Technology Demonstration and its Technology Innovation Office, is exploring ways in which standards can be based upon actual danger rather than simple detectability of contaminants. The intent is to give a chance to technologies that provide alternatives to costly incineration. Such policies will be even more firmly in place by the time phytoremediation enters the market. In addition, early pro-active communication and negotiation with state agencies, the EPA and international environmental agencies will further ensure that phytoremediation-specific benefits will be considered from the start.

REFERENCES

[1] G. Benjamin and B. Benjamin 1995, "The Ear" *Fundamentals of Industrial Hygiene* Plog, Nilan Quinlan. 4th ed. OSH., Chicago. National Safety Council/CRC Lewis Publication. pp. 83-101

[2] G. Benjamin 1995, "The Eye" *Fundamentals of Industrial Hygiene* Plog, Nilan Quinlan. 4th ed. OSH., Chicago. National Safety Council/CRC Lewis Publication. pp. 103 - 177

[3] G. Benjamin 1995, "The Lung" *Fundamentals of Industrial Hygiene* Plog, Nilan Quinlan. 4th ed. OSH., Chicago. National Safety Council/CRC Lewis Publication. pp. 35 - 47

[4] J. M Blaylock, D.E Salt, S. Dushenkov, O. Zakharova, G. Gussman, Y. Kapulink, B. Ensley, and Raskin Ilya. 1997 "Enhanced Accumulation of Pb In Indian Mustard by Soil-applied Chelatin Agent" *Environmental Science and Technology,* 3:31 860-865

[5] Code of Federal Regulation. 29CFR 1910.119; 29CFR 1910.1450

[6] R. Dogoni, Feb.10, 1997 "Molecular Magic with Microwaves"*: Journal of Science and Technology*, p. 26-33

[7] Economic Research uses USDA 1996 "Industrial Uses of Agricultural Materials" *Industrial Uses*/IUS-6: 32-36

[8] H. Gage 1993. "Modeling and System Development" *Man-machine System Design.* 1st. ed. NJIT Newark, NJ pp. 81 - 127

[9] J. W. Hole Jr. 1987, "The Cell" *Human Anatomy and Physiology*, 4th ed. Iowa. William C. Brown Publication pp. 75- 87

[10] C. D. Klassen & E. L. David. 1993, "Principles of Toxicology", *Toxicology* Casareh and Doull, 4th ed. New York. McGraw Hill. pp. 15 - 31

[11] C. D. Klassen and K. Rozman 1993 "Absorption, Distribution and Excretion of Toxicants". *Toxicology,* Casarah and Doull, 4th ed. New York. McGraw Hill. pp. 51-61

[12] Kumar, Dushenkov, Motto Ilya Raskin. 1995 "Phytoremediation: The use of plant to remove heavy metals from soil". *Environmental Science and Technology*, 29: 5: 1232-1238

[13] G. Miller. 1995 "Non-ionizing radiation." *Fundamentals of industrial hygiene.* Plog, Nilan Quinlan. 4th. Ed. OSH., Chicago. National Safety Council / Lewis Publication. pp. 295

[14] Niosh Pocket Guide to Chemical Exposure, US Department of Health and Human Services 1994

[15] National Safety Council. " Safety training" *Accident Prevention Manual; Business and Industry,* P. M Laing 10th. Ed. OSH, US

[16] R. M. Atlas April 3, 1995. "Bioremiadiation" *Chemical and Engineering News.* pp. 32-42

[17] J. S. Taylor 1995 "The Skin and Occupational Dermatoses" *Fundamentals of Industrial Hygiene,* PLOG, Nilan Quinlan. 4th. Ed. OSH., Chicago. National Safety Council / Lewis Publication.

[18] "Concrete and Masonry Construction" Osha 3106 US Department of Labor

[19] A.J. Vander, J.H. Sherman, D.S. Luciano, 1994. "Movement of Molecules Across Cell Membranes." *Human Physiology,* K. M. Prancan and J. W. Bradley 6th ed. New York. McGraw Hill. pp. 39-137