Chemical Safety and Security Industry (CSSI) Training

Yemen Chemical Industrialists

Amman, Jordan; 3-7 March 2013

SAND No. 2011-9012P

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sandia National Laboratories

Welcome, Introductions, CSP Overview and CSP Website

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Purpose of this Workshop

- Provide practical chemical risk management tools for use by chemical engineering faculty and students
- Provide information on identifying, evaluating, and controlling chemical hazards and threats
- Promote a culture of excellence in chemical risk assessment, mitigation, and management
- Determine needs for future training and support

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Chemical Security Engagement Program (CSP) Overview

US. Department of State
Washington, DC 20520

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Workshop Overview & Introductions

- CSP Sponsorship
- Purpose of Workshop
- Overview of Workshop
- Introductions

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

Chemical Security Engagement Program (CSP)

U.S. Department of State: CSP Program Objectives

- Raise awareness about the dual-use nature of chemicals
- Foster collaboration among chemical professionals worldwide
- Provide training opportunities, technical assistance, and conduct risk assessments in academic laboratories and industrial settings
- Support local and regional conferences on chemical security policy and regulation

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

CSP Activities

- Work with host countries to assess their current needs and priorities in chemical risk management
- Partner with :
  - National and regional chemical organizations (HKI, IKM)
  - Universities
  - International chemical organizations (OPCW, IUPAC, UNFAO)
  - Chemical industry associations (CICM, KN-RCI)
- CSP engages ministries/regulatory agencies in countries with:
  - Regional security concerns
  - Active producers/exporters of industrial chemicals

Himpunan Kimia Indonesia

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

CSP Website

https://www.csp-state.net/

- Offers networking opportunities
- Provides resources
- Discussion boards
  - Share best practices
  - Ask questions/get answers
- Upload/view photos from workshops
- View/download training materials
- See upcoming and past events

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

CSP Website – log in

Home

CSP
CHEMICAL SECURITY
ENGAGEMENT PROGRAM

Home | Workshops | Share Your Training | Discussion Board | Resources | Contacts

Please log in

Login Name

Password

Log in

Forgot your password?

If you have forgotten your password, click here to retrieve it.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Home Log in

CSP
CHEMICAL SECURITY
ENGAGEMENT PROGRAM

Home | Workshops | Grants & Funding | Discussion Board | Resources | Contacts

About Our Program

The Chemical Security Engagement Program (CSP) Partners With Chemical Professionals To:

Raise Awareness: Dual Use Nature of Chemicals

CSP works to reduce the risk of chemical threats by collaborating with partner governments, national and international chemical organizations, and chemical professionals to raise awareness about chemical security and safety, consistent with national and international guidelines, norms, and requirements.

Foster Collaboration among Chemical Professionals Worldwide

CSP works with chemical organizations and universities to facilitate collaboration between chemical professionals. CSP is particularly interested in funding collaboration that can improve laboratory safety and security.

Provide Training Opportunities and Technical Assistance to Improve Chemical Safety and Security in Laboratories

CSP seeks to work with chemical universities and professional organizations to develop and implement training modules to reinforce chemical security and safety best practice chemical curricula.

Facilities Training and Industrial Partnership to Improve Chemical Security Best Practices in CSP Partners' Local Chemical Industries

CSP partners with chemical industrial organizations to promote established best practices in chemical security, such as those reflected in the Responsible Care® Security Code and Responsible Care Management System. CSP also facilitates membership opportunities for CSP partners' local chemical companies in the area of chemical security.

Chemical Security Engagement Program is sponsored by the U.S. Department of State

Search Site | Search

Map of Participant Countries

Click on image for large, interactive map.

Upcoming Events

Home >Workshops >2012 Workshops

CSP
CHEMICAL SECURITY
ENGAGEMENT PROGRAM

Home | Workshops | Grants & Funding | Discussion Board | Resources | Contacts

Workshops

Click on the workshop name to view presentation materials used for that event. To view or upload photos of an event you attended, click on the Photo Gallery link and login with your user name and password. To request a user name and password, please email us at chemsecurity@sandia.gov.

Yemen CSSO - Jan 2012
Indonesia CSSI- March 2012
International Conference of Young Chemists, Jordan - April 2012
Indonesia CSSI April-May 2012
Malaysia CSSO- May 2012
Indonesia Total Laboratory Management Symposium May 2012
Malaysia CSSI June 2012
Advanced Chemical Management Training July 2012
Chemical Safety and Security Awareness - Malang, Indonesia September 2012
Advanced Chemical Safety and Security - Malang Indonesia Sept 2012
Chemical Safety and Security Officer (CSSO) Training - Algeria October 2012
Chemical Risk Management Training- Yemen October 2012
Chemical Safety and Security Officer (CSSO) Training - Philippines October 2012
Chemical Risk Management Training - Cairo, Egypt November 2012
Chemical Safety and Security Officer (CSSO) Training - Saudi Arabia December 2012

Chemical Security Engagement Program is sponsored by the U.S. Department of State

Search Site | Search

Workshops

- Photo Gallery

Workshops by year

- 2012
- 2011
- 2010
- 2009
- 2008

Where We've Been

- Map of Participant Countries
- Countries & Institutions

CSP
CHEMICAL SECURITY
ENGAGEMENT PROGRAM

Home | Workshops | Grants & Funding | Discussion Board | Resources | Contacts

Grants and Funding Opportunities

Travel Grant Funding

The Chemical Security Engagement Program travel grants provide short-term travel support to chemical scientists, engineers, technicians, and project managers to attend conferences and seminars for career enhancement and/or to network with other scientists, industry and academic organizations with the intent of developing collaborative projects and/or new research opportunities that improve chemical safety and security. To be considered for a travel grant, each submission must include a scanned copy of your valid passport (please include a copy of the first two pages of your passport) and Curriculum Vitae (CV) (or Resume).

More information and application

Chemical Security Improvement Grants (CSIGs)

The U.S. Department of State's Chemical Security Engagement Program (CSP) is pleased to offer grants to improve the physical and procedural security of chemical laboratories and facilities. These Chemical Security Improvement Grants (CSIG) contribute to the safety and security of industrial and academic chemical facilities, including their employees and their communities, and aim to prevent the accidental or intentional misuse of chemicals. CSIGs are one-time awards ranging from $2,000 to $30,000 in value with applications accepted on a quarterly basis. To be considered for a security improvement grant, applicants must submit a completed CSIG application form, CSIG budget form and a curriculum vitae (CV) for each individual compensated under the project.

CSIGs Application

Chemical Security and Safety Training (CSST) Awards

The U.S. Department of State's Chemical Security Engagement Program (CSP) is pleased to offer grants for alumni of prior CSP trainings to implement local chemical security and safety best practices trainings in academic and industrial settings. These trainings engage scientists, technicians, engineers and academics to convey international best practices for safe and secure chemicals

Chemical Security Engagement Program is sponsored by the U.S. Department of State

Search Site | Search

Map of Participant Countries

Click on image for large, interactive map.

Upcoming Events

- October 2012 | Philippines- Chemical Safety and Security Workshop

CSP Website – Discussion Board

CSP Website – Photos

Sandia National Laboratories

Sandia supports the CSP Program

Sandia National Laboratories
Albuquerque, New Mexico, USA

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Workshop Speakers and Introductions

What do you want to learn this week?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Aspects of Chemical Security
Dual-use Chemicals

SAND No. 2011-9013P

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Topics to be discussed

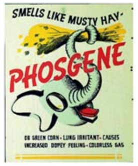
- What are dual use chemicals?
- Areas of focus for this talk
- Examples of each area:
  - Explosive / Chemical Weapons / Precursors (drug and weapons)
- International chemical controls

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

20

Chemical dual-use awareness

Dual use chemicals: Chemicals that can be used for both legal and illegal purposes.



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Areas of focus

Four Mains areas of focus:

1. Drug precursors
2. Chemical weapons
3. Explosives
4. Chemical weapon precursors

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Dual-use chemicals: Pseudoephedrine

- Pseudoephedrine is a common ingredient in cold medicines
- Precursor to crystal methamphetamine
- Recipes for conversion available on web

Illicit Methamphetamine Laboratory

US DEA

Clandestine meth labs in US during 2002
- Caused 194 fires, 117 explosions, and 22 deaths
- Cost $23.8 million for cleanup
- Dumped chemicals led to
  - deaths of livestock
  - contaminated streams
  - large areas of dead trees and vegetation

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Product of dual-use chemicals: Methamphetamine

Late 2005: Indonesian authorities raided a very large Meth Lab in Cikande, Indonesia 60km West of Jakarta.
- 75 kg of crystalline style Meth per batch
- 250,000 tablets of MDMA (Ecstasy) every 8hrs

MDMA=(3,4-methylenedioxymethamphetamine)

Meth reactor
~ 75kg "Ice"

MDMA reactors
~ 8kg Ecstasy

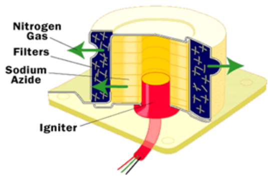
http://www.justice.gov/dea/programs/forensicsci/microgram/mg1106/mg1106.html

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Dual-use chemical: Sodium azide

- Industial Uses
  - Propellant in automobile airbags
    - ~ 50g Driver side
    - ~ 200g Passenger side
  - Biocide in hospitals and laboratories
  - Anticorrosion solutions
- Illegal Uses
  - Gas more deadly than Hydrogen Cyanide when reacted with an aqueous oxidizer
  - Toxic by ingestion
  - Detonator for powerful explosives

Air Bag Inflation Device



http://auto.howstuffworks.com/car-driving-safety/safety-regulatory-devices/airbag1.htm

Dual-use chemical: Cyanide

Therence Koh/AFP/Getty Images

* "Tylenol Crisis of 1982."

- Industrial Use
  - Cyanide consumption globally
    - 13% - mineral processing of gold, copper, zinc, silver
    - 87% - plastics, adhesives, and pesticides
- Illegal Use:
  - Product tampering*
    - Tylenol capsules
      - laced with KCN
      - 7 deaths, fall 1982, Chicago, Illinois, USA
      - Led to tamper-proof product packaging
  - Popular with criminals and terrorists because it is relatively easy to obtain
  - K/NaCN is an Australian Group CW agent

http://en.wikipedia.org/w/index.php?title=Tylenol_Crisis_of_1982&oldid=173056508>.

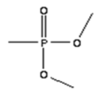
Dual-use chemicals: Chlorine

www.longwarjournal.org/archives/2007/03/al_qaedas_chlorine_w.php

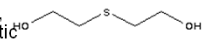
- Industrial Use
  - Manufacture of chlorine compounds
    - 63% - organic chlorine compounds
      - Examples: $C_2H_4Cl_2$ and C_2H_3Cl – (PVC)
    - 18% - inorganic chlorine compounds
      - Examples: HCl, HOCl, $AlCl_3$, $SiCl_4$, PCl_3
    - 19% - bleaches and disinfection products
- Illegal Use:
  - Incidents in which chlorine gas cylinders are blown up with explosives
    - Chlorine likely stolen/diverted from water purification plants or oil industry
    - Civilians and non-combatants injured
  - Chlorine first used in WWI as a chemical weapon

Dual-use chemicals: Precursors

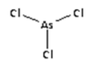
- Dimethyl methyl phosphonate (DMMP)
  - Flame retardant for:
    building materials, furnishings, transportation equipment, electrical industry, upholstery
  - **Nerve agent precursor**



- Thiodiglycol
  - Dye carrier, ink solvent, lubricant, cosmetics, anti-arthritic drugs, plastics, stabilizers, antioxidants, photographic, copying, antistatic agent, epoxides, coatings, metal plating
  - **Mustard gas precursor**



- Arsenic Trichloride
  - Catalyst in CFC manufacture, semiconductor precursor, intermediate for pharmaceuticals, insecticides
  - **Lewisite (Agent L, Schedule 1 CWC) precursor**



From: Chemical Weapons Convention: Implementation Assistance Programme Manual (on CD)

product of dual-use chemicals: TATP

- Triacetone triperoxide (TATP) or Acetone Peroxide
- Nicknamed “Mother of Satan” because of its deadly nature
- Made using acetone, hydrogen peroxide, and a strong acid (i.e. HCl, H_2SO_4)
- Invisible to detectors looking for N-based explosives
- Used as Primary High Explosive
  - Sept 2009 arrest of N. Zazi, NY and Denver
  - July 2005 London suicide bombs
  - 2001 Richard Reid “shoe bomber”
  - 1997 New York subway suicide bomb plot

CAS 17088-37-8

Wikipedia downloaded Oct 2009
http://en.wikipedia.org/wiki/Acetone_peroxide

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Dual-use Chemicals: Explosives

- Theft of conventional explosives
  - Chemical suppliers
  - Users such as mines or construction sites
- Diversion of industrial or laboratory chemicals
  - Chemical suppliers
  - Chemical factories
  - Academic teaching or research laboratories
  - Disposal sites

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

30

Diversion of chemicals: Oklahoma bombing

Photo: US DOD

- Bomb was made of:
  - 108 – 22.5kg bags of Ammonium nitrate fertilizer
  - 3 – 210L drums of liquid nitromethane
  - Several crates of Tovex
    - Water-gel mixture composed of ammonium nitrate and methyl-ammounium nitrate
  - 17 bags of ANFO – 94% ammonium nitrate / 4% fuel oil
  - 60L of diesel fuel
  - Cannon fuse
- How were the chemicals obtained?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

31

Diversion of chemicals: Bali bombing

- Van bomb was made of:
  - Potassium chlorate
  - Aluminum powder
  - Sulfur mixed with TNT (trinitrotoluene)
  - 150 meters of PETN (pentaerythritol tetranitrate) filled detonating cord
  - 94 RDX (cyclotrimethylenetrinitramine) electric detonators
- How where the chemicals obtained?

Photo: www.zgeek.com

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

32

International Chemical Controls

33

International chemical control organizations

Two Main Groups:

Organisation for the Prohibition of Chemical Weapons

- Implementing body of the Chemical Weapons Convention

The Australia Group

- Export controls

34

Organization for the Prohibition of Chemical Weapons (OPCW)

- International group headquartered in The Hague, Netherlands
  - https://www.opcw.org/index.html
- Chemical weapons convention (CWC)
  - International treaty which bans the development, production, stockpiling, transfer and use of chemical weapons
- Promotes international cooperation in peaceful uses of chemistry
- Provide assistance and protection to fellow member states

35

OPCW: International cooperation in peaceful uses of chemistry

- Associates program
- Analytical skills development course
- Conference support program
- Research projects program
- Internship Support Program
- Laboratory Assistance Program
- Equipment Exchange Program

36

OPCW: Assistance and protection to fellow members

- Each member state can request assistance from other member states in the event of a threat or attack, including chemical terrorism
- This can take the form of expertise, training, materials, and/or equipment

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

37

OPCW: Chemical Weapons Convention

Designated 3 class of controlled substances:

- Schedule 1 – chemicals have few or no uses outside of chemical weapons
- Schedule 2 – chemicals have legitimate small-scale applications
- Schedule 3 – chemicals have large scale uses apart form chemical weapons

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

38

Australia Group

- An informal arrangement to minimize the risk of assisting chemical and biological weapon (C&BW) proliferation.
  - Harmonizing participating countries' national export licensing measures
  - Started in 1985 when Iraq CW program was found to have diverted chemicals and equipment from legitimate trade
- 40 nations plus European Commission participate

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

39

Australia Group: Export Controls

- Controls exports of:
  - 63+ Chemical weapon agent precursor chemicals
  - Dual-use chemical manufacturing facilities and equipment and related technology
  - Dual-use biological equipment and related technology
  - Biological agents
  - Plant and animal pathogens
- Includes no-undercut policy
  - Countries will not approve an export that another member country denied

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

40

Dual-use summary

- Defined dual use chemicals
- Discussed examples in each area of focus:
  - Explosive / Chemical Weapons / Precursors (drugs and weapons)
- Discussed International chemical control groups
  - OPCW – schedule 1, 2, & 3
  - Australia group

Overview of Chemical Risk

SAND No. 2012-1606C

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

Overview of Presentation

- Chemical safety incidents
- Current regulations and standards
- Chemical security incidents
- Security threats
- Cyber security threats
- International security resolutions and organizations

Laboratory Safety Incidents

Recent accidents in U.S. research laboratories

- University of California Los Angeles (UCLA)
  - Scale up of flammable chemical t-butyl lithium
  - Quantities of flammables stored in lab exceeded U.S. regulations
  - Improper personal protective equipment
- Texas Tech University
  - Scale up of nickel hydrazine perchlorate from 300mg to 10grams
  - U.S. Chemical Safety Board investigated
    - Physical hazards of chemicals not assessed or controlled
    - Insufficient chemical safety management
    - Lessons from previous incidents not *Learned*

Texas Tech University Accident

Photo credit: U.S. Chemical Safety Board

US Chemical Safety Board Video

CSB Videos – http://www.csb.gov/videoroom/videos.aspx?cid=1
UCLA/Texas Tech/Dartmouth Incidents

Industrial Incidents

<u>Catastrophic process incidents:</u>

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

<u>More recently:</u>

- 2009-Fertilizer tank collapses
  - 2 critically injured
  - Responders exposed to ammonia
  - ~760 m^3 of fertilizer released
  - River contaminated
- 2007-Fire and Explosion
  - Filling ethyl acetate storage tank
  - Equipment not bonded and grounded

Photo credit. U.S. Chemical Safety Board.

Regulations and Standards

- Individual country regulations
  - European Union REACH
  - U.S. Risk Management Standard
- International chemical & labor organizations
  - ICCA Responsible Care
  - International Labor Organization
- International standards
  - ISO 14001:2004
  - OHSAS 18001
  - United Nations-GHS
  - SAICM

ICCA

International Labour Organization

ISO International Organization for Standardization

What about chemical security?

- Chemical theft
  - Precursors for drugs
  - Precursors for chemical weapons
  - Dual-use chemicals
    - Industrial chemicals
      - Flammable or toxic gases
      - Ammonium nitrate
      - Chlorine
      - Pesticides
- Plant sabotage
  - Deaths, injuries
  - Economic and environmental impact

Abandoned Bhopal Plant
Photo credit: AP/Saurabh Das

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What are the threats to chemical security?

- Unlimited access to facilities
  - Chemical storage areas
  - Analytical laboratories
  - Pesticide/chemical waste sites
  - Construction sites
- No controls or security checks on chemical procurement
- Shipping and receiving areas not protected
- Recruit young chemists
  - Tokyo subway Sarin attack

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Threats to Cyber Security

- SCADA control software is used by one-third of industrial plants
- Security technology may not work on plant proprietary networks
- Attacks may result in:
  - Loss of process control
  - Loss of production
  - Process safety incidents
- Examples:
  - 2005-Zolob worm shut down 13 Daimler Chrysler plants
  - Queensland, Australia sewage control system

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

International Resolutions & Organizations

- UN Security Council Resolution 1540
- Australia Group
- Organization for the Prohibition of Chemical Weapons
- American Chemistry Council

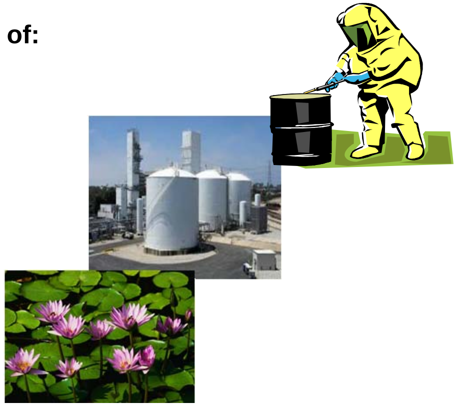
Responsible Care Security Code

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

How are chemical safety and chemical security related?

Both Ensure Protection of:

- Workers
- Plant facilities
- Plant processes
- Community
- Environment
- Economy



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Summary of Presentation

- Chemical safety incidents
- Current regulations and standards
- Chemical security incidents
- Security threats
- Cyber security threats
- International security resolutions and organizations

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Break

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Chemical Safety and Security Risk Assessment

SAND No. 2012-7128P
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Module Overview: Chemical Safety and Security Risk Assessment

- Module Learning Outcomes
- Risk Basics
- Chemical Safety Risk Assessment
- Chemical Security Risk Assessment
- Summary, Conclusions, and Evaluations

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

57

Module Outcomes: After this module, you should…

- Understand the definition of risk and the difference between hazard and risk
- Understand how other factors can influence risk perception
- Be able to assess and characterize the safety risks associated with chemical facilities
- Be able to assess and characterize the security risks associated with chemical facilities

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

58

Risk Basics Overview

- Hazard vs. Risk
- Definition of Risk
- Activity: Risk Perception
- Safety and Security
- Risk Characterization
- Risk Reduction

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

59

Risk Basics: Hazard vs. Risk

- There is a difference between ***hazard*** and ***risk***
  - Hazard
    - Something that has the potential to do harm
- Is there a hazard in this picture? If so, what type?

