Chemical

SAFETY AND SECURITY TRAINING

Chemical Safety and Security Workshop

Bangkok, Thailand

28 February- 4 March 2011

Sandia National Laboratories

Welcome and Introductions

Photo credit. U.S. Environmental Protection Agency

Chemical Safety and Security Overview

SAND No. 2009-8395P
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-4AL85000.

Why practice chemical safety?

- **Health and safety of the workers**
- **Prevent accidental releases**
  - **Potential regulatory fines, lawsuits**
- **Relationship with the local community**
- **Ensure a sustainable environment**

Industrial Safety Incidents

Catastrophic process incidents:

- **1976 Seveso Italy, 1984 Bhopal India, 2005 Texas City Texas**

More recently:

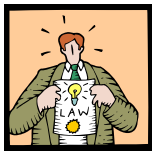
- **2010-Fire and Explosion**
  - **Refinery naphtha hydrotreater**
  - **Seven deaths**
- **2009-Fertilizer tank collapses**
  - **2 critically injured**
  - **Responders exposed to ammonia**
- **2007-Fire and Explosion**
  - **Filling ethyl acetate storage tank**
  - **Equipment not bonded or grounded**

Photo credit. U.S. Chemical Safety Board. http://www.csb.gov/

Safety Video: Bhopal India

Chemical safety is now under stricter control and scrutiny

- **Individual country regulations**
  - **US OSHA Process Safety Standard**
  - **US EPA Risk Management Plan Rule**
- **International chemical organizations**
  - **ICCA Responsible Care**
- **International standards**
  - ISO 14001:2004
  - OHSAS 18001
  - United Nations-GHS, SAICM
- **Increased public awareness**
- **Increased media coverage**
- **Less public tolerance**



What about chemical security?

- **Chemical theft**
  - **Precursors for drugs**
  - **Precursors for chemical weapons**
  - **Dual-use chemicals**
    - **Industrial uses**
    - **Attractive to criminals and terrorists**
    - **Toxic and reactive chemicals favored**
- **Attack on a facility**
  - **Economic and environmental impact**

Chemical Security Incidents

- **Sarin attack on Judges in Matsumoto, June 1994**
  - Sarin sprayed from truck at night
  - 7 deaths, 144 injuries
- **Sarin attack on Tokyo subway, March 1995**
  - 11 bags with 600 grams each on 3 main subway lines
  - 12 deaths, 3938 injuries
- **Hydrogen cyanide attacks on Tokyo subway, May 1995**
  - Bags of sodium cyanide and sulfuric acid
  - No deaths, 4 injuries

Chemical Security Incidents

- **March 2002, an anarchist (called himself "Dr. Chaos") was found at 2 am in a Chicago building carrying sodium cyanide**
- **Stored chemicals in a storage room at the Chicago subway**
  - **Chemicals stolen from an abandoned chemical warehouse**
  - **15 drums and 300 laboratory size chemical containers**
  - **Mercuric sulfate, sodium cyanide, potassium cyanide, and potassium chlorate**

- **Sentenced to prison for "possessing a chemical weapon", as well as other charges**

http://cns.miis.edu/db/wmdt/incidents/1190.htm, accessed 12/07

How are chemicals acquired for malevolent purposes?

- **Access to unprotected facilities**
  - **Warehouses**
  - **Plant storage facilities**
  - **Academic laboratories**
  - **Waste disposal sites**
  - **Construction sites**
- **No controls or security checks on procurement**
  - **Chemical supply companies**
  - **Shipping & receiving**
- **Recruit young chemists**
  - **Synthesize chemicals into weapons**

How are chemical safety and chemical security related?

Both Ensure Protection of:

- **Workers**
- **Facilities**
- **Processes**
- **Community**
- **Environment**
- **Economy**

Principles of Security

General principles should be followed to help ensure effective and appropriate security

- **Detect**
- **Deter**
- **Respond**

Chemical Security
International Resolutions, Organizations, Codes

- UN Resolution 1540
- Australia Group
- Organization for the Prohibition of Chemical Weapons
- American Chemical Council
  - *Responsible Care Security Code*

Individual chemical security standards differ from country to country

Reflect and Consider

What chemical safety and security practices and controls does your plant require?

…Are they <u>effective</u>?

…Could they be <u>improved</u>?

…<u>How</u>?