- Is it a risk? If so, how much of a risk?
  - Depends on the situation

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

60

Risk Basics: Hazard vs. Risk

- What is wrong?
  - Overloaded circuit
- What are the possible scenarios?
  - Blown fuse
  - Worker injury
  - Fire
- What is the likelihood?
  - Factors that lead to an event
    - Work habits, no electrical training
- What are the consequences?
  - Other factors and things that follow an event
    - Electrocution, fire, loss of experiment/process

Hazard

Risk

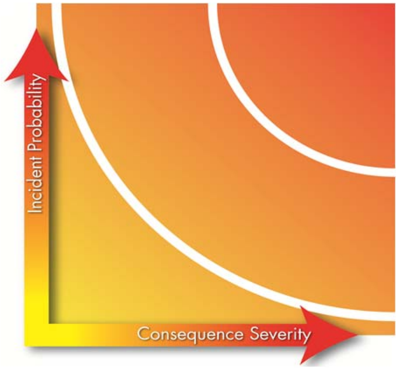
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

61

Risk Basics: Definition

Risk is a function of

- Probability that an incident will occur (**likelihood**)
- Severity if the event occurs (**consequence**)



Risk = *f* (Likelihood, Consequence)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

62

Activity: Risk Perception

- On the next page…
- Rank each action or technology according to your perception of its RISK
  - A rank of 1 means riskiest
  - A rank of 15 means least risky

Take about 10 minutes to do this

* Adapted from Slovic et al. "Facts and Fears: Understanding Perceived Risk." In R. C. Schwing and W. A. Albbers, Jr. (eds.) Societal Risk Assessment: How Safe is Safe Enough? New York: Plenum, 1980, 181-216.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

63

Rank these Items (#1 – #15) by Risk Level

Police work
Commercial Air
X-rays
Mountain climbing
Prescription antibiotics
Alcoholic beverages
Nonnuclear electric power
Railroads
Smoking
Pesticides
Motor vehicles
Spray cans
Bicycles
Swimming
Nuclear power

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

64

Activity: Risk Perception

College Students[1]

1. Nuclear power
2. Smoking
3. Pesticides
4. Motor vehicles
5. Alcoholic beverages
6. Police work
7. Spray cans
8. Traveling by commercial flight
9. X-rays
10. Nonnuclear electric power
11. Prescription antibiotics
12. Mountain climbing
13. Railroads
14. Bicycles
15. Swimming

Experts[2]

1. Motor vehicles
2. Smoking
3. Alcoholic beverages
4. X-rays
5. Pesticides
6. Nonnuclear electric power
7. Swimming
8. Bicycles
9. Travelling by commercial flight
10. Police work
11. Railroads
12. Nuclear power
13. Prescription antibiotics
14. Spray cans
15. Mountain climbing

1 Thirty US college students participated in this study
2 A group of fifteen risk assessment professionals in the US

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

65

Risk Basics: Definition

College Students

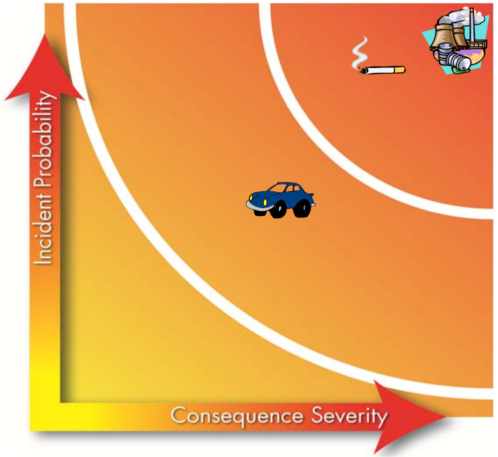
1. Nuclear Power
2. Smoking

4. Motor Vehicles

Experts

1. Motor Vehicles
2. Smoking

12. Nuclear Power



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

66

Activity: Risk Perception

- What do you think may have influenced your risk assessment besides your best guesses regarding ***likelihood*** and ***consequence***?
- Emotional Risk Perception Factors (examples)
  - Involuntary vs. Voluntary
  - Immoral vs. Moral
  - Unfamiliar vs. Familiar

What ***should*** be the basis for your professional Risk Assessment of Chemical Safety and Security?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

67

Risk Basics: Safety and Security

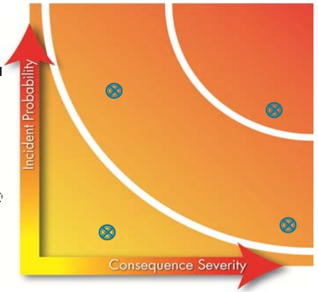
- Risk concept
  - Applies to both Chemical ***Safety*** and Chemical ***Security***
- Safety Incident
  - Spill
  - Accidental exposure
  - Uncontrolled reaction
- Security Incident
  - Theft or diversion of dual-use chemicals
  - Intentional release
  - Sabotage

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

68

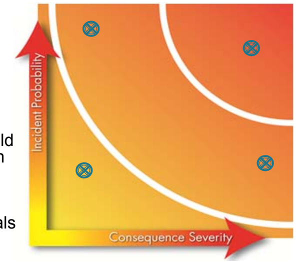
Chemical Safety Risk Characterization

1. **Low**
   - Procedures are routine; staff is trained and experienced; materials used are mostly benign and/or present in microscale amounts only
   - An incident would not likely be an emergency
2. **Moderate**
   - Procedures are not routine; staff may be partially trained or have limited experience; materials are reactive, flammable, toxic, and/or present in moderate quantity
   - An incident could constitute or develop into an emergency
3. **High**
   - Procedures are novel or extremely delicate; staff may be untrained or inexperienced; materials are highly reactive, toxic, explosive and/or present in large quantities
   - Process is under high temperature and/or pressure
   - An incident would be a life and facility-threatening emergency



Security Risk Characterization

1. **Low**
   - Assets are possibly targets for theft or diversion
   - Consequences of loss or release are minimal
2. **Moderate**
   - Assets are attractive for theft or diversion due to monetary value or dual-use
   - Consequences could threaten the public; misuse could be harmful or even lethal to a small number of people, and would certainly damage the institution, its programs, and reputation
3. **High**
   - Assets are very valuable or hard to acquire dual-use materials
   - Consequences of misuse could result in harm or death to many people



Safety and Security Risk Characterization

- What are the benefits of characterizing risks?
- Can risks ever be reduced to zero?
- What does it take to reduce CSS risk?
  - Are resources for risk reduction limitless?

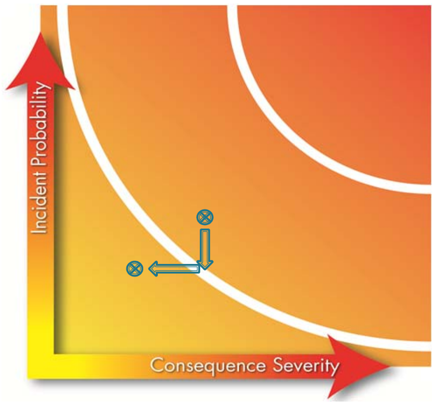
Characterizing CSS risks is a necessary step toward responsible and effective allocation of finite resources to reduce risk to acceptable levels

Risk reduction measures should always be applied in a graded manner

- **Large effort made to reduce high risks**
- **Smaller effort made to reduce low risks**

Risk Basics: Reduction

- Types of CSS Controls
  - Administrative
  - Operational
  - Engineering
  - PPE
- Decrease likelihood
- Decrease consequence



Risk = *f*(Likelihood, Consequence)

Module Overview: Chemical Safety and Security Risk Assessment

☑Module Learning Objectives

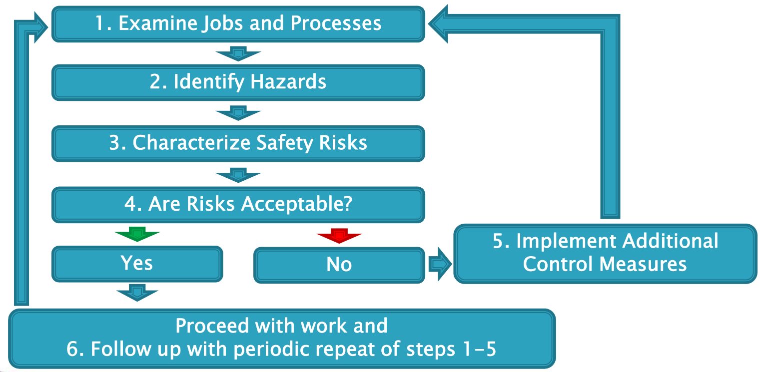
☑Risk Basics

- **Chemical Safety Risk Assessment**
- Chemical Security Risk Assessment
- Summary, Conclusions, and Evaluations

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

73

Chemical Safety Risk Assessment: Overview



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

74

Chemical Safety Risk Assessment

1. Examine jobs and processes

- Analyze for each step in the process
  - Who, what, where, when, and how?
    - Could exposure occur?
    - Could an accident occur?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

75

Chemical Safety Risk Assessment

1. **Examine jobs and processes**

Example: Precipitation of gold from cyanide solution
- 2 junior researchers in the laboratory with only minimal training and not accustomed to using PPE
- About twice a week, zinc powder is added to 100 mL of an aqueous, 0.10 M sodium cyanide solution containing dissolved gold
- The gold precipitates and is collected by filtration
- Work is performed on a crowded open benchtop alongside work on another project that involves preparing numerous HCl solutions

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

76

Chemical Safety Risk Assessment

2. Identify hazards

- On the basis of materials and equipment present

Example: 100 mL of a 0.10 M sodium cyanide solution
- Acute toxin
  - Harmful exposure can occur through ingestion, absorption through broken skin, or inhalation upon conversion to HCN gas by reaction with an acid

Chemical Safety Risk Assessment

3. Characterize safety risks

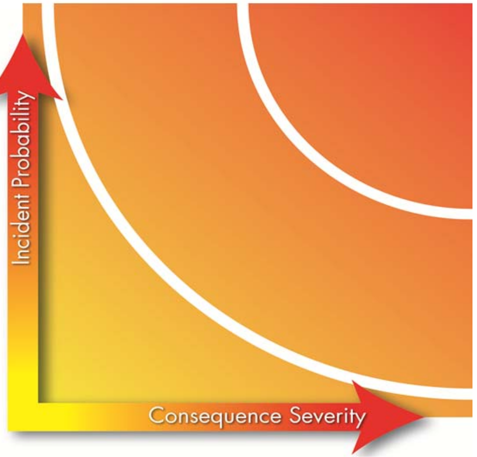
Example: regular work with sodium cyanide solutions
- What are the factors affecting the likelihood of exposure?
  - Do you think the likelihood of exposure is low, moderate, or high?
- What are the factors affecting the consequences of exposure?
  - Do you think the consequences of exposure are low, moderate, or high?

Chemical Safety Risk Assessment

3. Characterize safety risks

On the basis of *likelihood* and *consequence*, are the risks of exposure to NaCN low, moderate, or high?

Why?



Chemical Safety Risk Assessment

4. Are risks acceptable?

- Would you feel safe if you were doing this work?
  - Why/why not?
- Are current controls and practices reducing risk of exposure to acceptable levels?
  - Why or why not?
- Are there national standards for occupational exposure to cyanide?
- Are there other limits imposed by the institution?
  - If you don't know, how can you find out?
  - What do you do if there are not established limits?

Chemical Safety Risk Assessment

5. **Implement additional control measures** to reduce safety risks to acceptable levels

- What controls are needed to reduce the risk of exposure?
  - Substitution
  - Engineering
  - Administrative
  - PPE

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

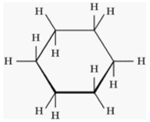
81

Controls

Change the process

eliminate the hazard

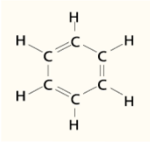
(e.g. Lower process temperature)



Substitution

less-hazardous substance

(e.g. – cyclohexane for benzene)



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

82

Engineering Controls

Enclose the hazard,

- **Use a barrier or**
- **Ventilate**
  - **Dilution ventilation**
  - **Local exhaust ventilation** (LEV)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

83

Administrative Controls

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

84

Personal Protective Equipment: PPE

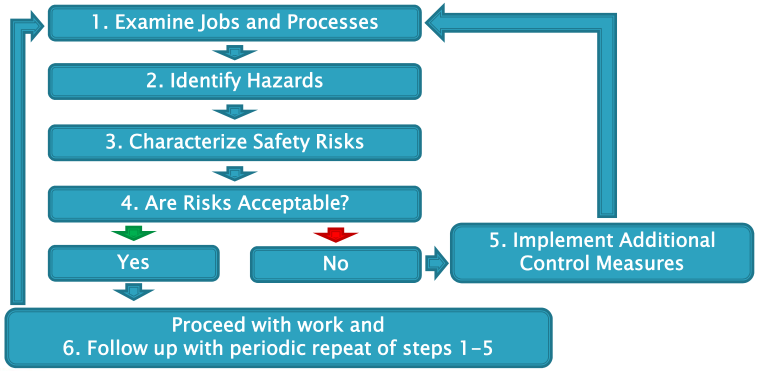
- PPE is the *least* desired control
- Does not eliminate the hazard
- Depends on worker compliance
- May create heat stress

Chemical Safety Risk Assessment

6. **Follow up** with periodic repeat of steps 1-5

- Have practices or people changed?
- Could further improvements be made?
- How often should follow-up assessments be performed?

Chemical Safety Risk Assessment: Overview



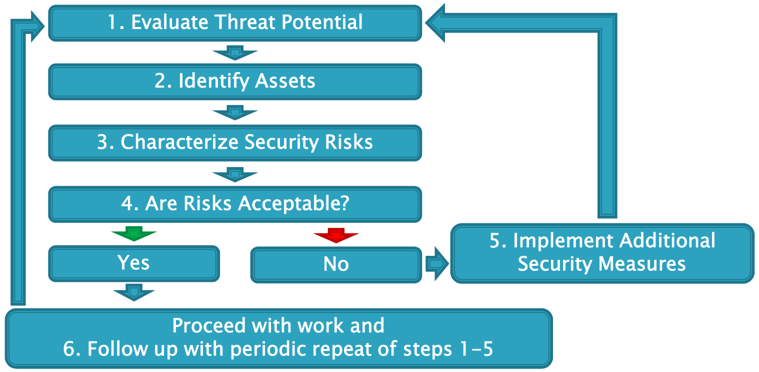
Activity: Chemical Safety Risk Assessment

- Get into three groups
- Identify one job or process that occurs in your laboratory or facility
- Perform a safety risk assessment
- Be prepared to discuss your results with the whole group

Module: Chemical Safety and Security Risk Assessment

- ☑Module Learning Objectives
- ☑Risk Basics
- ☑Chemical Safety Risk Assessment
- **Chemical Security Risk Assessment**
  - **Dual-Use Chemicals**
- Summary, Conclusions, and Evaluations

Chemical Security Risk Assessment: Overview



Chemical Security Risk Assessment

1. **Evaluate threat potential**

- Adversaries
  - Motive
  - Means
  - Opportunity
    - Outsiders — no authorized access
    - Insiders — authorized access
    - Collusion — between Outsiders and Insiders
- Actions
  - Sabotage
  - Theft
- Assets

Chemical Security Risk Assessment

2. **Identify security hazards - Assets**

- Information
- Equipment
- Expertise
- Dual-use materials
  - Need a working inventory
  - Need an understanding of dual-use materials
    - Likelihood and Consequences of malicious use
      - Ease or difficulty
      - Quantity
      - Location
      - How they are used

Chemical Security Risk Assessment

3. Characterize security risks

- Create and analyze scenarios
  - Adversary
  - Action
  - Asset

  - What are the factors affecting the likelihood of a security incident?
    - Do you think the likelihood is low, moderate, or high?

  - What are the factors affecting the consequences of a security incident?
    - Do you think the consequences are low, moderate, or high?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

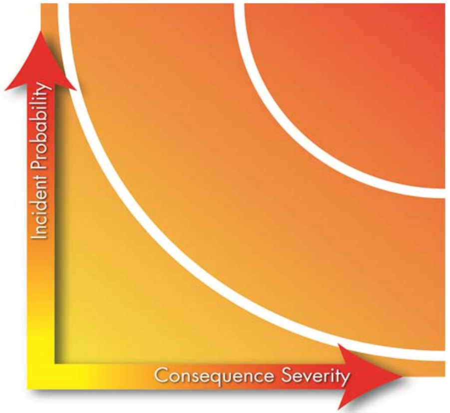
93

Chemical Security Risk Assessment

3. Characterize security risks

On the basis of *likelihood* and *consequence*, are the security risks low, moderate, or high?

Why?



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

94

Chemical Security Risk Assessment

3. Characterize security risks

- Is it possible to analyze, protect against, or even think of every possible scenario?
  - No

- So what should be done?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

95

Chemical Security Risk Assessment

4. Are risks acceptable?

- If you are accountable for the security of the assets, how do you establish an acceptable level of security risk?
  - Are there national security standards?
  - Are there other limits imposed by the institution?
    - If you don't know, how can you find out?
    - What do you do if there are not established limits?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

96

Chemical Security Risk Assessment

5. Implement additional control measures where needed to reduce security risks to acceptable levels

- What controls are needed to reduce the security risks?
  - Administrative
  - Operational
  - Engineering

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

97

Chemical Security Risk Assessment

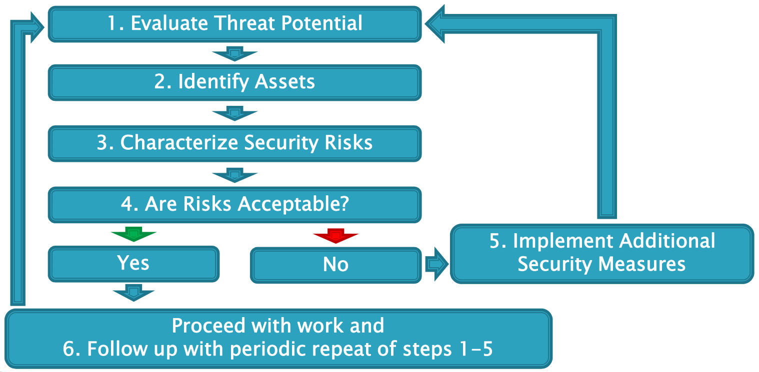
6. **Follow up** with periodic repeat of steps 1-5

- Have scenarios changed?
- Could further improvements be made?
- How often should follow-up assessments be performed?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

98

Chemical Security Risk Assessment: Overview



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

99

Chemical Security Risk Assessment

- Main points
  - Likelihood of a security threat scenario may be higher than you think
    - Of chemical, biological, nuclear, and radiological materials, ***chemicals*** are used maliciously ***the most often***
  - Consequences can range from low to high

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

100

Summary: Chemical Safety and Security Risk Assessment

☑Module Learning Objectives

☑Risk Basics

☑Chemical Safety Risk Assessment

☑Chemical Security Risk Assessment

- **Summary, Conclusions, and Evaluations**

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Conclusions

- Risk is a function of Likelihood and Consequence
  - Applies to both safety and security
- Chemical labs and plants need to be ***safe***, ***secure***, and ***productive***
  - Assessing and characterizing CSS risks allows controls to be applied in a graded manner
    - Larger efforts toward reducing high risks
    - Smaller efforts toward reducing low risks

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Deepwater Horizon Oil Spill

Case Study in Risk Assessment & Risk Management

SAND No. 2011-4999 P
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-AC04-94AL85000.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

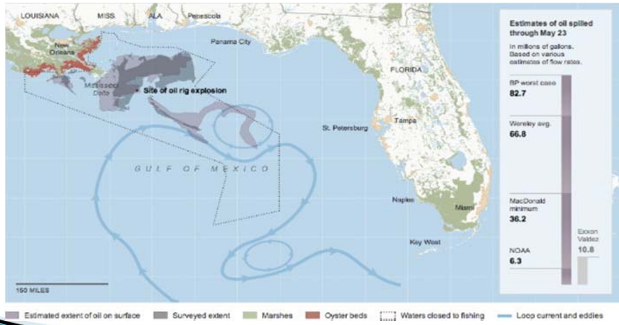
Deepwater Horizon Oil Spill

- Background
- Accident Investigation
- Critical Factors
- Key Findings from the Accident Investigation
- Management of Risks from the Investigation's Recommendations
- Mitigation of Risks
- Discussions

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Background

April 20, 2010 – the Deepwater Horizon, an offshore drilling rig owned by Transocean and under lease to BP, was performing drilling operations in the Gulf of Mexico 77 km (48 miles) off the Louisiana coast.



From the New York Times' Interactive Oil Spill Map, 24 May 2010. Deepwater Horizon Oil Spill.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

105

Background

During the operation a complex series of events permitted hydrocarbons from the well to enter into the wellbore and up into the Deepwater Horizon rig. The presence of hydrocarbons in the rig resulted in a series of explosions and fires in which;

- 11 people lost their lives,
- 17 others were injured,
- the rig burned and sank after 36 hours,
- Hydrocarbons continued to flow from the reservoir for 87 days until it was sealed on July 15, 2010,
- The estimated amount of oil spilled over the 87 days was 4.9 million barrels (780,000 m^3).

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

106

Background

Coast Guard Image of the Deepwater Horizon Oil Rig fire taken Wed 21 Apr 2010 08:20:15 AM EDT

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

107

Background

- *Deepwater Horizon Oil Rig* – a semi-submersible, dynamically positioned, ultra-deep water mobile off-shore drilling platform. It was built by Hyundai Heavy Industries in 2001 for R&B Falcon (which was acquired by Transocean Ltd.). The cost was US $340 million dollars. In 2010 it was insured for US $560 million.[1]
- *BP Plc British Petroleum* – BP is a global company. It is one of the world's leading international companies specializing in oil and gas exploration, and supply. Sales and other operating revenues were $297,107 million in 2010; 79,700 employees and active in 29 countries.[2]
- *Transocean Ltd.* – the world's largest offshore drilling contractor with 18,000 employees. They leased the Deepwater Horizon Oil Rig to BP and operated it.

1) Wikipedia – http://en.wikipedia.org/wiki/Deepwater_Horizon
2) www.bp.com

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

108

Background

- *Halliburton* – one of the world's largest providers of services and products to the oil industry. They have more than 60,000 employees worldwide and operate in 80 countries. They supplied the cement.
- *Cameron International Corp.* – provides flow equipment products, system and services worldwide to oil, gas and process industries. They have 18,000 employees worldwide and operate in more than 300 locations around the world. They designed and built the blow out preventer (BOP).
- *US Coast Guard* – performs annual inspections on US flagged rigs and annual examinations on foreign flagged rigs. For US flagged rigs they focus on safe manning and operation, inspect lifesaving, fire-fighting, hull integrity, vessel stability, occupational health & safety, electrical systems, etc. The flag state of the rig has the primary responsibility of ensuring compliance with international standards. The US can set certain requirements and conditions for foreign flagged rigs.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Accident Investigation

- Following the accident BP put together an investigation team.
- The team consisted of the following specialists:
  - safety, operations, subsea, drilling, well control, cement, modelers specializing in well flow dynamics, blow out preventer system specialists as well as process hazard analysts.
- The team used information from Transocean, Cameron, Halliburton and other companies to compile this report.

There was no one single cause for this accident; rather, a complex and interlinked series of mechanical failures, human judgments, engineering design, operational implementation and team interfaces that came together.[1]

1) BP Report - "Deepwater Horizon Accident Investigation Report", Sep. 8, 2010, p. 11, issued by BP, this document and accompanying appendices can be downloaded from the BP Website, http://www.bp.com/sectiongenericarticle.do?categoryId=9036598&contentId=7067574.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Critical Factors

The following critical factors were responsible for the accident and the aftermath to occur –

- Oil well integrity was not established or failed,
- Hydrocarbons entered the well undetected and well control was lost,
- The hydrocarbons ignited on the Deepwater Horizon Rig,
- The blow out preventer (BOP) malfunctioned and did not seal the well.

1) BP Report - "Deepwater Horizon Accident Investigation Report", Sep. 8, 2010, p. 31, issued by BP, this document and accompanying appendices can be downloaded from the BP Website, http://www.bp.com/sectiongenericarticle.do?categoryId=9036598&contentId=7067574.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Key Findings from the Accident Investigation

- The following key findings were taken from an internal report prepared by BP titled - "Deepwater Horizon Accident Investigation Report", Sep. 8, 2010 issued by BP (192 pages),[1]
- They also prepared a video titled "Deepwater Horizon Investigation". [1]

1) BP Report - "Deepwater Horizon Accident Investigation Report", Sep. 8, 2010 issued by BP, this document and accompanying appendices can be downloaded from the BP Website, http://www.bp.com/sectiongenericarticle.do?categoryId=9036598&contentId=7067574.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

8 Key Findings[1]

- Key Finding #1 – The annulus cement barrier did not isolate the reservoir hydrocarbons.
- Key Finding #2 – Two barriers that should have prevented hydrocarbons from entering the well bore failed (the shoe track and the float collar).
- Key Finding #3 – Personnel accepted a negative pressure test, but in fact well integrity had not actually been established.
- Key Finding #4 – Even though hydrocarbons had made their way into the wellbore the crew did not recognize it. They responded after the hydrocarbons had passed the BOP and into the riser.

1) BP Report - "Deepwater Horizon Accident Investigation Report", Sep. 8, 2010 issued by BP, this document and accompanying appendices can be downloaded from the BP Website, http://www.bp.com/sectiongenericarticle.do?categoryId=9036598&contentId=7067574.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

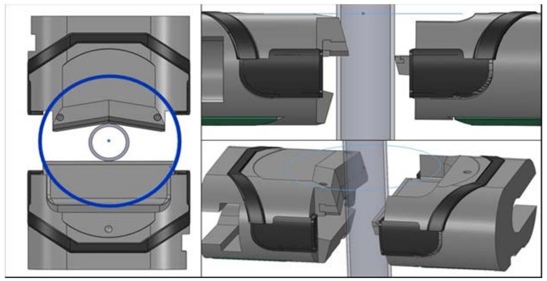
8 Key Findings – continued

- Key Finding #5 – Actions to gain control of the well failed when they did not close the BOP[1] and the diverter. The high pressure fluids should have been diverted overboard rather than into the mud gas separator (MGS).
- Key Finding #6 – By allowing the large quantity of mud and hydrocarbons to go into the MGS the MGS was overwhelmed and the hydrocarbons were vented into the rig. These flammable gases found their way to any number of ignition sources.
- Key Finding #7 – The oil rig as a whole was not electrically classified, only certain sections.
- Key Finding #8 – The BOP emergency mode operation failed to seal the well. There are three methods for operating the BOP during an emergency – all three failed.

1) Cameron Intl. Corp., who supplied the BOP, claimed that the BOP was not designed to operate at the extreme ocean depths where the Deepwater Horizon rig drilling at the Macondo well.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Blind Shear Ram



Source - DET NORSKE VERITAS Final Report for UNITED STATES DEPARTMENTOF THE INTERIOR BUREAU OF OCEAN ENERGY MANAGEMENT, REGULATION, AND ENFORCEMENT WASHINGTON, DC 0240
FORENSIC EXAMINATION OF DEEPWATER HORIZON BLOWOUT PREVENTER CONTRACT AWARD NO. M10PX00335
VOLUME I FINAL REPORT Report No. EP030842 20 March 2011

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Key Findings from the Accident Investigation

- BP's investigation team did not identify any single action or lack of any action that was the cause of the accident.
- They found that the accident was caused by a complex and interlinked series of –
  - Mechanical failures,
  - Human judgments,
  - Engineering design,
  - Operational implementation,
  - Team interfaces.

These factors all allowed the initiation and escalation of the accident.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

BP Investigation Team's Recommendations

From the Investigation Team's 8-Key Findings they outlined a series of recommendations that cover two areas –

1. Drilling and Well Operations Practice (DWOP) and Operating Management System (OMS) implementation
2. Contractor and service provider oversight and assurance

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

117

BP Investigation Team's Recommendations: DWOP & OMS Implementation Recommendations…

- Update, review and clarify Procedures and Engineering Technical Practices
- Strengthen Capability and Competency
  - Reassessing key personnel's roles in the areas of cementing,
  - Ensure adequate coverage of key personnel,
  - Develop programs to build key technical proficiencies,
  - Develop certification processes that include testing and demonstration of skills,
  - Develop advanced deepwater well control training programs,
  - Embed lessons learned from the Deepwater Horizon accident,
  - Request that the International Association of Drilling Contractors, review and consider developing formal certification programs.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

118

BP Investigation Team's Recommendations: DWOP & OMS Implementation Recommendations…

- Audit and Verification
  - Improve the rig audit process across BP-owned and BP-contracted rigs.
- Process Safety Performance Management
  - Establish leading and lagging indicators for the Drilling and Completion process for; well integrity, well control and critical safety equipment on rigs,
  - Require drilling contractors to have auditable integrity monitoring system to asses and improve well control equipment against a set of established standards (leading and lagging indicators).

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

119

BP Investigation Team's Recommendations: Contractor and Service Provider Oversight and Assurance…

- Cementing Services Assurance
  - Conduct an immediate review of the services provided by all cement suppliers and confirm adequate oversight and controls.
    - Cement service supplier should be compliant with BP and Industry Standards,
    - Ensure the competency of the supervisory personnel and engineers,
    - Effectively identify, communicate and be prepared to mitigate risks associated with the provider's services.
- Well control Practices
  - Assess and confirm that essential well control and well monitoring practices are clearly defined and rigorously applied on all BP-owned and BP-contracted offshore rigs.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

120

BP Investigation Team's Recommendations: Contractor and Service Provider Oversight and Assurance…

- Rig Process Safety
  - Require hazard and operability (HAZOP) reviews of the surface gas and drilling fluid systems for all BP-owned and BP-contracted rigs,
  - Include in the HAZOP reviews a study of all surface system hydrocarbon vents and review suitability of location and design.
- Blow Out Preventer Design and Assurance
  - Establish minimum levels of redundancy and reliability for BP's BOP systems,
  - Strengthen BP's minimum requirements for contractors BOP testing, include emergency systems,
    - Demonstrate that their maintenance management systems meet or exceed BP's minimum requirements,

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

BP Investigation Team's Recommendations: Contractor and Service Provider Oversight and Assurance…

Blow Out Preventer Design and Assurance continued…..

- Define BP's minimum requirements for drilling contractors' management of change (MOC) for subsea BOPs,
- Develop a clear plan for remotely operated vehicle (MOV) intervention as part of the emergency BOP operations,
- Require drilling contractors to implement a process to verify that shearing performance capabilities of blind shear rams (BSRs) are compatible with inherent variations of drill pipe inventory.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Important Findings in BP's Report: Risk Assessment

- In section 2.6 – Planning for Temporary Abandonment, page 66.
  - "The BP Macondo well team decided not to run a cement evaluation log prior to temporary abandonment, reportedly reflecting consensus among the various parties on the call. The investigation team has not seen evidence of a documented review and risk assessment with respect to well condition and duration of suspension, regarding the annulus cement barriers."
  - "By not conducting a formal risk assessment of the annulus cement barriers per the *ETP* recommendation, it is the investigation team's view that the BP Macondo well team did not fully conform to the intent of *ETP GP 10-60*.[1] Such a risk assessment might have enabled the BP Macondo well team to identify further mitigation options to address risks such as the possibility of channeling; this may have included running a cement evaluation log."

1) *BP's Engineering Technical Practice, GP 10-60.* Zonal Isolation Requirements.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Some Important Findings in the US Coast Guard's Investigation[1]

- The vessel's dual-command organizational structure impacted the crew's situational awareness, risk assessment and decision making.
- Training scenarios did not prepare the merchant marine officers and industrial drilling crew to function as a team under foreseeable hazards such as a well blowout.
- Failure of the onboard management team to demand that the BOP be maintained in accordance with the manufacture's recommendations.

1) United States Coast Guard – Report of Investigation into the Circumstances Surrounding the Explosion, Fire, Sinking and Loss of Eleven Crew Members Aboard the MOBILE OFFSHORE DRILLING UNIT *DEEPWATER HORIZON* In the GULF OF MEXICO, April 20 – 22, 2010.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Mitigation of Risks

Recall from BP's report that the accident was caused by a complex and interlinked series of –

- Mechanical failures,
- Human judgments,
- Engineering design,
- Operational implementation,
- Team interfaces.

How can these risks be lowered?

Mitigation of Risks

Risk	Mitigation
Mechanical failures	Inspections, strict adherence to servicing schedules, redundancies, follow standard operating procedures
Human judgments	Training, skills evaluations, certifications, build technical proficiencies, develop specialized training programs
Engineering design	Multiple reviews, internal oversight, outside review by experts
Operational implementation	Review operations and procedures and include all stakeholders, perform hazard scenario analyses
Team interfaces	Communication, team training across groups, provide redundancies in key personnel positions

Mitigation of Risks

Mechanical failures

- Routine inspection and a strict adherence to servicing schedules could have insured that the BOP would have functioned properly,
- Redundancies in the BOP (which are now required) could also have increased the chances that the well blowout and subsequent results could have been avoided.

Mitigation of Risks

Human judgments

- Rigorous training both for individuals and teams,
- Skills evaluations can help determine when more training and education is required,
- Certifications help insure that individuals have the skills and knowledge to perform their duties,
- Building technical proficiencies and specialized training programs helps advance the workforce to a higher level.

Mitigation of Risks

- Engineering design
  - Multiple reviews and internal oversight help avoid making critical mistakes,
  - Review by outside experts provides the opportunity for a "fresh set of eyes" to evaluate the design.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Mitigation of Risks

Operational implementation

- Reviewing operations and procedures to include all stakeholders avoids the possibility of miscommunication. This is important when multiple people/teams are working on different aspects of a process to achieve a goal or objective.
- By performing hazard scenario analyses the team(s) will know what to do in the in the event of an emergency or "off normal event" and will be able to implement emergency operation procedures.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Mitigation of Risks

Team interfaces

- Improve communication,
- Team training across groups can insure that operations (both routine and emergency) go according to plan,
- Provide redundancies in key personnel positions to insure coverage.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Discussion

Discuss how organizational structures might increase the risk of accidents.

What are some methods to reduce the risk of mechanical failures?

Comment on team training and emergency preparedness with respect to mitigating and controlling accidents.

What can government regulatory agencies do to help reduce the risk of inherently hazardous operations?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

References

- BP Internal Report, “Deepwater Horizon Accident Investigation Report”, Sep. 8, 2010 issued by BP (192 pages) and appendices.
- United States Coast Guard, “Report of Investigation into the Circumstances Surrounding the Explosion, Fire, Sinking and Loss of Eleven Crew Members Aboard the MOBILE OFFSHORE DRILLING UNIT *DEEPWATER HORIZON* In the GULF OF MEXICO”, April 20 – 22, 2010 (288 pages).
- Sutherland Asbill & Brennan LLP, “RESPONSE TO COAST GUARD DRAFT REPORT BY TRANSOCEAN OFFSHORE DEEPWATER DRILLING INC. AND TRANSOCEAN HOLDINGS LLC”, June 8, 2011 (112 pages).
- Rawle O. King, Congressional Research Service Report, “Deepwater Horizon Oil Spill Disaster: Risk Recovery, and Insurance Implications”, July 12, 2010 (24 pages).
- Final Report for US Dept. of the Interior Bureau of Ocean Energy and Management, Regulation, and Enforcement, by Det Norske Veritas, Washington, DC 0240; Forensic Examination of Deepwater Horizon Blowout Preventer, Contract Award No. M10PX00335 VOLUME I FINAL REPORT, Report No. EP030842 20 March 2011 (200 pages).

Lunch

International Risk Management Systems
Standards & Approaches

SAND No. 2011-7069C
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

Overview of Presentation

- Definitions
- Purpose
- Safety Concepts
- Standards
  - BS 8800
  - OHSAS 18001
  - ILO-OSH 2001
- Approaches
  - SAICM

Definitions

- Safety: "The state in which the possibility of harm to persons or of property damage is reduced to, and maintained at or below, an acceptable level through a continuing process of hazard identification and *safety risk management*. " (U.S. Federal Aviation Administration, 2009)
- A Safety Management System (SMS) is a *systematic way* to identify hazards and control risks while maintaining assurance that these risks are effective.
  - Provides for goal setting, planning, and measuring performance
  - SMS is a business imperative: ethical, legal and financial reasons for establishing a SMS (ICAO, 2009)

Reference: International Civil Aviation Organization (ICAO), Safety Management Manual, 2009; U.S. Federal Aviation Administration, System Approach for Safety Oversight, 2009

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

137

Purpose

- Ever-increasing pace of worldwide trade and economies
- Increase in occupational accidents and diseases
  - Over 1.2 million workers are killed due to work-related accidents and diseases annually
  - ~250 million occupational accidents annually
  - ~160 million work-related diseases annually
- The economic loss is estimated to be 4% of the world gross national product

Reference: International Labour Organisation, 2001

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

138

Safety Concepts

- Freedom from hazards
- Zero accidents or incidents?
- Instill safety culture towards unsafe acts and conditions
- Error avoidance
- Regulatory compliance

Reference: International Civil Aviation Organization, Safety Management Manual, 2009

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

139

Safety Concepts

- Traditional approach – prevent accidents
  - Focus is on outcomes (causes)
  - Focus is on unsafe acts by operational personnel
  - Assign blame/punish for failure to "perform safely"
  - Address identified safety concerns exclusively
- Traditional approach: WHAT? WHO? WHEN, but NOT: WHY? HOW?

Reference: International Civil Aviation Organization, Safety Management Manual, 2009

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

140

Evolution of Safety Concepts

Change in approach to incident causation:

- 1950s to 1970
  - Technical factors
- 1970s to 1990s
  - Human factors
- 1990s to present time
  - Organizational factors

Reference: International Civil Aviation Organization, Safety Management Manual, 2009

Safety Management Standards BS (British Standard) 8800

BS (British Standard) 8800 (1996)

- A guide to occupational health & safety management systems
  - Emphasizes good working practices to prevent accidents and ill health
  - Goal is to improve business performance and responsible image
  - Assists in continuous improvement beyond regulatory compliance

Safety Management Standards BS (British Standard) 8800

- Last edition: July 2004
- New and improved annexes cover:
  - Hazardous event investigation
  - Risk assessment and control
  - Integration with other quality and environmental management systems into an overall management system

Safety Management Standards OHSAS 18000

- OHSAS 18000 system specification comprises both OHSAS 18001 and OHSAS 18002.
- Created by leading national standards bodies, certification bodies, and specialist consultancies
- Intent—to remove confusion from the proliferation of certifiable occupational health & safety (OHS) specifications
- OHSAS publishes *The Essential Health and Safety Manual* for purchase.
- Emphasis is on policy and procedures

Safety Management Standards OHSAS 18001

Requirements:

- Identify occupational health and safety (OHS) hazards
- Assess the risks associated with OHS hazards
- Determine the controls necessary to reduce OHS risks to acceptable levels
- Proactive versus reactive approach to safety and health hazards

145

OHSAS 18001 Relationships to ISO

- OHSAS 18001 developed to be compatible with ISO 9001 and ISO 14001
- Facilitates the integration of quality, environmental, and OHS management systems
  - Document and data control
  - Auditing
  - Process controls
  - Record controls
  - Training
  - Corrective and preventive actions

146

OHSAS 18001 Elements

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

147

OHSAS 18001 Elements

- ***Employee Awareness***
  - Importance of conforming to OHS management system
  - Health & safety 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.

Employee involvement is KEY.

148

OHSAS 18001 Elements

Document Control

- Document procedures established and maintained
- Can be readily located
- Legible, identifiable and traceable
- 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

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

149

OHSAS 18001 Elements

Records and Reviews

- Compliance records
- Training records
- Accident Information
- Inspection, maintenance and calibration records
- Contractor and supplier information
- Incident reports
- Hazard analyses
- Audit results
- Management review records

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

150

OHSAS 18001 Elements

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

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

151

OHSAS 18001 Elements

Audit Program

- 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

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

152

OHSAS 18001 Elements

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

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

15
3

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.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

15
4

OHSAS 18001 Certification

Developing a program can be done with or without consultation:

- Without consultants:
  - Literature can be purchased to help guide through the process of designing and implementing the program.
- With consultants
  - Some consultants perform initial set-up, through development and implementation and certification.
  - Other consultants offer preliminary audits to diagnose implementation problems, and perform audits post-certification to monitor progress.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

15
5

International Labour Organisation (ILO)

OSH2001 Guidelines on Occupational Safety and Health Management Systems

- Voluntary guidelines
- Do not require certification
- Basic Components
  - Safety Management Policy
  - Organization
  - Planning and Implementation
  - Evaluation
  - Action for Improvement

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

15
6

ILO: OSH 2001

- Policy statement- state requirements in terms of resources, management commitment, and define OSH targets
- Organizing – describe organizational structure, responsibilities and accountabilities
- Planning and Implementation – define regulations and standards that are applicable and how they will be implemented
- Evaluation – define how OSH performance measured and assessed
- Continuous improvement processes described

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

157

Strategic Approach to International Chemical Management (SAICM)

- Adopted by the International Conference on Chemicals Management (ICCM), 2006
- Policy framework to foster safe management of chemicals
- Multi-sectoral, multi-stakeholder
- Goal: ensure that by 2020, chemicals are produced and used in ways that minimize the significant adverse impacts on the environment and human health (ICCM, 2006)

http://www.saicm.org/index.php?ql=h&content=home

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

158

Strategic Approach to International Chemical Management (SAICM)

Quick Start Programme:

- A voluntary, time-limited trust fund for developing countries, and economies in transition
- Priorities:
  - Development or updating of national chemical profiles
  - Identify capacity needs for sound chemicals management
  - Development and strengthening of national chemicals management institutions, plans, programmes and activities
  - Enable SAICM by integrating the sound management of chemicals in national strategies

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

159

Why Implement Safety Management Standards?

- Safety of workers
- Quality of product
- Increased efficiency
- Business image

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

160

Integrated Management Systems

- Integrated management systems combine quality, environmental *and* OHS management systems
- Integration may vary from:
  - Increasing compatibility of system elements, to
  - Embedding an integrated management system (IMS) in a culture of learning and continuous improvements
- Some national integrated management standards are being developed (ISO (2008). Integrated Use of Management System Standards).
- For business sustainability an IMS needs to include the entire product chain and all stakeholders
- Jorgensen, et al. (2006). *Integrated management systems – three different levels of integration*. Journal of Cleaner Production, 14(8), 713-722.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

161

Summary of Presentation

- Defined safety & safety management system
- Purpose of safety management systems
- Discussed safety concepts
- Described three safety management standards
  - BS 8800
  - OHSAS 18001
  - ILO-OSH 2001
- Described SAICM approach
- Described integrated management systems

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

162

Process Hazards, Incidents and Mitigation Strategies – I

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Key acronyms

PSM = *process safety management*

SDS = *safety data sheet*

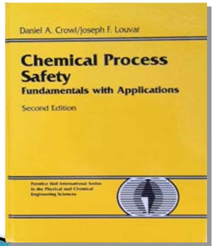
RAGAGEPs = *recognized and generally accepted good engineering practices*

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

164

Process Safety Resources

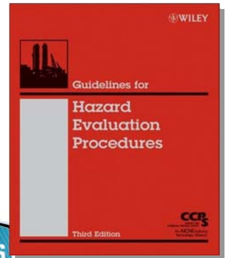
D.A. Crowl and J.F. Louvar 2001.
Chemical Process Safety: Fundamentals with Applications, 2nd Ed., Upper Saddle River, NJ: Prentice Hall.