Chemical Safety Principles and Management

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Definitions

- **Safety: "**The condition of being safe from undergoing or causing hurt, injury, or loss"
  - **Merriam-Webster**

    http://www.merriam-webster.com/dictionary/safety
- **Chemical Safety: "**Practical certainty that there will be no exposure of organisms to toxic amounts of any substance or group of substances: This implies attaining an acceptably low risk of exposure to potentially toxic substances."
  - **IUPAC Glossary of Terms Used in Toxicology**

    http://sis.nlm.nih.gov/enviro/iupacglossary/glossaryc.html

Hazard versus Risk

- **Hazard – *the potential to harm***
- **Risk – *the probability that harm will result***

Photo credit. Proctor and Gamble

Industrial Hazards

- ***Chemical hazards***
  - **Toxic, corrosive, carcinogenic substances**
  - **Flammable, explosive, and reactive substances**
- ***Other Industrial hazards***
  - **Mechanical-unguarded moving parts, belts, fans**
  - **Electrical**
  - **Pressure & temperature extremes**
  - **Elevated surfaces**
  - **Noise**
  - **Nonionizing radiation-lasers, ultraviolet light, radiofrequency**
  - **Ergonomic hazards**

Risk Assessment

Anticipation

Recognition

Evaluation

Control

→ **Hazards** →

Risk to:
Workers
Facility
Community

Anticipation

Advance Planning:

- **Outline proposed process**
  Describe step by step tasks
- **Acquire process**
  and safety information, equipment specifications, safety data sheets

•Team with engineers, team leaders, workers, safety professionals

Recognition

- **Identify and characterize chemical hazards**
  - Health hazard
  - Quantity
  - Solid, liquid, or gas
  - Flashpoint
  - Vapor pressure
  - Air or water reactivity
- **Identify other process hazards**
  - Process temperature and pressure
  - Mechanical
  - Electrical
- **Identify ergonomic hazards**

Evaluation

Risk Assessment

- **What are the tasks in the process**?
  - Filling, spraying, mixing, activities
  - Elevated pressure or temperature
  - Exposed liquid surface
  - Process chemical by-products

- **Process equipment maintained?**
- **Barriers and guards in place?**
- **Workers properly trained?**

- **What can go wrong in the process?**
- **Emergency shut-down equipment or ventilation**?

Controls

How are the risks controlled?

- •Eliminate the hazard
- •Substitution
- •Engineering controls
- •Operational practices
- •Personal Protective Equipment (PPE)

Controls

Change the process

eliminate the hazard

(e.g. Lower process temperature)

Substitution

non-hazardous substance for hazardous

(e.g. - toluene for benzene)

Engineering Controls

Isolate or enclose the hazard

Use a barrier

Or,

Ventilate

-Dilution ventilation

-Local exhaust ventilation (LEV)

Operational Practices

organizational *safety policies*

that apply to everyone

Personal Protective Equipment

PPE may include:

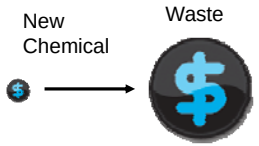
Full-body suits,
Aprons,
Eye protection,
Gloves,
Respirators,
Head & foot protection

Chemical Management

- Benefits
- Cradle to Grave Model
- Procurement
- Storage
- Use
- Disposal

Chemical Management Benefits

- Reduces cost of:
  - Raw materials
  - Hazardous waste disposal
- Facilitates plant sustainability
- Protects the environment
- Improves security
  - Theft
  - Sabotage



Chemical Management Cradle - to – Grave Model

Procure → **Store** →

Use → **Disposal**

Chemical Procurement

- Institute a ***procurement approval system***
  - Document how chemicals are ordered
  - Establish controlled procurement access
    - Chemical procurement approval form
  - Link ordering to a product review system
  - Track “chemicals of concern”

Chemicals Storage

Where are chemicals stored?

- Loading dock
- Warehouse
- Outside
- Storage tanks
- Waste facility

Guidelines for Safe Warehousing of Chemicals
Center for Chemical Process Safety (CCPS)

Chemical Storage

Design and Construction:

- International Code Council http://www.iccsafe.org/
- Combines many building and fire codes
- Incorporates
  - National Fire Protection Association (NFPA) Codes
  - NFPA Electric Code (70)
  - NFPA Life Safety Code (101)

Chemical Storage

Design and Construction:

- Safe path during normal and emergency conditions
- Separate personnel areas from warehouse
- Adequate aisle spacing
- Exit signage
- Emergency lighting
- Determine travel distance

Chemical Storage

Design and Construction:

- Spill containment
  - Maximum probable spill plus fire sprinkler water
  - Primary containment
    - Drains, trenches
  - Secondary containment
    - Recessed loading dock
    - Concrete berms, grates
- Separate incompatible chemicals
  - Oxidizers, corrosives, flammables

Chemical Storage

Design and Construction:

- Fire resistive building construction
  - For flammable chemical storage
- Fire rated separations
  - Fire wall, barrier, or partition
- Draft curtains, heat and smoke vents
- Powered ventilation systems
- Emergency power
- Temperature control

Chemical Storage

Chemical Storage

Natural peril mitigation:

- Earthquakes
  - Anchor racks
  - Store hazardous chemicals on lower racks
- Floods
  - Build flood walls/sandbags
  - Separate water reactives
- Lightning
- Wind storms
  - Roof construction

Chemical Storage

Gas Cylinders:

- Separate incompatibles
- Chain all gas cylinders
- Store in well-ventilated area
- Provide protection from direct sunlight
- Screw down cylinder caps when not in use

Chemical Storage

CSB Video: Compressed Gas Cylinder Fire

Chemical Storage

Tank Storage:

- Tank material **compatible** with the chemical stored
  - Mild Steel
  - Stainless steel
  - Cross-linked high density polyethylene
- Spill containment
  - Double walled tanks
  - Lined tanks
  - Berms
- Security Issues

Photo credit: Bailiff Enterprises, Inc. Houston, Texas

Drum Storage

Chemical Inventory Systems

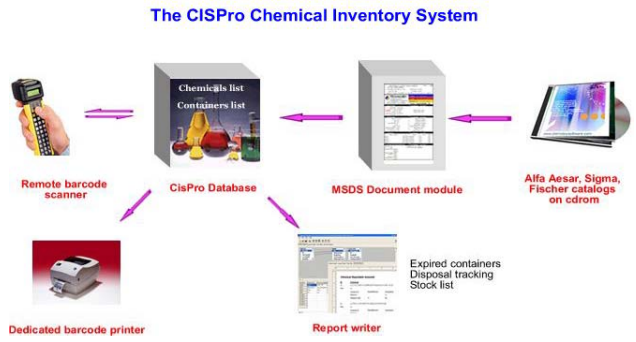
- **Home made** – Access™ or Excel™ programs
- **Freeware** – Web-based, Hypertext Preprocessor (PHP) software
- **Commercial** – Chemical inventory linked to Safety Data Sheets (SDS)
- **Radiofrequency Identification** (RFID) tracking

Chemical Inventory Systems

Should Include:

- **Barcode number**
- **Trade or IUPAC name**
- **CAS number**
- **Location**
- **Process unit**
- **Gas, liquid, or solid**
- **Quantity (units)**

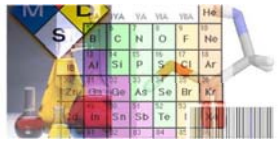
Inventory Systems Example: CISPro



Picture credit: ChemSW. http://www.chemistry-software.com/inventory/12220.htm

Inventory Systems Example: Chemoventory System

- **Chemoventory is a PHP- based online chemical inventory software**
- **Offers a free Lite version and one time paid standard version**
- **Chemoventory**
  1476 Creekside Dr #C108
  Walnut Creek, CA 94596



Chemoventory. http://www.chemoventory.com/index.php

Inventory Systems
Barcode Systems

- System of tracking is container-based
- Each container/tank/cylinder is provided with a barcode sticker
- Barcode labels may be printed using a direct thermal printer
- Requires a scanner

Photo credit: Fabian M. Dayrit and Jaclyn Elizabeth R. Santos

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Inventory Systems
Barcode Systems

Advantages:

- **Query for container location**
- **Link a chemical container to SDS**
- **Track chemicals of concern**
- **Document disposal or waste transfer**

- **Recommendations:**
  - **Perform a periodic site inspection**
    - **Assures accuracy of the inventory**
    - **Provides visual inspection of container condition**

Photo credit: Fabian M. Dayrit and Jaclyn Elizabeth R. Santos

Inventory Systems
Barcode Systems

BARCODE	LOCATION	DEPT	QUANTITY	UNIT	Purchase Date
AQ00600682	NM/518/1111	1725	50	kg	10/24/2006
AQ00602185	NM/518/1123	1111	50	kg	11/20/2006
AQ00582298	NM/518/1302	1131	25	kg	8/8/2006
AQ00602186	NM/518/1302	1131	200	Liters	11/20/2006
AQ00602187	NM/518/1302	1131	200	Liters	11/20/2006
AQ00582307	NM/518/1302	1131	200	Liters	8/8/2006

Using Chemicals
Hazard Communication

Label all chemical containers

-Product name
-Supplier name
-Chemical name
-Signal words (Danger, Warning)
-Hazard pictograms
-Hazard statements (FLAMMABLE LIQUID)

Symbol credit. NFPA. http://www.nfpa.org/faq.asp?categoryID=928&coo
Symbol credit. UNECE. http://www.unece.org/trans/danger/publi/ghs/pictograms.html

Using Chemicals
Hazard Communication

- **Pipe Labeling**
  - 2007 ANSI/ASME A13.1 *Scheme for the Identification of Piping Systems*
  - Does not apply to buried pipelines or electrical conduit
  - Label must state contents, hazard, direction of flow

Photo Credit: Seton Identification Products. http://www.seton.com/catalog/product/view/

Using Chemicals
Hazard Communication

Safety Data Sheet:

1. Identification
2. Hazard(s) identification
3. Composition information
4. First-aid measures
5. Fire-fighting measures
6. Accidental release measures
7. Handling and storage
8. Exposure control/personal protection

Using Chemicals
Hazard Communication

9. Physical/chemical properties
10. Stability and reactivity
11. Toxicological information
12. Ecological information
13. Disposal considerations
14. Transport information
15. Regulatory information
16. Other information

Chemical Security

- Only trained and approved personnel:
  - Have access to storage areas
  - Have access to procurement system and inventory database
- Locked doors and approved access for:
  - Reactive chemicals
  - Explosives
  - Dual use chemicals
  - Hazardous waste

Chemical Waste Management

- Solid waste
  - Hazardous waste
- Special categories
  - Metal waste
  - Radioactive and mixed waste
  - Biological waste
  - Unknown waste

Chemical Waste Management

- Substitute chemicals when process permits
- Recycle
- Dispose by incineration, if allowed
- Incineration is NOT the same as open burning

Exercise

- How are chemicals procured at your facility? Can anyone order a chemical?
- Are dual-use chemical quantities tracked?
- What safeguards are there for earthquakes, typhoons, floods?
- What labeling system is used?
- How do you access safety data sheets?
- How do you track chemical waste?