Chapter
2 • Toxicology
4 • Source Models
5 • Toxic Release and Dispersion Models
6 • Fires and Explosions
10 • Hazards Identification

Process Safety Resources

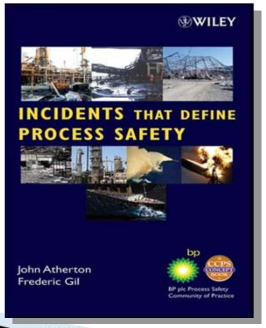
CCPS 2008a. Center for Chemical Process Safety, *Guidelines for Hazard Evaluation Procedures, Third Edition*, NY: American Institute of Chemical Engineers.



Chapter 3 • Hazard Identification Methods
3.1 Analyzing Material Properties and Process Conditions
3.2 Using Experience
3.3 Developing Interaction Matrixes
3.4 Hazard Identification Results
3.5 Using Hazard Evaluation Techniques to Identify Hazards
3.6 Initial Assessment of Worst-Case Consequences
3.7 Hazard Reduction Approaches and Inherent Safety Reviews

Process Safety Resources

CCPS 2008b. Center for Chemical Process Safety, *Incidents that Define Process Safety*, NY: American Institute of Chemical Engineers.



Process Safety Overview

1. What is *process safety*?
2. Opposite of process safety: Major incidents
3. The anatomy of process safety incidents
4. Overview of process safety strategies
5. Taking advantage of past experience
6. Defense in depth / layers of protection
7. Elements of process safety management

Process Safety Overview

1. What is *process safety*?

Process safety is ….

is the absence of loss and harm resulting from fires, explosions and hazardous material releases at process facilities.

(Event-focused definition)

Process safety is …

is the absence of loss and harm at process facilities by:

(a) identifying process hazards,

(b) containing and controlling them,

(c) countering abnormal situations with effective safeguards.

(Activity-focused definition)

Process Safety Overview

1. What is *process safety*?
2. Opposite of process safety: Major incidents

Major process incidents

Flixborough, UK (June 1974)

- Partial oxidation of cyclohexane
- Catastrophic failure of temporary 50cm diameter piping
- 40 tonnes of hot cyclohexane released in 30 s
- Vapor cloud explosion
- 28 fatalities, 53 injuries; 1800+ houses damaged; plant destroyed
- 18 of those fatally injured were in control room
- Hastened passage of UK "Health and Safety at Work Act"

See CCPS 2008b for details of these incidents

Major process incidents

Seveso, Italy (July 1976)

- Runaway reaction
- 2 kg of dioxin release from relief system
- Over 17 km^2 affected
- Locally grown food banned for several months
- Several inches of topsoil removed, incinerated
- 80,000 animals died or slaughtered
- Plant shut down and destroyed
- EU "Seveso Directive" prompted

Major process incidents

Mexico City, Mexico (November 1984)

- Large LPG / fuels storage facility
- Fires, vessel ruptures, boiling-liquid-expanding-vapor explosions (BLEVEs)
- Initiating cause unknown
- 600 fatalities, 7000 injuries
- Horizontal tanks rocketed as far as 1200 m away
- Fixed fire protection destroyed by blasts
- Fuels terminal destroyed

Major process incidents

Bhopal, India (December 1984)

- Pesticide production facility
- Water introduced into methyl isocyanate storage
- MIC toxic vapor release from vent system
- 2000 to 3000 early fatalities; ~200,000 injuries
- Plant shut down; Union Carbide eventually sold
- Seveso II, EPA Risk Management Program prompted

Major process incidents

Toulouse, France (September 2001)

- Ammonium nitrate storage at fertilizer plant
- Explosive decomposition initiated; cause unknown
- Equivalent blast energy 20-40 tons of TNT
- 30 fatalities; 2500+ injuries; US$ 2 billion in losses

Major process incidents

Texas City, Texas (March 2005)

- Refinery isomerization unit
- One valve not opened during unit re-start
- Release of hot flammable material from blowdown
- Ignition and vapor cloud explosion
- 15 fatalities, 170+ injuries; BP losses and impacts

Photo credit: U.S. Chemical Safety & Hazard Investigation Board

Major process incidents

Buncefield, UK (December 2005)

- Petrol (gasoline) tank farm
- Storage tank overflow
- Ignition, vapor cloud explosion and fires
- 40+ injuries; 20+ tanks destroyed
- Consequences could have been much worse

See www.buncefieldinvestigation.gov.uk/index.htm for details

DISCUSSION

When "major chemical incidents" is mentioned, what come first to your mind?

-
-
-
-
-

Process Safety Overview

1. What is *process safety*?
2. Opposite of process safety: Major incidents
3. **The anatomy of process safety incidents**

Process safety incident anatomy

Preface:

This presentation is adapted from course materials and from presentations used for several years for process safety lectures at the University of Cincinnati and The Ohio State University, with updates to reflect terminology used in the Third Edition of *Guidelines for Hazard Evaluation Procedures* (CCPS 2008a).

Incident – Definition

Incident:

An unplanned event or sequence of events that either resulted in, or had the potential to result in, adverse impacts.

Process industry incidents

- Fires
- Explosions
- Toxic Releases

- Fatalities
- Injuries
- Environ. Damage
- Property Damage
- Evacuations
- Business Losses
- Plant Closings
- Fines, Lawsuits

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

185

Process industry incidents

Loss Events

- Fatalities
- Injuries
- Environ. Damage
- Property Damage
- Evacuations
- Business Losses
- Plant Closings
- Fines, Lawsuits

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

186

Process industry incidents

Loss Events

Impacts

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

187

Key definition

Loss event:

Point in time in an abnormal situation when an irreversible physical event occurs that has the potential for loss and harm impacts.

– CCPS 2008a Glossary

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

188

Key definition

Loss event:

Point in time in an abnormal situation when an irreversible physical event occurs that has the potential for loss and harm impacts.

– CCPS 2008a Glossary

Examples:

- Hazardous material release
- Flammable vapor or dust cloud ignition
- Tank or vessel overpressurization rupture

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Key questions

- Why do loss events happen?
- How do loss events happen?
- What must be done to avoid them?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

WHY do loss events happen?

- We choose to handle dangerous process materials and energies
  - To make a living
  - To provide society with desirable products
- As long as we choose to handle them, a potential for loss events exists

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Analogy

- We choose to handle dangerous animals at the Zoo
  - To make a living
  - To provide society with desirable experiences
- As long as we choose to handle them, a potential for loss events exists
  - Things can be done to reduce their likelihood and severity to negligible or tolerable levels

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Process safety

is the absence of loss and harm at process facilities by:

(a) **identifying process hazards**,

(b) containing and controlling them,

(c) countering abnormal situations with effective safeguards.

Process hazard – Definition

Presence of a stored or connected material or energy with inherent characteristics having the potential for causing loss or harm.

3 types of process hazards

- Material hazards
- Energy hazards
- Chemical interaction hazards

3 types of process hazards

- **Material hazard**: A contained or connected process material with one or more hazardous characteristics
- Energy hazard
- Chemical interaction hazard

Inherent characteristics

Presence of a stored or connected material or energy with <u>inherent characteristics</u> having the potential for causing loss or harm.

Material hazards

<u>Inherently hazardous characteristics</u>:

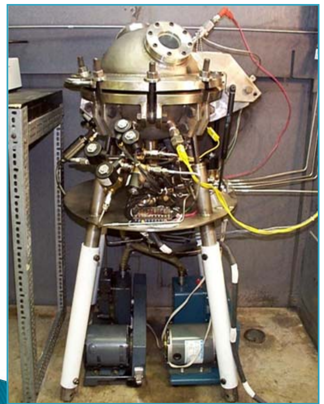
 Flammability

 Instability

 Toxicity

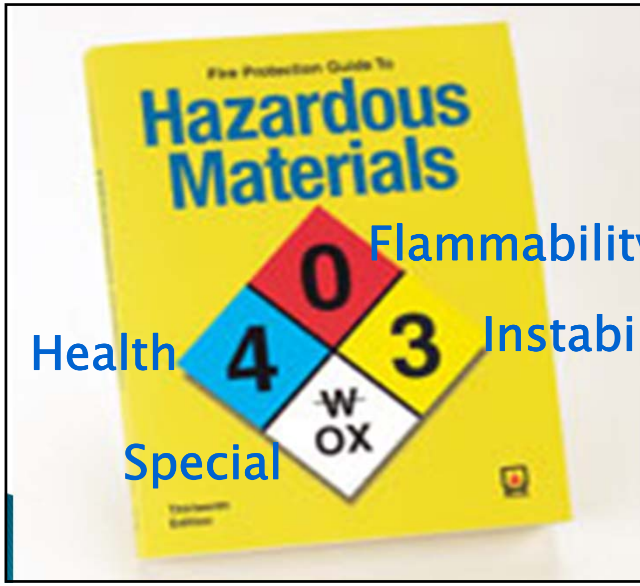
 Corrosivity

E.g., Flammable materials



Inherent characteristics:

- Flash point (volatility)
- Heat of combustion
- Ease of ignition
  - Flammability limits
  - Minimum ignition energy
  - Autoignition temperature



NFPA 704

Summary of material hazards for emergency response

Safety Data Sheets

"SDSs"

- More complete summary of hazards
- Required to be accessible in workplace
- All hazardous materials on-site
- Available from suppliers, internet sources
- Give only basic chemical reactivity info
- Often inconsistent from source to source

Limitations

NFPA 704 diamonds and SDSs only give properties of individual hazardous materials.

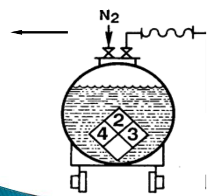
- Hazardous energies not identified
- Some hazardous chemical interactions not identified
- Connected hazards may not be identified

3 types of process hazards

- Material hazard
- Energy hazard: Some form of physical energy contained within or connected to the process with the potential for loss or harm
- Chemical interaction hazard

Process hazard

Presence of a
stored or connected
material or energy with
inherent characteristics
having the potential for
causing loss or harm.



Forms of energy with injury potential

Electrical (voltage, capacitance)	**Chemical** – Health Haz (NFPA 2 to 4)
Mechanical (spring, machine parts)	**Chemical** – Flammable (NFPA 3 to 4)
Kinetic (moving or rotating mass)	**Chemical** – Combustible(NFPA 2 to 4)
Positional (elevated part or equipment)	**Chemical** – Reactive (NFPA 2 to 4)
Hydraulic (liquid under pressure)	**Thermal** – Hot material (steam, hot oil)
Pnematic (gas/vapor under pressure)	**Thermal** – Cryogenic Fluid (liquid N2)

LOCKOUT/TAGOUT ENERGY CONTROL PROCEDURE Page 1 of 1

Drawing No. X-100-101
Equipment Name Methanol Flowmeter
Location Bldg 1, Inside dike wall

Form of Energy with Injury Potential (examples)	Connected Energy Source and Magnitude	Residual and/or Stored Energy?
Electrical (voltage, capacitance)		
Mechanical (spring, machine parts)		
Kinetic (moving or rotating mass)		
Positional (elevated part or equipment)		
Hydraulic (liquid under pressure)	MeOH pump discharge, 3 bar g	
Pneumatic (gas/vapor under pressure)		
Chemical–Health Hazard (NFPA 2 to 4)	MeOH, up to 10,000 liters	Yes
Chemical–Flammables (NFPA 3 or 4)	MeOH, up to 10,000 liters	Yes
Chemical–Combustibles (NFPA 2)		
Chemical–Reactive (NFPA 2 to 4)		
Thermal–Hot Material (steam, hot oil)		
Thermal–Cryogenic Fluid (liquid N_2)		

ISOLATE CONNECTED ENERGY SOURCES
Energy Isolating Device #1 Ball Valve
Location Between MeOH transfer pump and flowmeter
Use of Device Close valve
LOTO Lockout and tagout **Initials**________

LOCKOUT/TAGOUT ENERGY CONTROL PROCEDURE Page 1 of 1

Drawing No. X-100-101
Equipment Name Methanol Flowmeter
Location Bldg 1, Inside dike wall

...

ISOLATE CONNECTED ENERGY SOURCES
Energy Isolating Device #1 Ball Valve
Location Between MeOH transfer pump and flowmeter
Use of Device Close valve
LOTO Lockout and tagout **Initials**________

...

BLEED OFF RESIDUAL OR STORED ENERGIES

Bleed-Off Procedure:
Drain residual flammable liquid into grounded catch pan.
Initials________

VERIFY ISOLATION AND DEENERGIZATION

Verification Procedure:
Visually check for pockets of flammable liquid while disassembling.
Initials________

3 types of process hazards

- Material hazard
- Energy hazard
- **Chemical interaction hazard:** Presence of materials with the potential for loss or harm upon their interaction in an unintentional or uncontrolled manner

Reactive interactions

Example Compatibility Chart for an Acetic Anhydride Handling Facility

Will These Two Materials React?	Acetic Acid	Acetic Anhydride	Cooling Water	Sulfuric Acid	50% Caustic	Lube Oil	Cleaning Solution
Acetic Acid							
Acetic Anhydride	*Reactive*						
Cooling Water	*Not reactive*	*Reactive*					
Concentrated Sulfuric Acid	*Reactive*	*Reactive*	*Reactive*				
50% Caustic	*Reactive*	*Reactive*	*Reactive*	*Reactive*			
Lube Oil	*Not reactive*	*Not reactive*	*Not reactive*	*Reactive*	*Reactive*		
Cleaning Solution	*Find out what the cleaning solution contains, then determine reactions*						

From CCPS 2001

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

209

Process hazard

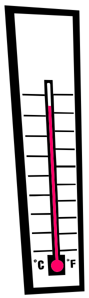
Presence of a
stored or connected
material or energy with
inherent characteristics
having the potential for
causing loss or harm.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

210

Degree of hazard

- More hazardous material
  → *greater degree of hazard*
- Farther from zero energy state
  → *greater degree of hazard*



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

211

EXERCISE

Which has more available energy?

1 t heptane at 98 ºC

or

2 t heptane at 20 ºC (ambient temperature)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

212

EXERCISE

1 t heptane, 98 ºC

Chemical energy = 44,600 MJ
Thermal energy = 200 MJ
Total = 44,800 MJ

2 t heptane, ambient temperature

Chemical energy = 89,200 MJ
Thermal energy = 0 MJ
Total = 89,200 MJ

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

213

Energy and its Zero energy state

Energy	Zero Energy State
Electrical (voltage, capacitance)	0 volts
Mechanical (spring, machine parts)	Sprung
Kinetic (moving or rotating mass)	At rest
Positional (elevated part or equipment)	Ground level
Hydraulic (liquid under pressure)	0 bar gauge
Pneumatic (gas/vapor under pressure)	0 barg, 0m3
Chemical–Health Hazard (NFPA 2 to 4)	Nontoxic
Chemical–Flammables (NFPA 3 or 4)	Nonflammable
Chemical–Combustibles (NFPA 2)	Nonflammable
Chemical–Reactive (NFPA 2 to 4)	Nonreactive
Thermal–Hot Material (steam, hot oil)	Ambient
Thermal–Cryogenic Fluid (liquid N_2)	Ambient

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

214

Break

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

215

Process Hazards, Incidents and Mitigation Strategies, continued

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Key questions

- Why do loss events happen?
- How do loss events happen?
- What must be done to avoid them?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

217

HOW do loss events happen?

- Anatomy of an incident
- Unsafe act & condition precursors

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

218

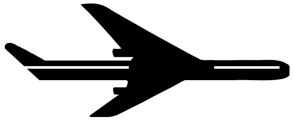
Incident sequence: *Hazard*

- *(Hazard)*
  - *Cause*
    - *Deviation*
      - *Loss event*
        - *Impacts*

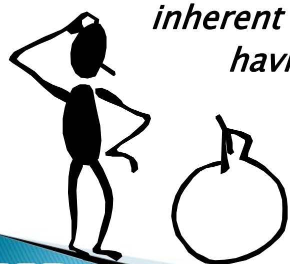
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

219

Process hazard



***Presence** of a*
stored or connected
material or energy with
inherent characteristics
having the potential for
causing loss or harm.



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

220

Normal operation

During normal operation, all hazards are contained and controlled…

Normal operation

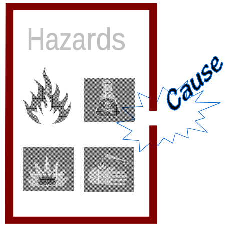
During normal operation, all hazards are contained and controlled, *but they are still present*.

Incident sequence: *Cause*

- *(Hazard)*
  - ***Cause***
    - *Deviation*
      - *Loss event*
        - *Impacts*

Initiating cause

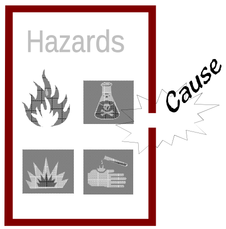
Every incident starts with an *initiating cause* *(also called an initiating event or just a "cause".*



Example initiating causes:
- Feed pump fails off
- Procedural step omitted
- Truck runs into process piping
- Wrong raw material is received
- Extreme low ambient temperature

Initiating cause

Once an *initiating cause* occurs, normal operation cannot continue without a process or operational response.

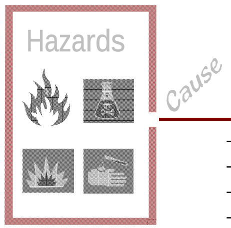


Incident sequence: *Deviation*

- *(Hazard)*
  - *Cause*
    - ***Deviation***
      - *Loss event*
        - *Impacts*

Deviation

The immediate result of an initiating cause is a ***deviation.***



Deviation

- No Flow
- Low Temperature
- High Pressure
- Less Material Added
- Excess Impurities
- Transfer to Wrong Tank
- Loss of Containment
- etc.

Abnormal situations

- Most engineering focuses on designing a process to *work:* (normal situation)
- We must also consider how a process can *fail,* starting with an "abnormal situation"

Deviation

A *deviation* is an abnormal situation, outside defined design or operational parameters.

Hazards

Cause

Deviation

- No Flow
- Low Temperature
- **High Pressure** *(exceed upper limit of normal range)*
- Less Material Added
- Excess Impurities
- Transfer to Wrong Tank
- Loss of Containment
- etc.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

229

Incident sequence: *Loss event*

- *(Hazard)*
  - *Cause*
    - *Deviation*
      - ***Loss event***
        - *Impacts*

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

230

Loss event

A *loss event* will result if a deviation continues uncorrected and the process is not shut down.

Hazards

Cause

Deviation

Loss Event

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

231

Loss event

Loss events are generally irreversible process material/energy releases.

Hazards

Cause

Deviation

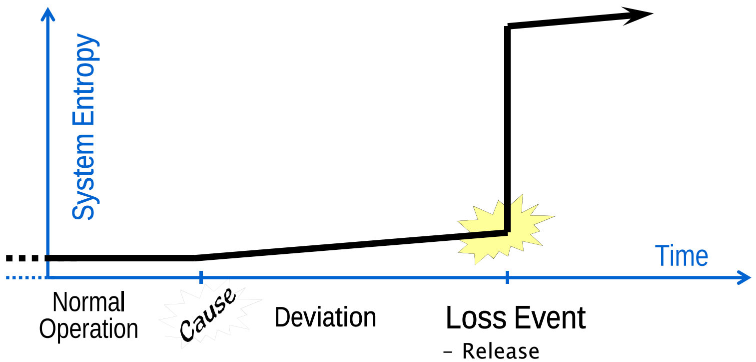
Loss Event

- Release
- Fire
- Explosion

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

232

Loss event: Step change in system entropy

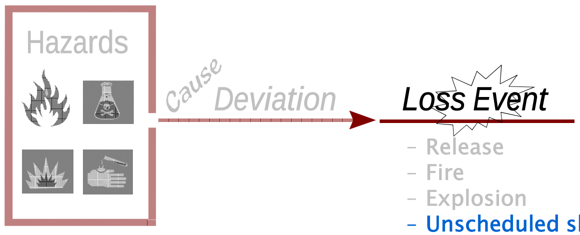


Loss Event
- Release
- Fire
- Explosion

233

Loss event

Loss events may also be related to production or equipment failures.



- Release
- Fire
- Explosion
- Unscheduled shutdown
- Ruined batch
- Compressor failure

234

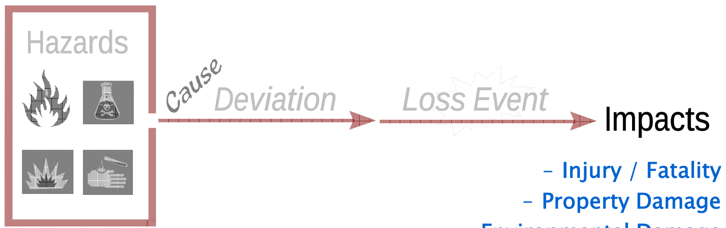
Incident sequence: *Impacts*

- *(Hazard)*
  - *Cause*
    - *Deviation*
      - *Loss event*
        - ***Impacts***

235

Impacts

Impacts are the losses and injuries that can result from a loss event.

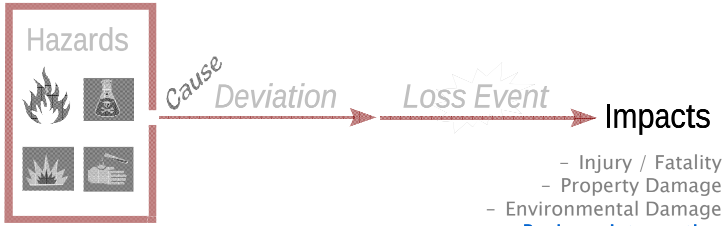


- Injury / Fatality
- Property Damage
- Environmental Damage

236

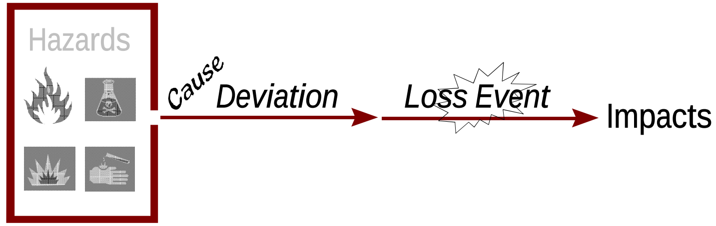
Impacts

There are often other, less tangible impacts as well.



- Injury / Fatality
- Property Damage
- Environmental Damage
- **Business Interruption**
- **Market Share Loss**
- **Reputation Damage**

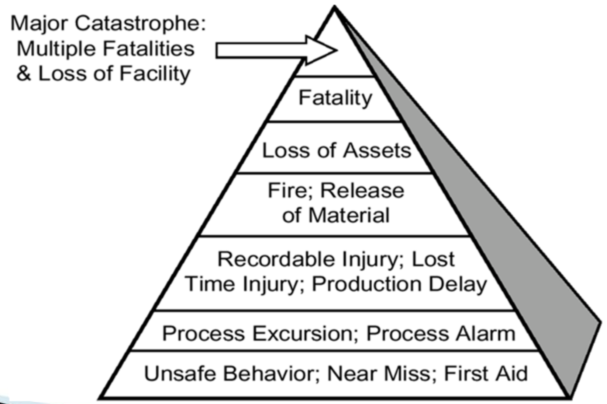
Incident sequence without safeguards



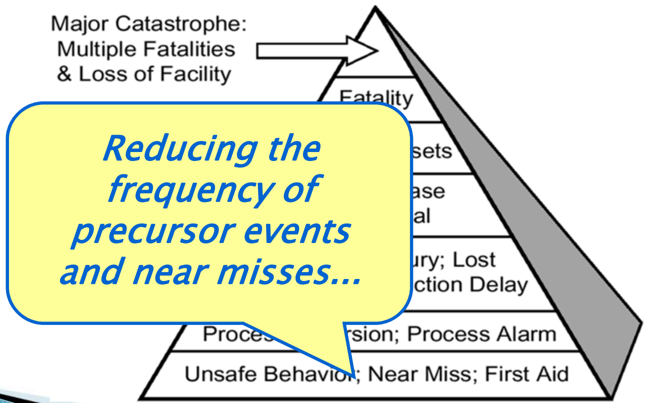
HOW do loss events occur?

- Anatomy of an Incident
- Unsafe act & condition precursors

Unsafe act & condition precursors



Pyramid principle of safety



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Pyramid principle of safety

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Key questions

- Why do loss events happen?
- How do loss events happen?
- What must be done to avoid loss events?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Process Safety Overview

1. What is *process safety*?
2. Opposite of process safety: Major incidents
3. The anatomy of process safety incidents
4. Overview of process safety strategies
5. Taking advantage of past experience
6. Defense in depth / layers of protection
7. Elements of process safety management

What must be done (items 4–7)

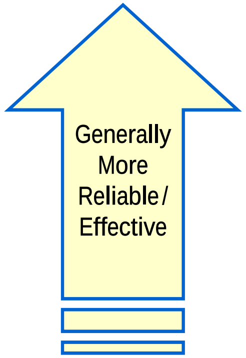
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Process Safety Overview

1. What is *process safety*?
2. Opposite of process safety: Major incidents
3. The anatomy of process safety incidents
4. Overview of process safety strategies

Process safety strategies

- Inherent – Hazard reduction
- Passive – Process or equipment design features that reduce risk without active functioning of any device
- Active – Engineering controls
- Procedural – Administrative controls



Process Safety Overview

1. What is *process safety*?
2. Opposite of process safety: Major incidents
3. The anatomy of process safety incidents
4. Overview of process safety strategies
5. Taking advantage of past experience

Using past experience

"Those who cannot remember the past are condemned to repeat it." *– George Santayana*

Learning from past (usually bad) experiences have been embodied in various forms:

- Regulations
- Codes
- Industry standards
- Company standards
- "Best practices"
- Handbooks
- Guidelines
- Procedures
- Checklists
- Supplier Recommendations

Using past experience

- One term commonly used for non-regulatory codes and standards is "RAGAGEPs"
- From U.S. OSHA's Process Safety Management Standard (Process Safety Information element):
  - 29 CFR 1910.119(d)(3)(ii) The employer shall document that equipment complies with recognized and generally accepted good engineering practices.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

249

Using past experience

- One term commonly used for non-regulatory codes and standards is "RAGAGEPs"
- From U.S. OSHA's Process Safety Management Standard (Process Safety Information element)
- Example: International consensus standard IEC 61511 [ANSI/ISA-84.00.01 (IEC 61511 Mod)], "Functional Safety: Safety Instrumented Systems for the Process Industry Sector"

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

250

RAGAGEPs

Recognized and Generally Accepted Good Engineering Practices

- Take advantage of wealth of experience
- Pass on accumulated knowledge
- Reduce recurrence of past incidents
- Enable uniformity of expectations
- Reduce liabilities when followed

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

251

Example: Anhydrous ammonia

- Regulatory requirements:
  E.g., U.S. OSHA Standard 29 CFR 1910.111, "Storage and Handling of Anhydrous Ammonia"
- Industry standards
  - CGA G-2, "Anhydrous Ammonia"
  - ANSI/CGA K61.1, "American National Standard Safety Requirements for the Storage and Handling of Anhydrous Ammonia"
- Other standards apply to specific applications, e.g., EN 378 for ammonia refrigeration

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

252

RAGAGEPs Alphabet Soup

- IEC
- NFPA
- ASME
- ISA
- UL
- FM
- CGA
- BS
- DIN
- ASHRAE
- IIAR
- ASTM
- API
- AIChE/CCPS
- IRI
- Chlorine Institute
- SOCMA
- etc.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

253

DISCUSSION

With what RAGAGEPs are you most familiar?

-
-
-
-
-

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

254

Process Safety Overview

1. What is *process safety*?
2. Opposite of process safety: Major incidents
3. The anatomy of process safety incidents
4. Overview of process safety strategies
5. Taking advantage of past experience
6. Defense in depth / layers of protection

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

255

Layers of protection

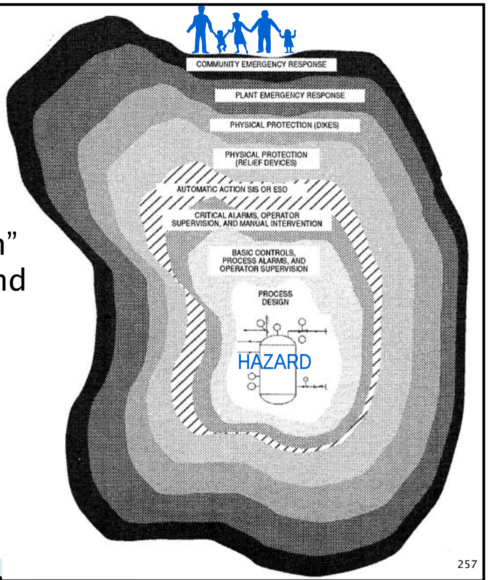
- Also called "Safety layers"
- Multiple layers may be needed, since no protection is 100% reliable
- Each layer must be designed to be effective
- Each layer must be maintained to be effective
- Some layers of protection are ***contain and control measures***
- Other layers of protection are ***safeguards***

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

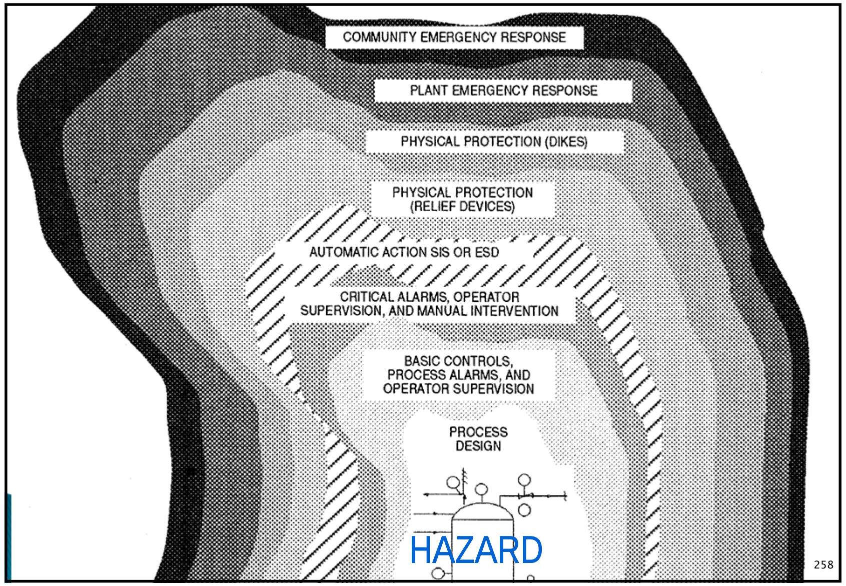
256

“Layers of protection” between hazards and receptors =

“Defense in depth”



257



258

Layers of protection

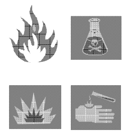
- Also called “Safety Layers”
- Multiple layers may be needed, since no protection is 100% reliable
- Each layer must be designed to be effective
- Each layer must be maintained to be effective
- Some layers of protection are ***contain and control measures***
- Other layers of protection are ***safeguards***

259

Contain & control

Contain & Control

Hazards



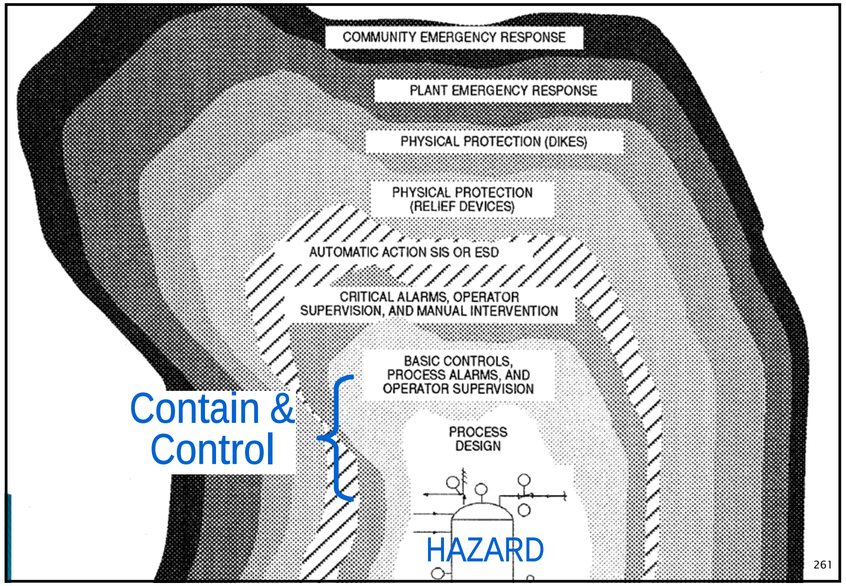
Operational Mode: Normal operation

Objective: Maintain normal operation; keep hazards contained and controlled

Examples of ***contain & control*** measures:

- Basic process control system
- Inspections, tests, maintenance
- Operator training
  - How to conduct a procedure or operate a process correctly and consistently
  - How to keep process within established limits
- Guards, barriers against external forces
- Management of change

260



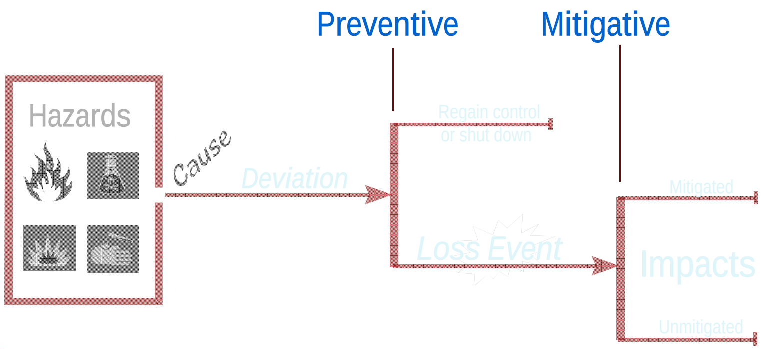
Key definition

Safeguard:

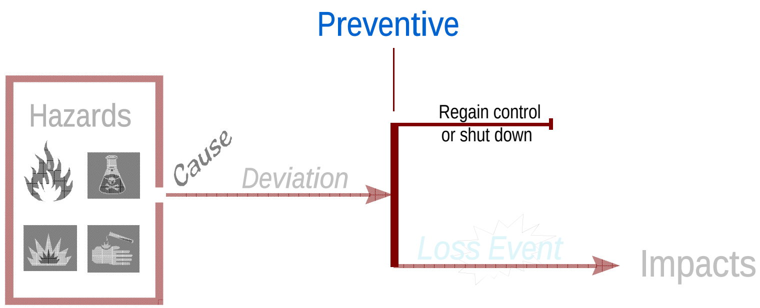
Any device, system, or action that would likely interrupt the chain of events following an initiating cause or that would mitigate loss event impacts.

– CCPS 2008a Glossary

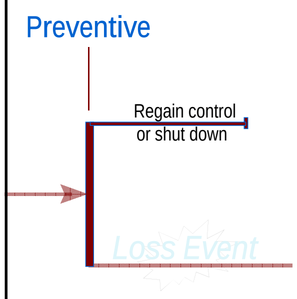
Two types of safeguards



Preventive safeguards



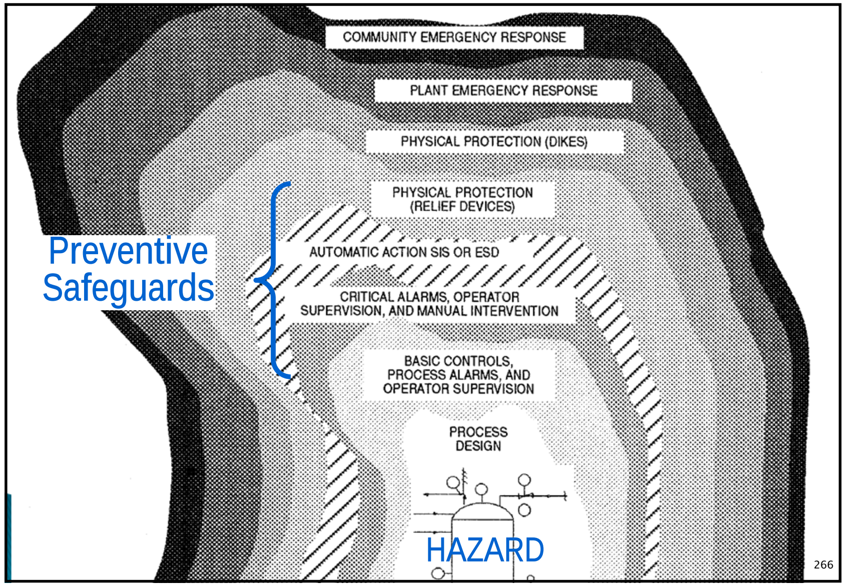
Preventive safeguards



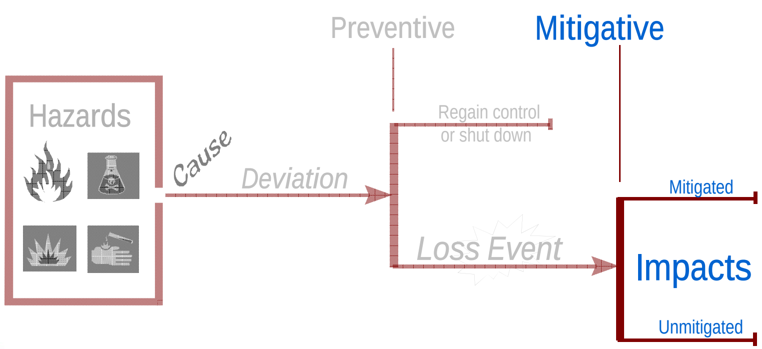
Operational Mode: Abnormal operation

Objective: Regain control or shut down; keep loss events from happening

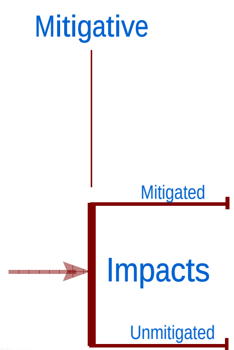
Examples of Preventive Safeguards:
- Operator response to alarm
- Safety Instrumented System
- Hardwired interlock
- Last-resort dump, quench, blowdown
- Emergency relief system



Mitigative safeguards



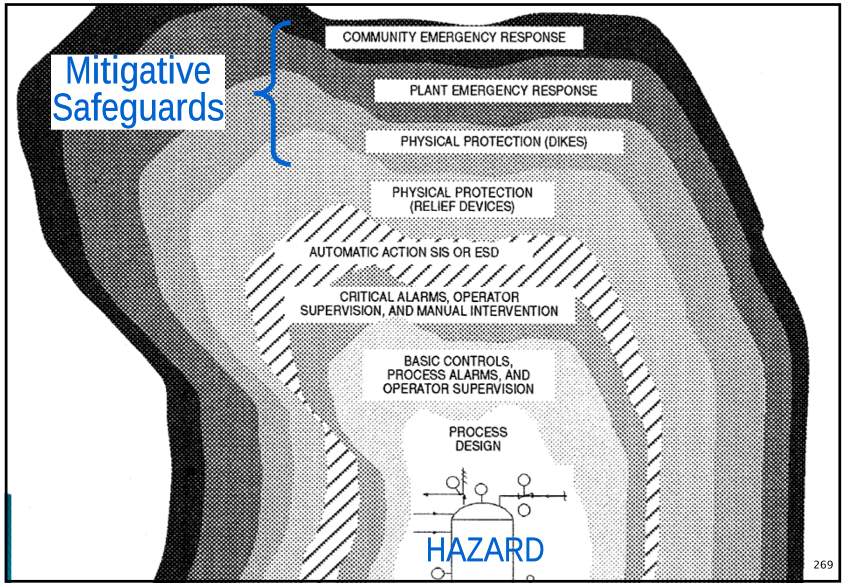
Mitigative safeguards

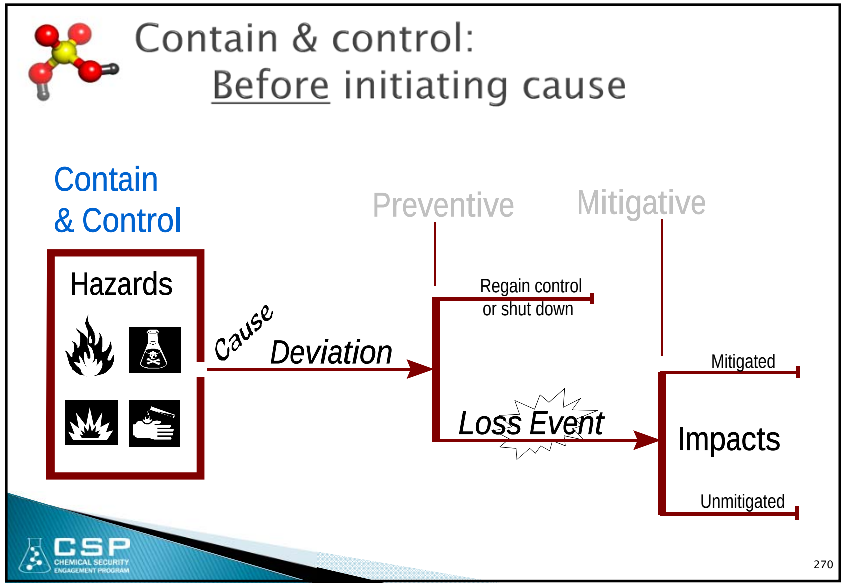


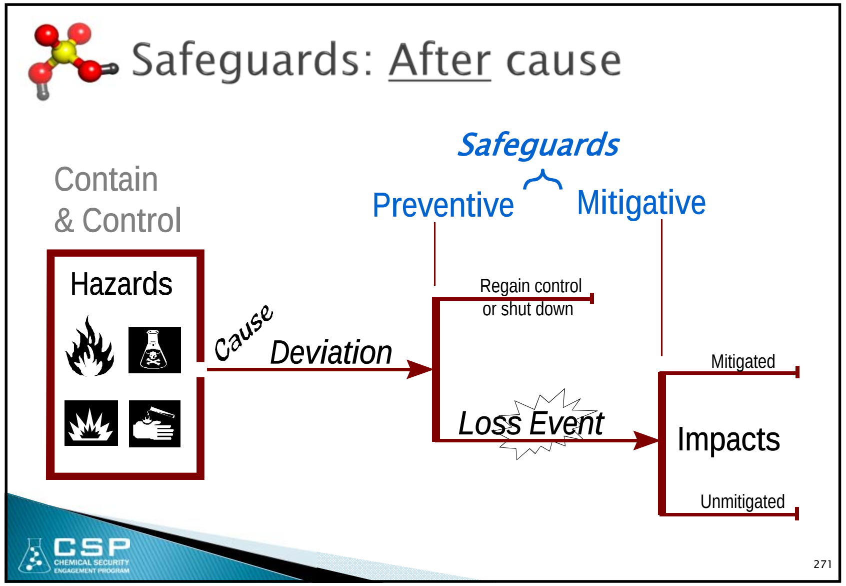
Operational Mode: Emergency

Objective: Minimize impacts

Examples of Mitigative Safeguards:
- Sprinklers, monitors, deluge
- Emergency warning systems
- Emergency response
- Secondary containment; diking/curbing
- Discharge scrubbing, flaring, treatment
- Shielding, building reinforcement, haven
- Escape respirator, PPE







Process Safety Overview

1. What is *process safety*?
2. Opposite of process safety: Major incidents
3. The anatomy of process safety incidents
4. Overview of process safety strategies
5. Taking advantage of past experience
6. Defense in depth / layers of protection
7. Elements of process safety management

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

272

Comprehensive PSM program elements

- Management systems
- Employee participation
- Process safety information
- Process hazard analysis
- Operating procedures
- Training
- Contractor safety
- Pre-startup safety reviews
- Mechanical integrity
- Safe work practices
- Management of change
- Emergency planning and response
- Incident investigation
- Compliance audits

PSM elements covered in this course

- Management systems
- Employee participation
- Process safety information
- **Process hazard analysis**
- Operating procedures
- Training
- Contractor safety
- **Pre-startup safety reviews**
- **Mechanical integrity**
- **Safe work practices**
- **Management of change**
- **Emergency planning and response**
- **Incident investigation**
- Compliance audits

DISCUSSION

What **PSM elements** do you think industrial facilities would find the most challenging to implement?