Tea Break

OHSAS 18001: International Occupational Health and Safety Assessment Specification and Management System

Developed by BSI, BVQ1 and SGS certification bodies

Embraces BS8800

SAND No. 2011-0549C
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for the United States Department of Energy's National Nuclear Security Administration
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OHSAS 18001 Requirements

- Identify OHS hazards
- Assess the risks associated with OHS hazards identified
- Determine the controls necessary to reduce OHS risks to acceptable levels

OHSAS 18001 Relationships to ISO

- Uses same principles as ISO 9001/14001
  - Document and data control
  - Auditing
  - Process controls
  - Record controls
  - Training
  - Corrective and preventive action and statistics
  - Structure about identical to ISO 14001

ISO 9001 and OHSAS 18001

- ISO 9001, the world's most widely established quality standard, focuses on satisfying customer requirements.
  - However, neither ISO 9001 nor ISO 14001 explicitly address risk management.
- OHSAS 18001 expands customer requirements of ISO 9001 and:
  - Includes regulatory and other mandatory OHS requirements
  - Is a system for monitoring, controlling and improving performance regarding current regulations and legislation.
    - Does NOT replace these regulations and legislation.

BS (British Standard) 8800

- Written by industry, safety practitioners and the Health and Safety Executive (HSE) Board to:
  - Minimize risk to employees by developing good working practices to prevent accidents and ill health
  - Improve business performance and responsible image
  - Assist in continuous improvement beyond legal compliance
  - Help organizations comply with its OHS policies and objectives

BS 8800 (2004)

- New and improved annexes:
  - Promoting an effective OHS management system
  - Hazardous event investigation
  - Risk assessment and control
  - Integration with other management systems into an overall management system

OHSAS 18001 Integration with ISO Standards

- Can be partially of fully integrated with ISO 9001/14001 programs.
- Some elements are common to ISO; others have no common basis.
- Successful integration requires a mature ISO 9001/14001 program(s).
- Can be run in parallel with ISO; integration not for all.

Relationships

- OHSAS 18001 sets OHS specifications.
- OHSAS 18002 provides guidelines for implementation of OHS 18001.
- BS8800 explains various elements in developing and maintaining an OHS management system.
  - Offers guidance in promoting safety management system, risk assessment and hazardous event investigation.

Applicability of OHSAS 18001

- Applies to any organization, regardless of:
  - Size
  - Process
  - Regulatory requirements
  - Economic situation
  - Geographic location

Why Implement OHSAS 18001?

There are costs to implementing OHSAS 18001, but if they can be justified the benefits (both tangible and intangible) exceed the costs:

- Safety of workers
- Quality of product
- Increased efficiency
- Good for business

Benefits of OHSAS 18001

- Tangible
  - Reduce lost time
  - Reduce litigation risk
  - Adequate health & safety insurance provisions
  - Regulatory flexibility

Benefits of OHSAS 18001

- Intangible
  - Continuity of operations
  - Operational efficiency
  - Quality work force
  - Improved community goodwill
  - Competitive advantages
  - Employee motivation and pride

OHSAS 18001 Management Plan

- Integrated with other business activities
- Dedicated to continuous improvement
- Develops corporate commitment
- Establishes emergency preparedness response
- Satisfies legislative requirements
- Not intended to address product or services safety

OHS Management Program

- Designates responsibility and authority
- Defines means through which objectives are to be achieved, and timeline for achieving them.
- Must be reviewed at regular, planned intervals
- Must be amended to address relevant changes in activities, products/services or operating conditions
- Top management must provide necessary resources

OHSAS 18001 Requirements

- Must establish and maintain procedures for ongoing identification of hazards, risk assessment and control measures for:
  - Routine and non-routine activities
  - Activities of all personnel having access to the facility
  - For all facilities, regardless whether provided by the organization or others

Proactive, Not Reactive

- Consistent with operating experiences and capabilities of risk control measures and provide input into:
  - Determination of facility requirements
  - Identification of training needs
  - Development of operational controls
  - Monitoring of actions to ensure effectiveness and timeline to implementation
  - Classification of risks (LOW-HIGH)

Regulations

- Specific to the activity (e.g. site operating permits)
- Specific to the organizations products and/or services
- Specific to the industry; general OHS safety laws and authorizations, licenses and permits
- Must consider the legal and regulatory requirements of ALL activities (not just high risk).