-
-
-
-
-

Day 2

Chemical Risks in the Process Industry

SAND No. 2011-0720P
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Topics

- Definition of hazards
- Types of hazards and potential consequences
  - Toxic/corrosive, asphyxiation, combustion, detonation, chemical reactivity, rapid phase transition, bursting vessel and other hazards
- Approaches and methods for systematically identifying process hazards
- Chemical hazard data
- Discussions
- Resources
- Summary

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Key points of this module

- Identify hazards and determine the potential consequences,
- Learn methods to manage hazards and reduce the risks,
- Learn where to obtain reference and resource materials.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Key acronyms

BLEVE = boiling-liquid-expanding-vapor explosion
VCE = vapor cloud explosion
LFL = lower flammable limit
UFL = upper flammable limit
LOC = limiting oxygen concentration
AIT = auto ignition temperature
DHS = Department of Homeland Security (USA)
MOC = minimum oxygen concentration
MSOC = maximum safe oxygen concentration
MIE = minimum ignition energy
TNT = trinitrotoluene
CCPS = Center for Chemical Process Safety
CAMEO = computer-aided management of emergency operations
NIOSH = National Institutes of Occupational Safety and Health
NOAA = National Oceanic and Atmospheric Administration

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Identification of Hazards and Potential Consequences

- "Process hazard" defined
- Types of hazards and potential consequences
- Approaches and methods for systematically identifying process hazards
- Chemical hazard data

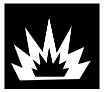
US Chemical Safety Board

Identification of Hazards and Potential Consequences

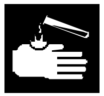
- "Process hazard" defined
- Types of hazards and potential consequences
- Approaches and methods for systematically identifying process hazards
- Chemical hazard data

US Chemical Safety Board

Process hazard definition



Presence of a stored or connected material or energy with inherent characteristics having the potential for causing loss or harm.



Identification of Hazards and Potential Consequences

- "Process hazard" defined
- Types of hazards and potential consequences

US Chemical Safety Board

Types of Process Hazards and Potential Consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

These are not mutually exclusive categories.

Types of Process Hazards and Potential Consequences

- Toxicity and corrosivity hazards
- Simple asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

Toxicity/corrosivity hazards

Nature of hazard	Potential exposure of people to materials having toxic and/or corrosive properties
What is required	Presence or generation of toxic/corrosive material + mechanism for physical contact
Typical examples	Chlorine used for water treatment; hydrogen sulfide as hydrocarbon impurity; sulfuric acid used for pH control
Consequences	Contact with toxic/corrosive material can cause various health effects, depending on material characteristics, concentration, route of exposure and duration of contact (see Day 1 information)

Toxicity/corrosivity hazards

Video example	www.youtube.com; search term "Seward ammonia spill"
Area of effect	Liquid releases usually very localized; toxic vapor releases can extend many km
How calculated	• Toxic release dispersion models can be used to calculate release rates, downwind and cross-wind distances with various meteorological conditions • Some models can also calculate indoors concentration as a function of time
Free program	http://www.epa.gov/emergencies/content/cameo/aloha.htm

Types of Process Hazards and Potential Consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

Asphyxiation hazards

- An *asphyxiant* is a gas that can cause unconsciousness or death by suffocation (*asphyxiation*).
  - *Chemical asphyxiants* chemically interfere with the body's ability to take up and transport oxygen
  - *Physical asphyxiants* displace oxygen in the environment
- *Simple asphyxiants* have no other health effects
- Most simple asphyxiants are colorless and odorless.

Asphyxiation hazards

- Common industry asphyxiant: Nitrogen N_2
- Other simple asphyxiants:
  - Hydrogen H_2
  - Argon, helium, neon Ar
  - Hydrocarbon gases (for example: methane, ethane, ethylene, acetylene, propane, propylene, butane, butylene) CH_4
  - Carbon dioxide CO_2

Asphyxiation hazards

What is required	Reduced-oxygen atmosphere **+** situation allowing breathing of the atmosphere
Typical examples	Entry into vessel inerted with nitrogen; oxygen depletion by rusting over time; oxygen depletion by combustion; natural gas leak into enclosed room or area
Video	http://www.csb.gov/videoroom/detail.aspx?vid=11&F=0&CID=1&pg=1&F_All=y
Boundaries	• US OSHA: oxygen deficiency exists if concentration is less than 19.5% • ACGIH®: deficiency exists below 18% oxygen at 1 atm (equivalent to a partial pressure pO_2 of 135 torr)

Types of Process Hazards and Potential Consequences

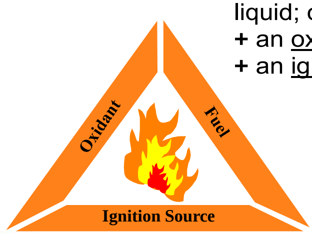
- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Combustion hazards

Nature of hazard: Potential for uncontrolled release of the heat of combustion upon rapid oxidation of a combustible material

What is required: A fuel (pyrophoric or flammable gas; pyrophoric, flammable or combustible liquid; or finely divided combustible solid) + an oxidant (usually atmospheric O_2) + an ignition source (unless pyrophoric)



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Combustion hazards

Nature of hazard: Potential for uncontrolled release of the heat of combustion upon rapid oxidation of a combustible material

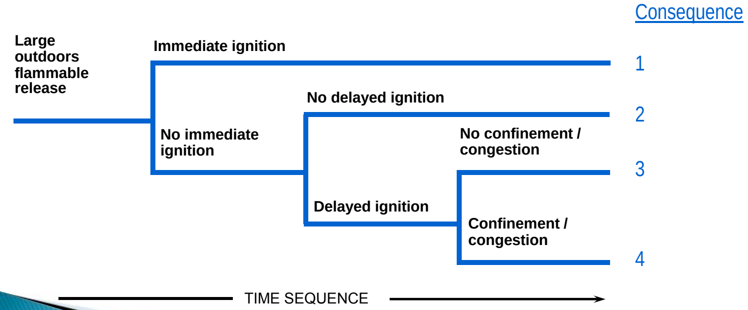
What is required: A fuel (pyrophoric or flammable gas; pyrophoric, flammable or combustible liquid; or finely divided combustible solid) + an oxidant (usually atmospheric O_2) + an ignition source (unless pyrophoric)

Possible consequences:
- **Flash fire**, **pool fire** and/or **jet fire**
- **Confined vapor explosion**
- **Vapor cloud explosion**
- **Dust or mist explosion**
- Toxic combustion products

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

EXERCISE

Describe each of the four possible outcomes.



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Some definitions

Combustion	A propagating rapid oxidation reaction.
Oxidation	In this context, a reaction in which oxygen combines chemically with another substance.
Oxidizer	Any material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials.
Explosion	A rapid or sudden release of energy that causes a pressure discontinuity or blast wave.

Some definitions

Spontaneously combustible	Capable of igniting and burning in air without the presence of an ignition source.
Pyrophoric	Capable of igniting spontaneously in air at a temperature of 130°F (54.4°C) or below.
Hypergolic	Hypergolic behavior is characterized by immediate, spontaneous ignition of an oxidation reaction upon mixing of two or more substances.

Reference: Johnson et al. 2003

Combustion hazards

Area of effect	Small fires usually have very localized effects; a large fire or a combustion-related explosions can destroy an entire facility and affect nearby surroundings
How calculated	Available combustion energy:
	Mass of combustible x heat of combustion *or* Mass rate of combustion x heat of combustion
	E.g., Ethanol pool fire in a 50 m^2 dike:

[Pool area x burning rate x liquid density] x heat of combustion
= (50 m^2) (0.0039 m/min) (789 kg/m^3) (26900 kJ/kg) = $4x10^6$ kJ/min

Note: Only ~ 20% of this will be released as thermal radiation.

Combustion hazards

Free program	www.epa.gov/emergencies/content/cameo/aloha.htm
	(can be used to calculate release rates, extent of a flammable vapor cloud, and vapor cloud explosion effect distances)
Online reference	Gexcon Gas Explosion Handbook, www.gexcon.com/handbook/GEXHBcontents.htm
Other references	**CCPS 2010; Crowl and Louvar 2001**
	(See also the Chemical Data Sources at the end of this presentation)

Flammability limits

LFL **Lower flammability limit**

Below LFL, mixture will not burn, it is too lean.

UFL **Upper flammability limit**

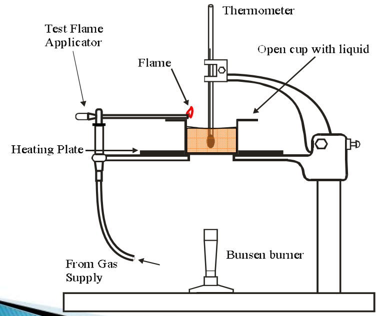
Above UFL, mixture will not burn, it is too rich.

- **Defined only for gas mixtures in air**
- **Both UFL and LFL defined as volume % fuel in air**

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Flash point

Flash Point Temperature above which a liquid produces enough vapor to form an ignitable mixture with air



(Defined only for liquids at atmospheric pressure)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Example values

	LFL	UFL
Methane	5%	15%
Propane	2.1%	9.5%
Butane	1.6%	8.4%
Hydrogen	4.0%	75%

	Flash point
Methanol	12.2 °C
Benzene	-11.1 °C
Gasoline	-40 °C
Styrene	30.5 °C

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Limiting oxygen concentration

Limiting oxygen concentration (LOC): Oxygen concentration below which combustion is not possible, with any fuel mixture, expressed as volume % oxygen.

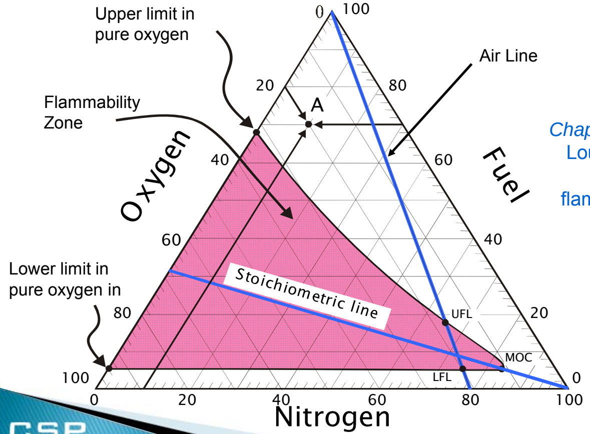
Also called: Minimum Oxygen Concentration (MOC)
Max. Safe Oxygen Concentration (MSOC)

Examples:

	LOC (volume % oxygen)
Methane	12 %
Ethane	11 %
Hydrogen	5 %

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Flammability diagram



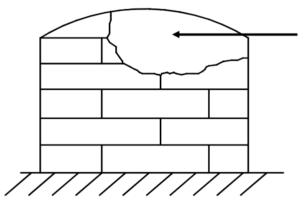
Chapter 6 of Crowl and Louvar shows how to prepare and use flammability diagrams

Design Criteria

1. Avoid flammable mixtures
2. Eliminate ignition sources

Inerting and purging

Purpose: To reduce the oxygen or fuel concentration to below a target value using an inert gas (for example: nitrogen, carbon dioxide)



For example reduce oxygen concentration to < LOC

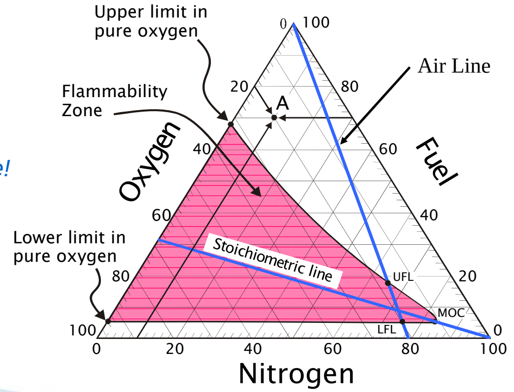
Inerting and purging options

- Vacuum Purge - evacuate and replace with inert
- Pressure Purge - pressurize with inert, then relieve pressure
- Sweep Purge - continuous flow of inert
- Siphon Purge - fill with liquid, then drain and replace liquid with inert
- Combined - pressure and vacuum purge; others

See Chapter 7 of Crowl and Louvar for details

Flammability diagram

OBJECTIVE:
Stay out of Flammability Zone!



Ignition sources

- Obvious (for example: flames, welding, hot surfaces)
- Spontaneous ignition at moderate temperatures
- Electrical sources
  - Powered equipment
  - Static electricity
  - Stray currents
  - Radio-frequency pickup
  - Lightning
- Chemical Sources
  - Catalytic materials
  - Pyrophoric materials
  - Thermite reactions
  - Unstable chemical species formed in system

- Physical sources
  - Adiabatic compression
  - Heat of adsorption
  - Friction
  - Impact

Minimum ignition energy

Minimum ignition energy (MIE) The electrical energy discharged from a capacitor that is just sufficient to ignite the most ignitable mixture of a given fuel-mixture under specific test conditions.

Typical values: (wide variation expected)

Vapors	**0.25 mJ**
Dusts	**about 10 mJ**

- **Dependent on test device, so not a reliable design parameter**
- **Static spark that you can feel: about 20 mJ**

Autoignition temperature

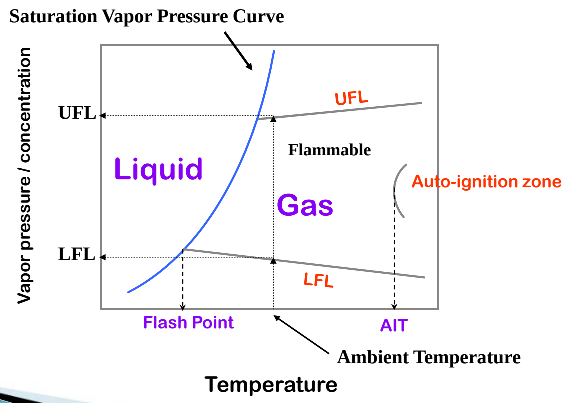
Autoignition Temperature (AIT): Temperature above which adequate energy is available from the environment to start a self-sustaining combustion reaction.

	AIT (°C)
Methane	632
Ethane	472
1-Pentene	273
Toluene	810
Acetaldehyde	185

There is great variability in reported AIT values! Use lowest reported value.

See Appendix B of Crowl and Louvar 2002 for a table of AITs

Flammability relationships



Ignition source control

- Identify ignition sources
  - Continuous ignition sources: for example fired equipment
  - Potential/intermittent ignition sources: for example traffic
- Identify what could be ignited
  - Flammable atmospheres
  - Potentially flammable atmospheres
  - Likely leak/release locations
  - Avenues to unexpected locations: drains, sumps
- Analyze for adequate control

DISCUSSION

Which of these two design criteria can be more easily and reliably attained?

1. Avoid flammable mixtures
2. Eliminate ignition sources

Types of Process Hazards and Potential Consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

Detonation hazards

Nature of hazard	Potential for generating a damaging blast wave by extremely fast chemical reaction
What is required	One of two typical mechanisms: (1) Direct initiation of a solid or liquid explosive material or mixture, or (2) Acceleration of a propagating gas-phase reaction to detonation velocity
Typical examples	(1) TNT; picric acid; unstable peroxides; commercial explosives (2) Vapor cloud explosion; flame acceleration in a long pipeline containing a flammable mixture

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Detonation hazards

Possible consequences	• **Blast wave** (sometimes more than one) • Shrapnel (usually small fragments) • Toxic decomposition products See calculation example for Bursting vessel explosion hazards
Video	www.youtube.com; search term **Pepcon explosion**

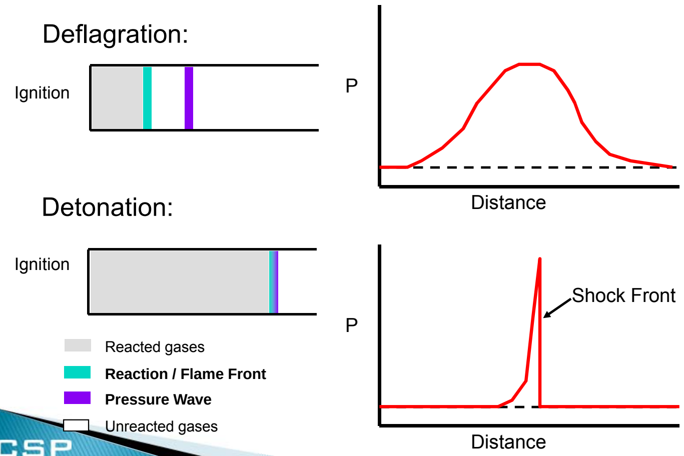
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Some definitions

Deflagration	A chemical reaction propagating at less than the speed of sound relative to the unreacted material immediately ahead of the reaction front.
Detonation	A chemical reaction propagating at greater than the speed of sound relative to the unreacted material immediately ahead of the reaction front.
Deflagration-to-Detonation Transition (DDT)	Increase in the propagating velocity of a chemical reaction until the velocity exceeds the speed of sound relative to the unreacted material immediately ahead of the reaction front.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Deflagration *vs.* Detonation



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Types of Process Hazards and Potential Consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

Chemical reactivity hazards

Nature of hazard	Potential for an uncontrolled chemical reaction that can result in loss or harm
Also known as	*Reactive chemical hazards*
What is required	Any situation where the energy and/or products released by a chemical reaction are not safely absorbed by the reaction environment
Typical examples	• Loss of control of an intended reaction • Initiation of an unintended reaction
Consequences	Fire, explosion, toxic gas release and/or hot material release

Chemical reactivity hazards

Video	"Introduction to Reactive and Explosive Materials"
Types of chemical reactivity hazards	• Water-reactive • Oxidizing • Spontaneously combustible / pyrophoric • Peroxide forming • Polymerizing • Decomposing • Rearranging • Interacting (i.e., incompatible)
Reference	Johnson et al. 2003 ***See also:*** Day 3 presentation on Chemical Reactivity Hazards

Types of Process Hazards and Potential Consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

Rapid phase transition hazards

Nature of hazard	Near-instantaneous phase transition from liquid to gas, with large volume increase
Also known as	Boiling-liquid-expanding-vapor explosion (BLEVE)
What is required	Any liquefied gas stored under pressure above its boiling point
Typical example	Propane storage tank engulfed in fire with flame impinging on vapor space of tank, weakening the metal to point of failure
Consequences	Blast energy from both phase transition and bursting vessel; large tank fragments; huge fireball also if flammable liquid

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Rapid phase transition hazards

Videos	www.youtube.com; search term **BLEVE**
Area of effect	Can be 1 km or more, depending on size of storage tank(s)
How calculated	Calculate each mechanism separately and determine which has greatest effect; multiple mechanisms increases severity: • Bursting vessel explosion • Phase transition volume expansion • Missiles / flying debris • Fireball thermal radiation if flammable • Follow-on ("domino") effects
Reference	CCPS 2010

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Types of Process Hazards and Potential Consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Bursting vessel explosion hazards

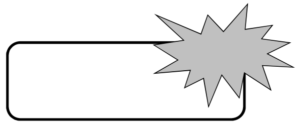
Nature of hazard	Near-instantaneous release of energy stored by a compressed vapor or gas
Also known as	Containment overpressurization; Vessel rupture explosion
What is required	Vapor or gas at elevated pressure inside some form of containment
Typical examples	Overpressurization of a reaction vessel from an unrelieved runaway reaction; ignition of flammable vapors in a tank
Consequences	Blast energy from bursting vessel; large vessel fragments thrown; expelling of remaining tank contents; follow-on effects

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Bursting vessel explosion hazards

Videos	www.csb.gov; several examples in Video Room, including **Explosion at T2 Labs**
Area of effect	Highly dependent on amount of stored energy at time of rupture
How calculated	Calculate each mechanism separately and determine which has greatest effect; multiple mechanisms increases severity: • Bursting vessel explosion (gas / vapor volume expansion) • Missiles / flying debris • Release of vessel contents • Follow-on ("domino") effects
References	**CCPS 2010; Crowl and Louvar 2002**

Bursting vessel explosion hazards



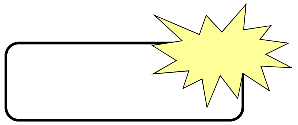
One equation used for calculating blast energy:

$$W_e = R_g T \left[\ln\left(\frac{P}{P_E}\right) - \left(1 - \frac{P_E}{P}\right) \right]$$

Maximum Mechanical Energy

where W_e is the energy of explosion, P is absolute gas pressure in vessel, P_E is abs. ambient pressure, T is absolute temperature.