Objectives

- Should be quantified whenever possible
- There must be a continuous improvement commitment
- Consider:
  - Legal requirements
  - OHS hazards and risks
  - Technological options
  - Financial, operations and business requirements
  - Views of interested parties

Employee Awareness

- Employees must understand:
  - Importance of conforming to OHS management system
  - OHS consequences of their work activities
  - Individual roles & responsibilities
  - Potential consequences of non-conformance to operating procedures
- Employees should be involved in review of policies/procedures for managing risks and consulted on changes that affect workplace.
- Employees should be aware of organization's OHS representative.

Employee involvement is KEY.

- Employees must take responsibility for conforming to OHS standards on a daily basis.
  - Therefore, it is important that they respect the process.
- More likely to follow procedures they are involved in designing, and will have greater respect for the process if they are recognized as active participants/encouraged to share opinions.
- Interaction between management and employees, as well as with OHS representative, should be encouraged.

Authorization of OHS Management System by Top Management is Crucial

- Appropriate to nature and scale of OHS risks
- Include commitment to continuous improvement
- Documented and communicated to all employees
- Available to interested parties
- Reviewed periodically
- At least comply with current OHS legislation

Document Control

- Procedures established and maintained such that all documents and data required by OHSAS specifications:
  - Can be readily located.
  - Are reviewed periodically and updated if necessary.
  - Are available at all locations where the OHS management system operates.
  - Documents may be integrated with other corporate documents where appropriate .
    - e.g. org charts, site emergency plans, etc.

Document Control (continued)

- Applies to documents including records, audits and reviews:
  - Must be legible, identifiable and traceable
  - Must be stored as to be readily retrievable and protected against loss or damage
  - Retention time must be established and recorded

Records and Reviews

- Compliant records
- Training records
- Accident Information
- Inspection, maintenance and calibration records
- Contractor and supplier information
- Incident reports
- Risk information
- Audit results
- Management review records

Emergency Situations

- Identify potential emergency situations and response measures.
- There must be review of response measures after any incidents occur.
- Emergency response measures must be tested periodically.

Responsibility and Authority

- Procedures must be defined for response to and investigation of accidents and incidents
- Procedures must be in place for taking action to mitigate consequences from accidents and incidents
- Corrective and preventive action procedures must be initiated and completed
- There must be confirmation of effectiveness of corrective and preventive actions taken

Audit Program and Procedures

- Determines whether OHS management plan has been properly implemented and maintained and meets policy and objectives
- Reviews results of previous audits
- Provides audit information to (top) management
- Should be conducted by independent (not necessarily external) personnel

Management Reviews

- Should be at specified periodic intervals, documented, and cite any need for changes to policy or objectives
- Should include:
  - Audit results
  - Extent to which objectives are met
  - Confirmation of continued suitability of OHS management system
  - Concerns from any relevant interested parties

OHSAS 18001 Certification

Steps to certification are similar to those for ISO 9001/14001:

- **Commit to developing OHSAS 18001 system.**
- **Develop plan for implementation.**
  - **Understand legal/regulatory requirements.**
  - **Identify risks/hazards, and controls for them.**
- **Implementation and training.**
  - **Training for management/employees can be done in-house or through consultants.**
  - **Allow enough time for system to be correctly/effectively implemented.**
- **Once system is in place, consider options for certification.**

OHSAS 18001 Certification

Developing a program can be done with or without consultation:

- **Without – literature can be purchased to help guide through the process of designing/implementing.**
  - Hiring a consultant to check progress may be beneficial.
- **With – Groups like SGS and BVQI, who were involved in the creation of OHSAS 18001, offer in-depth consulting services.**
  - SGS offers its services from the initial set-up, through development and implementation, all the way to certification.
  - BVQI offers preliminary audits to diagnose implementation problems, and audits post-certification to monitor progress.

Chemical Health Hazards Exposure Standards

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Chemical Health Hazards

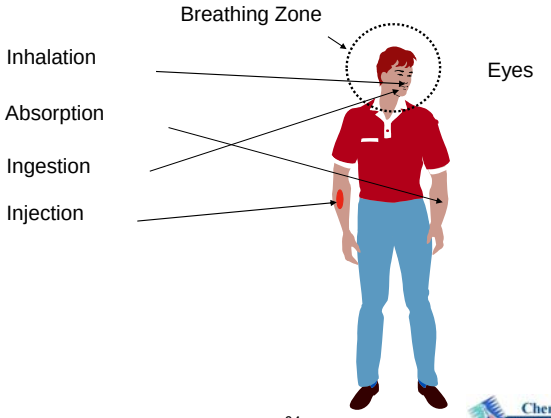
- **Definitions**
- **Exposure**
- **Dose response**
- **Health effects**
- **Exposure limits**
- **Evaluating exposure**
- **Exercises**

Definitions

- **Toxicology: the study of the adverse effects of chemicals (xenobiotics) on living organisms.**
- **Toxicity: ability of a chemical to produce an unwanted effect.**
- **Hazard: the probability that the chemical will produce the unwanted effect**
- **Exposure: Contact with the chemical substance.**
- **Dose: the amount of the chemical that has the potential to produce injury or death.**