Bursting vessel explosion hazards



Another equation used for calculating blast energy:

$$W_e = \frac{(P - P_E)\, V}{\gamma - 1}$$

Brode's Equation

where W_e is the energy of explosion, P is absolute gas pressure in vessel, P_E is abs. ambient pressure, V is vapor volume, and γ is the ratio of specific heats

Bursting vessel explosion hazards

EXAMPLE

- The vapor space of a 30 m^3 flammable liquid storage tank is nitrogen-inerted.
- The nitrogen regulator fails open, exposing the tank vapor space to the full 4 bar gauge nitrogen supply pressure. The tank relief system is not sized for this failure case.
- If the tank ruptures at 4 bar gauge when it is nearly empty of liquid, how much energy is released?

Bursting vessel explosion hazards

Data

P = 4 bar gauge = 400 Pa gauge = 501325 Pa abs

P_E = 0 bar gauge = 0 Pa gauge = 101325 Pa abs

V = 30 m^3

γ = 1.4 for nitrogen (dimensionless)

Bursting vessel explosion hazards

Calculation

Using Brode's equation:

$$W_e = \frac{(501325 \text{ N/m}^2 - 101325 \text{ N/m}^2) \cdot 30 \text{ m}^3}{1.4 - 1}$$

$$W_e = 3 \times 10^7 \text{ N-m} = 3 \times 10^7 \text{ Joules}$$

Bursting vessel explosion hazards

Comparison

TNT (trinitrotoluene) has a heat of explosion of 4686 J/g, so a blast energy of 3 x 10^7 J is equivalent to

3 x 10^7 / 4686 = 6400 g TNT = 6.4 kg TNT

Bursting vessel explosion hazards

Consequences

Figure 6-23 in Crowl and Louvar 2001 (page 268) gives a correlation of scaled overpressure vs scaled distance.

If a control room building is 30 m away from the storage tank, the scaled distance is

$$z_e = 30 \text{ m} / (6.4 \text{ kg TNT})^{1/3} = 16.2$$

From Figure 6-23, the scaled overpressure p_s = 0.1, and the resulting overpressure is (0.1)(101 kPa) = 10 kPa

Bursting vessel explosion hazards

Consequences

Table 6-9 of Crowl and Louvar 2001 (p. 267) indicates that 10 kPa is sufficient to:

- break windows,
- cause serious damage to wood-frame structures,
- distort the steel frame of clad buildings.

Types of Process Hazards and Potential Consequences

- Toxicity and corrosivity hazards
- Simple asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

Other physical hazards

Physical hazard	Typical examples
Hydraulic pressure	High-pressure hydraulic fluid: *Jet spray from pinhole leak can cause severe cuts*
Vacuum	Contained sub-atmospheric pressure: *Pumping out of a tank or condensing steam with inadequate venting can cause tank implosion*

A railcar steam cleaning team went to lunch - but before they left, they put the man-way back on the car on a cool and cloudy day. The steam condensed and created a vacuum.

CCPS CENTER FOR CHEMICAL PROCESS SAFETY An AIChE Industry Technology Alliance

Process Safety Beacon

http://www.aiche.org/ccps/safetybeacon.htm

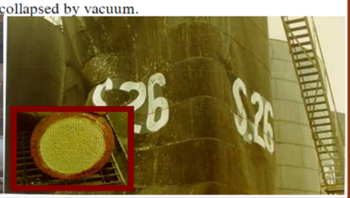
Messages for Manufacturing Personnel

Sponsored by CCPS Supporters

February 2007

Vacuum Hazards - Collapsed Tanks

The tank on the left collapsed because material was pumped out after somebody had covered the tank vent to atmosphere with a sheet of plastic. Who would ever think that a thin sheet of plastic would be stronger than a large storage tank? But, large storage tanks are designed to withstand only a small amount of ***internal*** pressure, not vacuum (external pressure on the tank wall). It is possible to collapse a large tank with a small amount of vacuum, and there are many reports of tanks being collapsed by something as simple as pumping material out while the tank vent is closed or rapid cooling of the tank vapor space from a thunder storm with a closed or blocked tank vent. The tank in the photograph on the right below collapsed because the tank vent was plugged with wax. The middle photograph shows a tank vent which has been blocked by a nest of bees! The February 2002 Beacon shows more examples of vessels collapsed by vacuum.



Other physical hazards

Physical hazard	Typical examples
Elevated temperature	High gas, liquid or surface temperature: *Contact with hot surface or leaking hot material can cause severe burns; prolonged exposure to high area temperature can cause heat exhaustion*
Cryogenic temperature	Liquid nitrogen; flashing liquefied gas: *Skin contact can cause cryogenic burns*

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Other physical hazards

Physical hazard	Typical examples
Mass storage	Very large liquid storage tanks, silos: *Catastrophic failure can lead to fatalities*

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

CCPS Process Safety Beacon (continued)

Do you know?

• You might think that an incident that occurred over 80 years ago is not relevant to today's industry. But, we still have catastrophic failures of storage tanks today (see pictures below), and for similar reasons.

• A large quantity of any liquid, even a non-hazardous material such as molasses or water, can be dangerous if rapidly released in large quantities, simply because of its volume and mass.

What You Can Do

• If you observe leakage, corrosion, or other indication of potential failure in a storage tank, report it immediately to management.

• Make sure that any new tank, or one being returned to service following repair or inactivity, is properly inspected and tested before filling.

• Ensure you know the operating capacities of your tanks and double check the level before filling.

• Don't throw out your old incident reports. Read them again, and remember the lessons. We can learn a lot from things that happened a long time ago.

January 1988 – Floreffe, Pennsylvania, USA, tank failure releases over 4 million US gallons (15,000 cu. m) of diesel oil into the Monongahela River.

January 2000 – Cincinnati, Ohio, USA, tank failure releases 365,000 gallons (1400 cu. m) of fertilizer solution into the Ohio River.

Remember the lessons of the past!

Other physical hazards

Physical hazard	**Typical examples**
Obscuring vapor cloud	Acid gases, titanium tetrachloride, cryogenic liquids: *Dense vapors, dust or condensed humidity can obscure vision and lead to e.g. vehicle collisions*

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

Identification of Hazards and Potential Consequences

- "Process hazard" defined
- Types of hazards and potential consequences
- Approaches and methods for systematically identifying process hazards

US Chemical Safety Board

Approaches/methods to systematically identify process hazards

Some "HAZID" approaches and methods:

- Analyze material properties
- Analyze process conditions
- Use company and industry experience
  - Knowledge of the process chemistry
  - Experience at a smaller scale - pilot plant
  - Examination of relevant previous incidents
  - Use relevant checklists - CCPS 2008a Appendix B
- Develop chemical interaction matrices

Approaches/methods to systematically identify process hazards

Typical hazard identification results:

- List of flammable/combustible materials
- List of toxic/corrosive materials and by-products
- List of energetic materials and explosives
- List of explosible dusts
- List of hazardous reactions; chemical interaction matrix
- Fundamental hazard properties: flash point, toxic endpoint
- Others: simple asphyxiants, oxidizers, etc.
- Total quantities of each hazardous material
- List of chemicals and quantities that would be reportable if released to the environment
- List of physical hazards (pressure, temperature, etc.) associated with a system
- List of contaminants and process conditions that lead to a runaway reaction

Reference: CCPS 2008a, Table 3.4

One format for a "hazard inventory"

Last Updated:	PROCESS HAZARDS					

CHEMICAL PROCESS HAZARDS						Inherent Safety:
Chemical, Concentration*	Quantity Stored or Rate Processed	Volatility	Health Hazards	Flammability; Fire Hazards	Chemical Reactivity; Other Hazards	Recommendation No.

*Include materials that may have dust or mist explosion hazards, as well as toxicity, fire, explosion, and other reactivity hazards

PHYSICAL PROCESS HAZARDS						Inherent Safety:
Contained and Controlled Process Energy	Location Within or Connected To Process	Units of Measure	Range	Design	Comment	Recommendation No.
Pressurized Gas						
Hydraulic Pressure						
Vacuum						
Thermal Energy						
Radiant Energy						
Cryogenic Liquid						
Liquefied Gas						
Kinetic Energy; Material Movement						
Potential Energy; Mass Storage or Elevated Material						

A "chemical interaction matrix" format

Last Updated:	CHEMICAL REACTIVITY MATRIX

Abbreviation	Meaning
NR	Not reactive; no conditions identified for this process that would result in a chemical reaction between these materials
NS	No scenario identified that would result in this combination of materials coming into contact in this process
?	Unknown whether chemical reaction would occur between these materials at conditions found in this process
corr	One material corrosive to the other if these materials are combined
ht	Heat generation by chemical reaction or heat of solution; may cause pressurization if these materials are combined
R	Energetic chemical reaction, flammable gas generation, and/or toxic gas generation if these materials are combined
H#, F#, I#, W, OX	NFPA **H**ealth rating (0-4), **F**lammability rating (0-4), **I**nstability rating (0-4), vigorously or violently water reactive (**W**), oxidizer (**OX**)

Material	Abbv										
		F_ H_ I_									
			F_ H_ I_								
				F_ H_ I_							
					F_ H_ I_						
						F_ H_ I_					
							F_ H_ I_				
								F_ H_ I_			
									F_ H_ I_		
										F_ H_ I_	
											F_ H_ I_

Chemical interaction potentials based on scenarios and reactivity data listed [on separate page]

Reactivity represents only binary combinations.
See ASTM E 2012, "Standard Guide for the Preparation of a Binary Chemical Compatibility Chart," for methodology and example.

Identification of Hazards and Potential Consequences

- "Process hazard" defined
- Types of hazards and potential consequences
- Approaches and methods for systematically identifying process hazards
- Chemical hazard data

US Chemical Safety Board

Chemical hazard data

Some sources of chemical hazardous property data:

- Safety Data Sheets from chemical supplier
- Chemical-specific sources (Chlorine Institute)
- Many books and handbooks (Sax, Bretherick's)

DISCUSSION

- Select a familiar type of simple chemical process.
- Identify what *process hazards* are present - generate a hazard inventory.
- Discuss what could happen if the hazards were not contained and controlled.

353

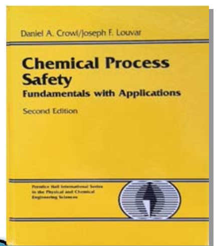
Chemical hazard data

Some internet-accessible data sources:

- International Chemical Safety Cards www.ilo.org/legacy/english/protection/safework/cis/products/icsc/dtasht/index.htm
- CAMEO Chemicals cameochemicals.noaa.gov
- Chemical Reactivity Worksheet response.restoration.noaa.gov/CRW
- NIOSH Pocket Guide to Chemical Hazards www.cdc.gov/niosh/npg
- Wireless Information System for Emergency Responders wiser.nlm.nih.gov

Resources

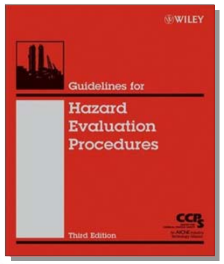
D. A. Crowl and J. F. Louvar 2001.
Chemical Process Safety: Fundamentals with Applications, 2nd Ed., Upper Saddle River, NJ: Prentice Hall.



Chapter
- 2 • Toxicology
- 4 • Source Models
- 5 • Toxic Release and Dispersion Models
- 6 • Fires and Explosions
- 10 • Hazards Identification

Resources

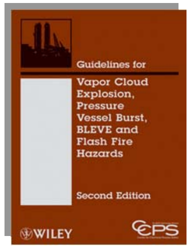
CCPS 2008a. Center for Chemical Process Safety, *Guidelines for Hazard Evaluation Procedures, Third Edition*, NY: American Institute of Chemical Engineers.



Chapter 3 • Hazard Identification Methods
- 3.1 Analyzing Material Properties and Process Conditions
- 3.2 Using Experience
- 3.3 Developing Interaction Matrixes
- 3.4 Hazard Identification Results
- 3.5 Using Hazard Evaluation Techniques to Identify Hazards
- 3.6 Initial Assessment of Worst-Case Consequences
- 3.7 Hazard Reduction Approaches and Inherent Safety Reviews

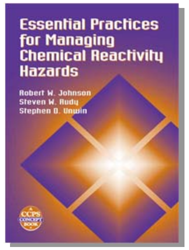
Resources

CCPS 2010. Center for Chemical Process Safety, *Guidelines for Vapor Cloud Explosion, Pressure Vessel Burst, BLEVE and Flash Fire Hazards, 2nd Edition*, NY: AIChE.



Resources

Johnson *et al.* 2003. *Essential Practices for Managing Chemical Reactivity Hazards*, NY: AIChE, accessible free after registration on www.knovel.com.



Summary

- Identified different types of hazards and determine the potential consequences,
- Discussed methods to manage hazards and reduce the risks,
- Information on where to obtain reference and resource materials.

Break

Globally Harmonized System of Classification

SAND No. 2012-5234C
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-AC04-94AL85000.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Labeling Basics

- Proper Labeling of Laboratory Hazards
  - Chemical
  - Physical
  - Biological
  - Radiological

Just ignore the label...
The worst stuff isn't listed anyway.

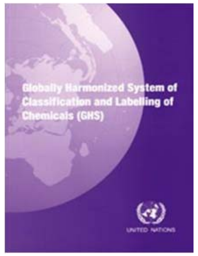
- Globally Harmonized System (GHS) Hazard Labels

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

362

Globally Harmonized System (GHS): Classification and Labeling of Chemicals

- A system for standardizing and harmonizing the classification and labeling of chemicals
- Not a regulation or a standard.
  - establishes agreed hazard classification and communication provisions with explanatory information on how to apply the system
- GHS Labels and Safety Data Sheets (SDS)



http://www.osha.gov/dsg/hazcom/ghs.html

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

363

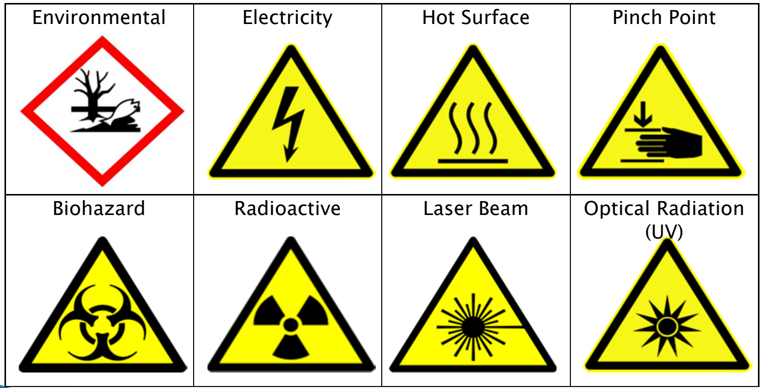
Globally Harmonized System (GHS): Hazard Labels

Corrosive	Irritant	Health Hazard	Acute Toxicity
			
Flammable	Explosion	Oxidizer	Compressed Gas
			

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

364

Globally Harmonized System (GHS) and Other Hazard Labels

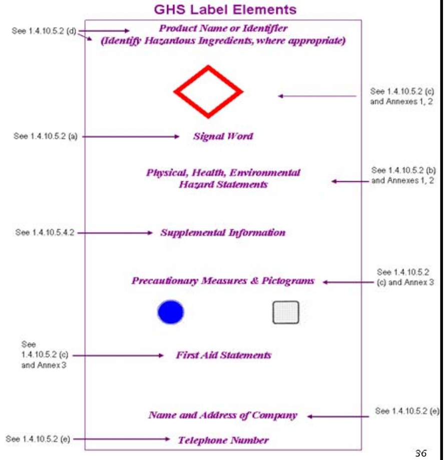


CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

365

GHS Labels Elements

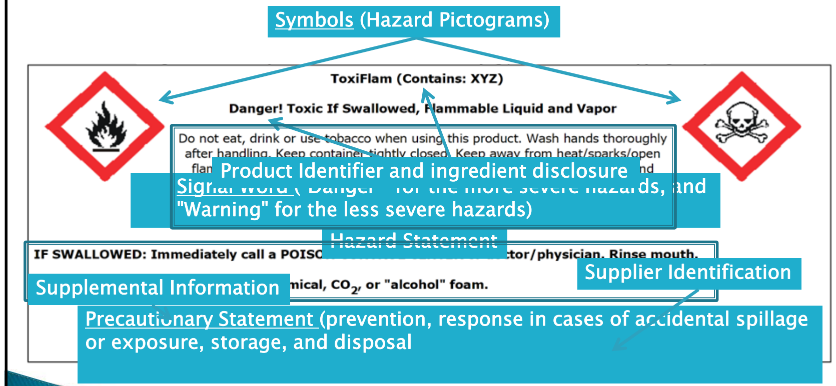
- Symbols (hazard pictograms)
- Signal words
  - "Danger" for the more severe hazards, and
  - "Warning" for the less severe hazards
- Hazard statement
- Precautionary Statements and Pictograms
  - prevention, response in cases of accidental spillage or exposure, storage, and disposal
- Product Identifier (ingredient disclosure)
- Supplier identification
- Supplemental information



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

366

GHS Labels Elements: Example Bottle Label

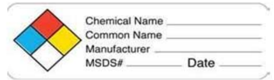


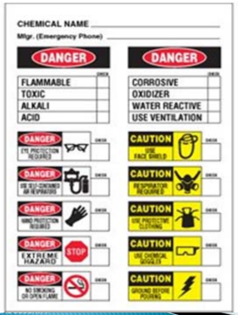
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

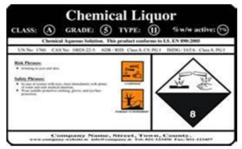
367

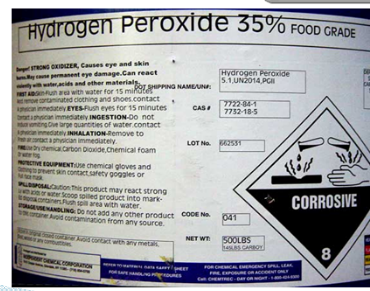
Example Labels

- Label Creation









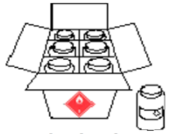
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

368

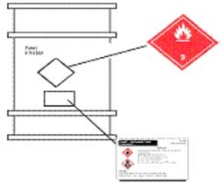
Other Labeling Considerations

- Chemical Resistance
- Environmental Resistance
  - Heat, Fridge, Freezer
- Age
- Size
  - Label
  - Container
- Attachment to Bottle

Transportation: Package Labels

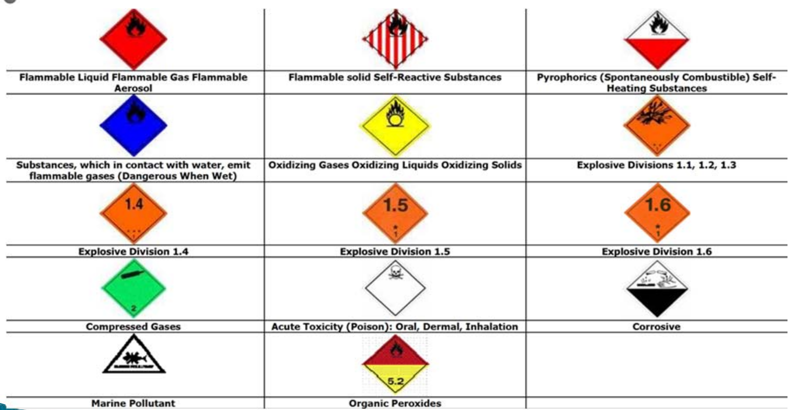


Combination Packaging (Outer box with inner bottles)



Combination Packaging (Outer box with inner bottles)

Transportation: Pictograms



Example: Outer Shipping Container

ToxiFlam **Flammable liquids, toxic, n.o.s.**

Danger! Toxic If Swallowed **(contains XYZ)**
Flammable Liquid and Vapor **UN 1992**

Do not eat, drink or use tobacco when using this product. Wash hands thoroughly after handling. Keep container tightly closed. Keep away from heat/sparks/open flame. - No smoking. Wear protective gloves and eye/face protection. Ground container and receiving equipment. Use explosion-proof electrical equipment. Take precautionary measures against static discharge. Use only non-sparking tools. Store in cool/well-ventilated place

IF SWALLOWED: Immediately call a POISON CONTROL CENTER or doctor/physician. Rinse mouth.

In case of fire, use water fog, dry chemical, CO_2, or "alcohol" foam.

See Material Safety Data Sheet for further details regarding safe use of this product.