Klassen, C. (2001). Casarett and Doulls Toxicology
Plog, B. (2002). Fundamentals of Industrial Hygiene

Exposure



Exposure
Inhalation

- **Most important route of exposure for workers**
  - Gases, solvent vapors, acid mists, dusts, particles, and metal fumes
- **Exposure is dependent on:**
  - Duration and frequency of task
  - Breathing rate
  - Concentration of the chemical
  - Particle size
    - Respirable size = 0.1 μm to 10 μm
  - Solubility of gases & vapors
    - Formaldehyde versus chloroform

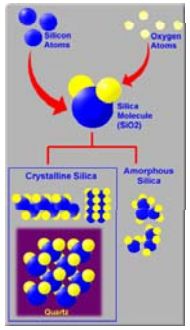
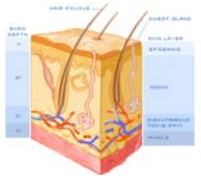


Photo Credit: US OSHA

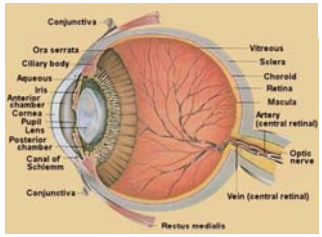
Exposure
Skin Absorption

- **Depends on skin location and thickness**
  - Palms of the hands are thickest
  - Skin on abdomen is thin
- **Depends on skin condition**
  - Dry and broken skin more susceptible
  - Sweat increases absorption
- **Duration of contact**
- **Properties of the chemical**
  - Concentration
  - Solubility (in fat or water)
  - Molecular size (nanoparticles)



Exposure
Eyes

- **Corneal irritation or trauma**
  - Gases, particles
- **Corneal burns**
  - Acids, ammonia
  - Mustard agents
- **Optic nerve damage**
  - Thallium, methanol (ingested)



Exposure
Ingestion

- **Rare exposure route, but possible**
  - Swallow chemicals after inhaling
    - -Mucociliary action of respiratory tract
  - Eating, drinking, smoking in work areas
- **Factors affecting absorption**
  - Ionized versus nonionized form of compounds
  - Weak base absorbed in intestines
  - Weak acid absorbed in stomach

Pharmacokinetics

- **Absorption**
  - **Chemical enters the body by exposure route**
- **Distribution or storage**
  - **Distributed to organs, or**
  - **Stored in bone, proteins, fat**
- **Metabolism**
  - **Liver, kidney enzymes**
  - **May metabolize to a more toxic chemical**
- **Excretion**
  - **Sweat, urine, feces**

Dose Response

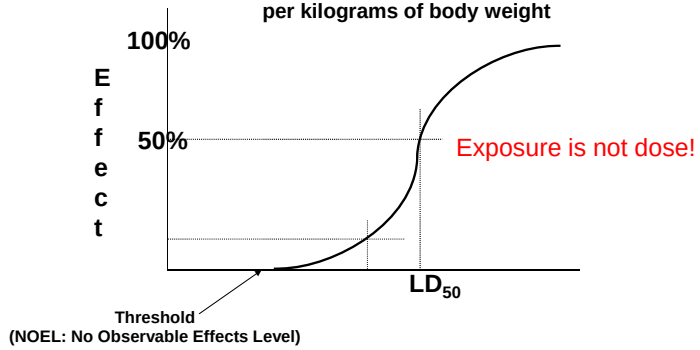
"All substances are poisons; There is none which is not a poison. The right dose differentiates a poison from a remedy…" – Paracelsus (1493-1541)

Dose Response Terminology

- TD_{lo} – Toxic dose low - lowest dose for effect
- LD_{10} – Lethal dose 10% - dose that causes death in 10% of the test population
- LD_{50} – Lethal dose 50% - dose that causes death in 50% of the test population
- TC_{lo} – Toxic concentration low - used to express toxic concentration *via* inhalation
- LC_{10} – Lethal concentration 10% - concentration that causes death in 10% of the test population *via* inhalation
- LC_{50} – Lethal concentration 50% - concentration that causes death in 50% of the test population *via* inhalation

Dose Response

Dose is measured in milligrams of toxicant per kilograms of body weight



Dose Response

Chemical	Beneficial Dose	Toxic Dose
Aspirin	300-1000 milligrams	30,000 milligrams
Vitamin A	500 units	50,000 units
Oxygen	20% in air	50-100% in air

Health Effects

- **Acute Health Effects-severe injury or death**
  - High dose of chemical over short time period
  - Chemicals with acute effects:
    - Toxic gases: hydrogen sulfide, phosgene
    - Asphyxiants gases: nitrogen, methane
    - Corrosive gases and liquids: chlorine, acids
- **Chronic Health Effects-chronic disease**
  - Low dose of chemical over long time period
  - Chemicals with chronic effects:
    - Carcinogens: benzene, asbestos, arsenic
    - Reproductive agents: glycol ether acetates, lead, carbon disulfide
    - Sensitizers-glutaraldehyde, toluene diisocyanate

Health Effects

- **Local**
  - Effect occurs at site of contact
  - Skin rash, burns, coughing
  - Chemicals with local effects:
    - Cutting oils, solvents, acids
    - Cotton dust, aluminum oxide
- **Systemic**
  - Chemical distributed by circulation
  - Effect occurs in body organs
  - Chemicals with systemic effects:
    - Methylene chloride to heart muscle
    - Lead to bone and brain

Health Effects

Chemicals affect people differently:

- Age
- Gender
- Genetic makeup
- Disease or stress
- Nutrition
- Lifestyle
- Interactions between chemical toxicants

Health Effects
Chemical Interactions

- **Additive Effect**
  - Combined effect of 2 chemicals equals sum of each agent alone…(2 + 3 = 5)
  - Example: Parathion, methyl-parathion pesticides
- **Synergistic Effect**
  - Combined effect of 2 chemicals is greater than sum of each agent alone…(2 + 3 = 20)
  - Example: Carbon tetrachloride & ethanol

Health Effects
Chemical Interactions

- **Potentiation**
  - One substance does not have a toxic effect on certain organ or system, but when added to another chemical, it makes the latter more toxic…(0 + 2 = 10)
  - Example: Carbon tetrachloride & isopropanol
- **Antagonism**
  - 2 chemicals, when given together, interfere with each other's actions or one interferes with the action of the other chemical…(4 + 6 = 8)
  - Example: BAL (chelating agent) and lead

Health Effects
Target Organs

Toxins	Target organ	Signs & Symptoms	Examples
HEPATOTOXIN	LIVER	JAUNDICE	CARBON TETRACHLORIDE
NEPHROTOXINS	KIDNEY	EDEMA	CADMIUM MERCURY
NEUROTOXINS	NERVOUS SYSTEM	NARCOSIS NERVE DAMAGE	METHYL ETHYL KETONE
HEMATOPOIETIC SYSTEM	BLOOD	CYANOSIS DEATH	CARBON MONOXIDE HYDROGEN CYANIDE
LUNG AGENTS	LUNGS, BRONCHI	EDEMA, SILICOSIS	CHLORINE, SILICA
REPRODUCTIVE TOXICANT	REPRODUCTIVE SYSTEM	BIRTH DEFECTS	LEAD
SKIN AGENTS	SKIN	RASHES,IRRITATION	ISOCYANATES
EYE HAZARDS	EYES	BURNS	INORGANIC ACIDS

Industrial Exposures and Health Effects

Industrial Exposures
Metals

Exposure primarily by inhalation:

- **Particulates**
  - Processes: grinding, cutting, sanding,
  - Examples: copper, nickel, zinc
- **Fumes**
  - Processes: welding, smelting
  - Examples: lead, manganese, hexavalent chromium, zinc
- **Mists (soluble metal compounds)**
  - Processes: spraying anticorrosives, metal plating

Examples: hexavalent chromium, nickel chloride

http://www.millerwelds.com/

Health Effects
Metals

- **Sensitizers (skin and lungs)**
  - Nickel, beryllium, chromium
- **Metal fume fever**
  - Oxides of zinc, magnesium, and copper
- **Organ toxicity**
  - Arsenic—neurotoxicity, liver injury
  - Cadmium—kidney, lung fibrosis
  - Lead-nervous system, blood, kidney, reproductive
- **Carcinogens**
  - Arsenic, soluble nickel, hexavalent chromium

Industrial Exposures
Solvents

Exposure by inhalation and skin absorption:

- Process: transfer, mixing, spraying, high vapor pressure solvents
  - Examples: ethers, ketones, chloroform, methylene chloride
- Process: Heating solvents
  - Examples: styrene, dimethyl formamide
- Process: skin immersion in process baths, parts cleaning
  - Examples: acetone, n-methyl pyrollidone, dimethyl sulfoxide (DMSO)

Health Effects
Solvents

- Skin irritants, dermatitis
  - Acetone, alcohols
- Organ toxicity
  - N-hexane—neurotoxicity
  - Chloroform, vinyl chloride—liver toxicity
  - Methylene chloride—heart toxicity
- Carcinogens
  - Benzene, formaldehyde
- Reproductive toxicants
  - Glycol ether acetates

Occupational Exposure Limits

Evaluating Exposure

Exposure Limits

<u>Goals of exposure limits:</u>

- Compare measured concentration of hazardous chemical or level of a physical agent against a standard
  - Inhalation exposure to chemicals
  - Exposure to noise, lasers, nonionizing radiation, heat & cold stress
- Chemical exposure limits are milligrams/cubic meter (mg/m^3) or parts per million (ppm)
- Apply to workers only, <u>NOT</u> the general public
- Exposure limits may be required by law

Exposure Limits

Exposure limits (OELs) are country specific:

- **DFG MAK – Maximum Workplace Concentrations**
  - **German legal limits**
- **PEL – Permissible Exposure Limits**
  - Occupational Safety and Health Administration **(**OSHA)
  - **USA legal limits**
- **REL – Recommended Exposure Limits**
  - National Institute of Occupational Health & Safety (NIOSH)
  - USA recommendations to OSHA
- **ACGIH TLV® – Threshold Limit Values®**
  - American Conference of Governmental Industrial Hygienists
  - USA recommendations

Exposure Limits

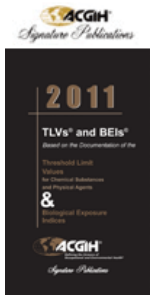
Permissible Exposure Limit (PEL)

- Exposure limits are published by the U.S Occupational Safety and Health Administration (OSHA)
- Intended to control health effects from exposures to air contaminants
- Applies only to workplaces covered by OSHA
- Action Levels published for highly toxic chemicals
  - ½ the PEL
  - Benzene, asbestos, vinyl chloride, formaldehyde

Exposure Limits

ACGIH TLVS®:

- ACGIH is a private, non-governmental corporation
- ACGIH TLVS are published as *guidelines*
- Not legal standards
- ACGIH TLVs are *often* lower than PELs
- Reviewed and revised annually



Exposure Limits

ACGIH TLVS®:

- 8 Hour time-weighted average (TWA)
- 15 minute short-term exposure limit (STEL)
- Ceiling value (C)

- **TLV Examples:**
  - Carbon dioxide = 5000 ppm TWA
  - Osmium tetroxide = 0.0002 ppm TWA
  - Hydrogen chloride = 2 ppm C
  - Ammonia = 35 ppm STEL

Calculation for Unit Concentration

$$\text{TLV (ppm)} = \frac{\text{TLV (mg/m}^3\text{)} \quad 24.45}{\text{(molecular weight)}}$$

$$\text{TLV (mg/m}^3\text{)} = \frac{\text{TLV (ppm) (MW)}}{24.45}$$

Time Weighted Average (TWA)

Average exposure for an individual over a working period of time, determined by taking one or more samples during the working period:

$$\text{TLV – TWA*} = \frac{C_1T_1 + C_2T_2 + \ldots + C_NT_N}{T_1 + T_2 + \ldots + T_N}$$

Where:
C = airborne concentration
T = time

*** A TLV expressed as a TWA**

8-Hr Time Weighted Average

Average exposure for an individual over an 8-hr working period of time, determined by taking one or more samples during the 8-hr working period:

$$\text{TLV – TWA}_8 = \frac{C_1T_1 + C_2T_2 + \ldots + C_NT_N}{8 \text{ hrs}}$$

Example

A degreaser operator is monitored for exposure to Stoddard solvent. The monitoring data is:

TIME PERIOD (NUMBER)	*CONCENTRATION (PPM)*	*TIME (HOUR)*
1	80	2
2	110	4
3	55	2

Solution

$$TLV - TWA_8 = \frac{C_1T_1 + C_2T_2 + \ldots + C_NT_N}{8 \text{ hrs}}$$

$$TLV - TWA_8 = \frac{(80 \times 2) + (110 \times 4) + (55 \times 2)}{8 \text{ hrs}}$$

EIGHT HOUR TLV-TWA = 89 ppm

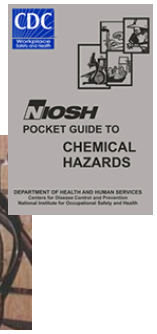
Over exposed?
(TLV = 100 ppm)

Other ACGIH TLV Notations …

- "Skin" potential exposure by the dermal route, including mucous membranes and the eyes
  - Examples: some solvents, phenol, pesticides
- "SEN" potential to produce sensitization
  - Example: toluene diisocyanate

Evaluating Exposure

- **Qualitative assessment**
  - **Observe task**
    - **Airborne contaminants?**
    - **Skin immersion ?**
  - **Evaluate toxicity**
    - **Safety data sheets**
    - **NIOSH Pocket Guide**
    - **http://www.cdc.gov/niosh/npg/**
- **Quantitative**
  - **Model exposure**
  - **Perform air sampling**



Evaluating Exposure

- **Quantitative**
  - **Model the contaminant concentration in the room**
  - **Exercise: What concentration, in parts per million (ppm) would be produced by the release of 1 gram (g) of benzene in a 125 cubic meter room (m^3)?**

Mass of contaminant/volume of room

1g/125 m^3 = 1000 milligrams/125 m^3 = 8 mg/m^3

ACGIH STEL for benzene is 8 mg/m^3

(15 minute short term exposure)

Evaluating Exposure

Air monitoring:

- Results must be analyzed
- Results are compared against a standard OEL
- Methods:
  - Air sampling pump and media or badges
    - Filters-for metals, particulates
    - Charcoal tubes-for solvents
    - Silica gel tubes-for acids

Photo credits: Sensidyne , SKC Inc.

Evaluating Exposure

Other air monitoring methods:

- Direct reading instruments
  - Photoionization detectors-solvents
  - Particle counters-dusts
  - Portable gas detection
    - Operate with hand pump
    - Color coded detector tubes
    - Detect 500 gases and vapors

LUNCH