MyCompany, MyStreet, MyTown NJ 00000, Tel: 444 999 9999

GHS Safety Data Sheets

- Serve the same function as an MSDS does in ISO, EU and ANSI requirements
- Most comprehensive source of information
  - Hazards, including environmental hazards
  - Advice and safety precautions
    - Transportation, emergency responders, poison centers
- Product related and not specific to workplace or task
  - Written and supplied by manufacturer
- Only for pure substances and some mixtures

http://www.osha.gov/dsg/hazcom/ghs.html

373

SDS Format

16 Sections

1. Identification
2. Hazard(s) identification
3. Composition/information on ingredients
4. First-aid measures
5. Fire-fighting measures
6. Accidental release measures
7. Handling and Storage
8. Exposure controls/ personal protection
9. Physical and chemical properties
10. Stability and reactivity
11. Toxicological information
12. Ecological information
13. Disposal considerations
14. Transport information
15. Regulatory information
16. Other information

374

Safety Data Sheet Example: Benzene

SDS Section 2: Hazards Identification

- OSHA Hazards
  - Flammable liquid, Carcinogen, Target Organ Effect, Irritant, Mutagen
- GHS Classification
  - Flammable liquids (Category 2)
  - Acute toxicity, Oral (Category 5)
  - Skin irritation (Category 2)
  - Eye irritation (Category 2A)
  - Germ cell mutagenicity (Category 1B)
  - Carcinogenicity (Category 1A)
  - Aspiration hazard (Category 1)
  - Acute aquatic toxicity (Category 2)
- GHS Label elements, including precautionary statements
- Signal word: Danger

375

Safety Data Sheet Example: Benzene

SDS Section 4: First Aid Measures

- General advice
  - Consult a physician. Show this safety data sheet to the doctor in attendance. Move out of dangerous area.
- If inhaled
  - If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.
- In case of skin contact
  - Wash off with soap and plenty of water. Consult a physician.
- In case of eye contact
  - Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.
- If swallowed
  - Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

376

Safety Data Sheet Example: Benzene

SDS Section 4: Accidental release measures

- Personal precautions
  - Use personal protective equipment. Avoid breathing vapors, mist or gas. Ensure adequate ventilation. Remove all
  - sources of ignition. Evacuate personnel to safe areas. Beware of vapours accumulating to form explosive concentrations. Vapours can accumulate in low areas.
- Environmental precautions
  - Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided.
- Methods and materials for containment and cleaning up
  - Contain spillage, and then collect with an electrically protected vacuum cleaner or by wet-brushing and place in container for disposal according to local regulations.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

377

Safety Data Sheet Example: Benzene

SDS Section 8: Exposure Controls/PPE

Exposure Limits

- TWA = 0.5 ppm USA. ACGIH Threshold Limit Values (TLV)
- Leukemia Substances for which there is a Biological Exposure Index or Indices (see BEI® section)
- Confirmed human carcinogen Danger of cutaneous absorption
- STEL = 2.5 ppm USA. ACGIH Threshold Limit Values (TLV)
- TWA = 10 ppm USA. Occupational Exposure Limits (OSHA) - Table Z2

Respiratory protection

- Where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

378

Safety Data Sheet Example: Benzene

SDS Section 8: Exposure Controls/PPE

Hand protection

- Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.
- Immersion protection
  Material: Fluorinated rubber
  Minimum layer thickness: 0.7 mm
  Break through time: > 480 min
  Material tested:Vitoject® (Aldrich Z677698, Size M)
- Splash protection
  Material: Fluorinated rubber
  Minimum layer thickness: 0.7 mm
  Break through time: > 30 min
  Material tested:Vitoject® (Aldrich Z677698, Size M)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

379

Safety Data Sheet Example: Benzene

SDS Section 13: Disposal

- Product
  Burn in a chemical incinerator equipped with an afterburner and scrubber but exert extra care in igniting as this material is highly flammable. Offer surplus and non-recyclable solutions to a licensed disposal company. Contact a licensed professional waste disposal service to dispose of this material.
- Contaminated packaging
  Dispose of as unused product.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

380

GHS Safety Data Sheets (SDS)

- Benefits of the SDS
  - The SDS contains comprehensive information for chemical management in one place
- Drawbacks
  - Not always current
  - Lack of toxicity information for most chemicals
  - Industry focus, not specific to laboratory scale
  - Sometimes inconsistent
- Keep a SDS for each chemical in your inventory
- Ensure all SDSs are accessible to workers and auditors

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Chemical Toxicity and Exposure Standards

2012-1601C
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-AC04-94AL85000.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Overview

- Definitions
- Exposure
- Dose response
- Exposures
- Health effects
- Exposure limits
- Evaluating exposure
- Control banding

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

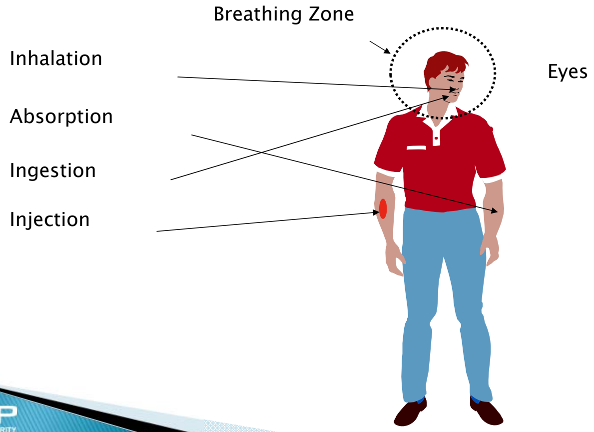
Definitions

- Toxicology: the study of the adverse effects of chemicals (xenobiotics) on living organisms.
- Toxicity: ability of a chemical to produce an unwanted effect.
- Hazard: presence of an agent that has inherently hazardous properties and the potential to cause harm.
- 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

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Exposure



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

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
    - Inhalable size = 0.1 µm to 10 µm
  - Solubility of gases & vapors
    - Formaldehyde versus chloroform

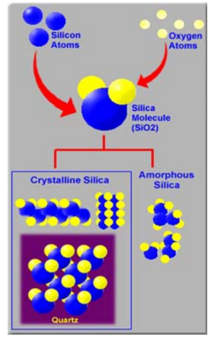
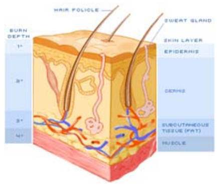


Photo Credit: US OSHA

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Exposure: Skin absorption

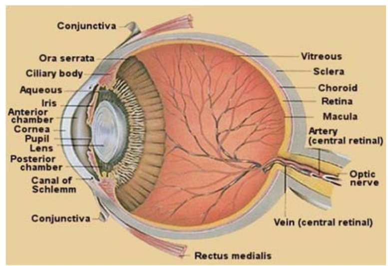
- Depends on skin location and thickness
  - Palms of the hands are thickest
  - Skin on abdomen is thin
- Depends on skin condition
  - Dry and broken skin more susceptible
  - Sweat increases absorption
- Duration of contact
- Properties of the chemical
  - Concentration
  - Solubility (in fat or water)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



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

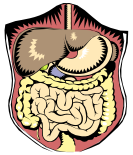
Exposure: Eyes

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



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Exposure: Ingestion



- Rare exposure route, but possible
  - Swallow chemicals after inhaling
  - 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

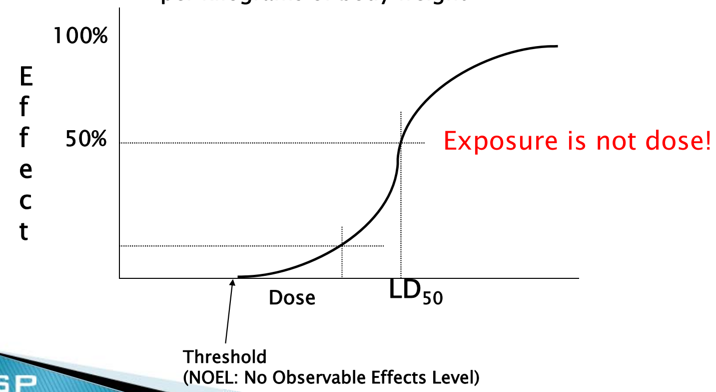
"All substances are poisons;
There is none which is not a poison.
The right dose differentiates a
poison from a remedy…"
—Paracelsus (1493-1541)

Dose Response Terminology

- TD_{lo} – Toxic dose low – lowest dose for effect
- LD_{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_{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



393

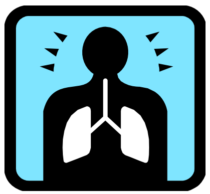
Health Effects

- Acute Health Effects–severe injury or death
  - High concentration 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 concentration over long time period
  - Chemicals with chronic effects:
    - Carcinogens: benzene, asbestos, arsenic
    - Reproductive agents: glycol ether acetates, lead, carbon disulfide
    - Sensitizers–glutaraldehyde, toluene diisocyanate

394

Health Effects

- Local
  - Effect occurs at site of contact
  - Skin rash, burns, coughing
  - Chemicals with local effects:
    - Solvents, acids
    - Nickel allergy
- Systemic
  - Chemical distributed by circulation
  - Effect occurs in body organs
  - Chemicals with systemic effects:
    - Methylene chloride to heart muscle
    - Lead to bone and brain

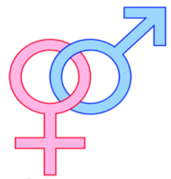


395

Health Effects

<u>Chemicals affect people differently</u>:

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



396

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 toxic effect on certain organ or system, but when added to another chemical, it makes the latter more toxic…(0 + 2 = 10)
  - Example: Isopropanol & carbon tetrachloride
- 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

Exposures

Exposures: Metals

Exposure primarily by inhalation:

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

http://www.millerwelds.com/

Health Effects of Metals

- Sensitizers (skin and lungs)
  - Skin rash, asthma
  - Nickel, beryllium, chromium
- Metal fume fever
  - Flu-like symptoms
  - Oxides of zinc, magnesium, and copper
- Organ toxicity
  - Damage specific organs
  - Arsenic—nervous system, liver
  - Cadmium—kidney, lungs
  - Lead-nervous system, blood, kidney, reproductive systems
- Carcinogens
  - Cause cancer
  - Arsenic, soluble nickel, hexavalent chromium

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

401

Exposures: Solvents

Exposure is by inhalation and skin absorption:

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

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

402

Health Effects: Solvents

- Skin irritants, dermatitis (rash)
  - Acetone, alcohols
- Organ toxicity
  - Nerve damage-hexanes
  - Liver-chloroform, vinyl
  - Heart damange-methylene
- Carcinogens
  - Benzene, formaldehyde
- Reproductive toxicants
  - Cause women to miscarry
  - Glycol ether acetates

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

403

Exposures: Pesticides

Exposure primarily by skin absorption and inhalation of aerosols:

- Processes: mixing, spraying (aerosols), waste handling
- Organochlorine (DDT, Chlordane, Dieldrin)
  - NOTE: poorly absorbed through the skin
- Carbamates (Aldicarb, Carbofuran),
- Organophosphates (Malathion, Parathion)

Exposure by ingestion from pesticide residue on foods

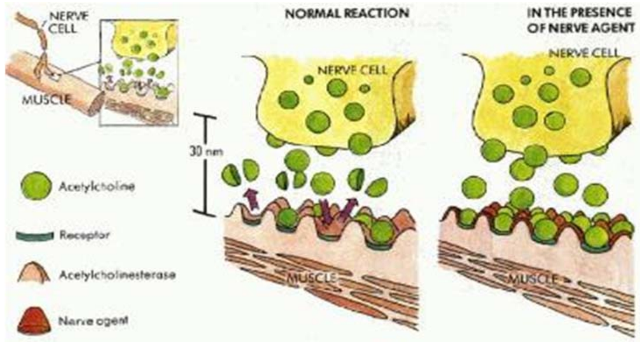
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

404

Health Effects: Pesticides

- Organochlorines
  - Animals: Estrogenic
  - Animals: Suppression of immune system
  - Humans: dizziness, nausea, vomiting, skin rash
- Carbamates and Organophosphates
  - Neurotoxicity is the principal toxicity
    - Affect skeletal muscle, smooth muscle and central nervous system (brain)
  - Used in suicide attempts

Inhibition of Acetycholinesterase: Carbamate/Organophosphate Insecticide Exposure



Occupational Exposure Limits:

Evaluating Exposure

Occupational Exposure Limits (OELs)

- Government regulation or professional standard organizations set OELs
- OELS apply to workers only, <u>NOT</u> the general public
- Primarily limits for inhalation exposure
- Expressed in milligrams/cubic meter (mg/m^3) or parts per million (ppm)
- Exposure must be measurable for comparison with the OEL
- Some publish exposure standards for noise, lasers, non-ionizing radiation, heat & cold stress, as well as chemicals

International Occupational Exposure Limits

- Indicative OEL Values (IOELVs)
  - Specified by the Council of the European Union
  - Based on advice from Scientific Committee on Occupational Exposure Limits (SCOEL)
  - 2009 –Third list of IOELVs published
  - Member states have until 12/2011 to implement legislation
- European Union Reach
  - Worker derived no-effect levels (DNELs)
  - Must be calculated for quantities >10 tons/year
  - Safety margins higher than the IOELVs
- German Exposure Limits
  - DFG MAK – Maximum Workplace Concentrations

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

409

U.S. Exposure Limits

- PEL – Permissible Exposure Limits
  - Occupational Safety and Health Administration (OSHA)
  - USA legal limits
- REL – Recommended Exposure Limits
  - National Institute of Occupational Safety & Health (NIOSH)
  - Recommended, not legal limits
- ACGIH TLV® – Threshold Limit Values®
  - American Conference of Governmental Industrial Hygienists
  - Recommended, not legal limits
- AIHA WEEL – Workplace Environmental Exposure Limits American Industrial Hygiene Association (AIHA)
  - Recommended, not legal limits

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

410

Exposure Limits

<u>Permissible Exposure Limit (PEL)</u>

- 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 <u>only</u> to workplaces covered by OSHA
- Action Levels published for highly toxic chemicals
  - ½ the PEL
  - Benzene, asbestos, vinyl chloride, formaldehyde

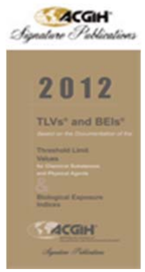
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

411

Exposure Limits

<u>ACGIH TLVs®:</u>

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



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

412

Exposure Limits

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

ACGIH TLV® Examples:
- Carbon dioxide = 5000 ppm TWA
- Osmium tetroxide = 0.0002 ppm TWA
- Hydrogen chloride = 2 ppm ceiling
- Ammonia = 35 ppm STEL

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

413

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

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

414

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:

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

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

415

Example: 8-hour Time-Weighted Average

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**

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

416

Solution

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

$$\text{TLV - TWA}_8 = \frac{(80 \times 2) + (110 \times 4) + (55 \times 2)}{8 \text{ hrs}}$$

EIGHT HOUR TLV–TWA = 89 ppm

Over exposed?

(TLV–TWA = 100 ppm)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

417

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

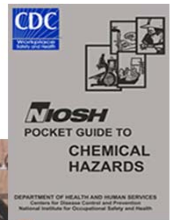
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

418

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



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

419

Evaluating Exposure

Quantitative

- Model the contaminant concentration in the room
- Example: What concentration, in mg/m^3 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

$1 \text{ g}/125 \text{ m}^3 = 1000 \text{ milligrams}/125 \text{ m}^3 = 8 \text{mg}/\text{m}^3$

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

420

Calculation for PPM Concentration

$$\frac{(8\ \text{mg/m}^3)\quad(24.45)}{78.11\ \text{(Molecular Weight)}} = 2.5\ \text{ppm}$$

ACGIH STEL for benzene is 2.5 ppm
(15 minute short term exposure)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

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

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

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

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Evaluating Exposure: Control Banding

- Initiatives:
  - World Health Organization (WHO)
  - International Labor Organization (ILO)
- Over 17 million organic and inorganic substances
- 170,000 chemicals may require registration under EU REACH regulations
- Shift in traditional industrial hygiene approach towards exposure

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Evaluating Exposure: Control Banding

What is control banding?

- A complementary approach to traditional industrial hygiene
- Focuses resources on exposure controls rather than exposure assessment
- Provides technical expertise to chemical users through simplified guidance

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

425

Evaluating Exposure: Control Banding

- Web Page: National Institute of Occupational Safety and Health (NIOSH)
  - www.cdc.gov/niosh/topics/ctrlbanding/
- Publications:
- AIHA (2007)
  - *Guidance for Conducting Control Banding Analysis*
- ACGIH (2008)
  - *Control Banding: Issues and Opportunities*
- NIOSH (2009)
  - *Qualitative Risk Characterization and Management of Occupational Hazards*

    http://www.cdc.gov/niosh/docs/2009-152/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

426

Summary of Presentation

- Provided definitions of dose/exposure
- Explained the dose response relationship
- Summarized exposure and health effects of metals and solvents
- Summarized international exposure limits
- Described methods for evaluating exposure
- Described control banding

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

427

Lunch

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

428

Implementing Inherently Safer & Secure Design

SAND No. 2012-7064C
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

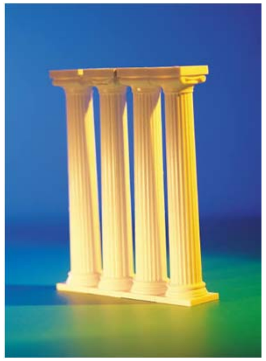
Part of formal IST definition

- IST is an iterative process that considers such options, including eliminating a hazard, reducing a hazard, substituting a less hazardous material, using less hazardous process conditions, and designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional harm.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Pillar One

Minimize
Substitute
Moderate
Simplify

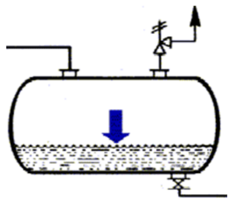


CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Minimize

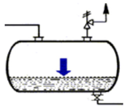
To *minimize* is to reduce the amount of potential energy present (get the system closer to a zero energy state),

this reduces the potential impacts if containment or control of the hazard is lost.



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Minimize

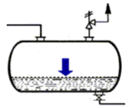


Some strategies for making a process inherently safer by *minimization*:

- Inventory reduction:
  - less material stored ⟸ *requires administrative control*
  - fewer tanks; just-in-time delivery
  - less vapor volume
  - generate on demand (chlorine, MIC, ammonia, hydrogen...)
  - receive by pipeline instead of by truck or rail
- Process intensification
- Process operation closer to ambient conditions

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Minimize



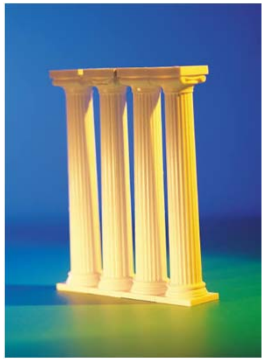
Ultimate case:

- Elimination of the hazard:
  - Eliminating use of a particular hazardous material
  - Operating the system at a zero energy state with respect to a particular hazard
  - Shutting down the process
  - Using a toll manufacturer (risk *transfer*)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Pillar Two

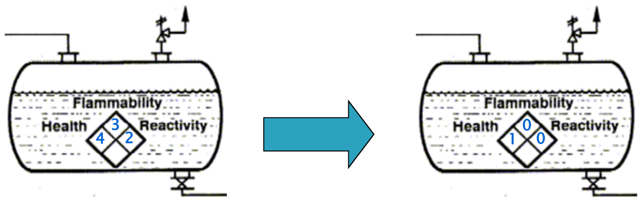
Minimize
Substitute
Moderate
Simplify



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Substitute

To *substitute* is to replace with a less hazardous material or condition.



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Substitute

Some strategies for making a process inherently safer by *substitution*:

- Commercially available alternatives
- Alternative raw material or intermediate that can be transported and stored more safely
- Alternative chemistry– Biosynthesis routes

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

437

Substitute

Solvent substitutes:

- Water-based paints, adhesives
- Aqueous cleaning systems
- Less volatile solvents; higher flash point
- Dibasic esters for paint stripping

Web resources are available

- "Substitutes in Non-Aerosol Solvent Cleaning," www.epa.gov/ozone/snap/solvents/solvents.pdf

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

438

Substitute

Some chlorine alternatives: *Cl_2*

- Sodium hypochlorite
- Calcium hypochlorite
- Hydrogen peroxide
- Chlorine dioxide
- Bromine
- Mixed oxidants
- Other technologies (UV radiation)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

439

Pillar Three

Minimize

Substitute

Moderate

Simplify

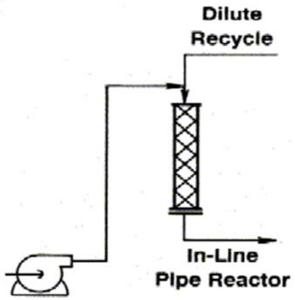
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Moderate

To *moderate* (or *attenuate)* is to handle a material under less hazardous conditions.

Dilution
Refrigeration
Less severe processing conditions

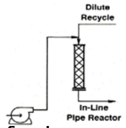
Note: Available energy may be the same, but potential loss event impacts can be reduced



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

441

Moderate



Some strategies for making a process inherently safer by *moderation* :

- **Dilution:**
  - using in aqueous instead of anhydrous form
  - Using in solution such that the solute would boil off before a runaway reaction temperature was achieved
  - Lower concentration of benzoyl peroxide in paste
  - Mixing coal dust with rock dust
- **Refrigeration:**
  - storing anhydrous ammonia as a refrigerated liquid instead of as a liquefied gas

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

442

Moderate

- Aqueous ammonia instead of anhydrous
- Aqueous HCl in place of anhydrous HCl
- Sulfuric acid in place of oleum
- Wet benzoyl peroxide in place of dry
- Dynamite instead of nitroglycerine

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

443

Less severe processing conditions

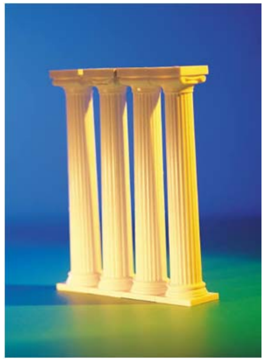
- Ammonia manufacture
  - 1930s – pressures up to 600 bar
  - 1950s – typically 300-350 bar
  - 1980s – plants operating at pressures of 100-150 bar were being built
- Result of understanding and improving the process
- Lower pressure plants are cheaper, more efficient, as well as safer

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

444

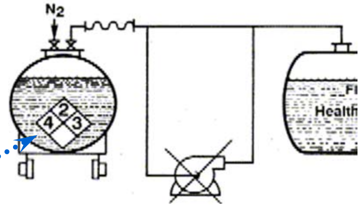
Pillar Four

Minimize
Substitute
Moderate
Simplify



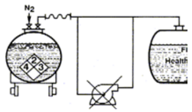
Simplify

To ***simplify*** is to eliminate unnecessary complexity.



(<u>Not</u> "first-order" inherent safety, since the underlying hazard is still there.)

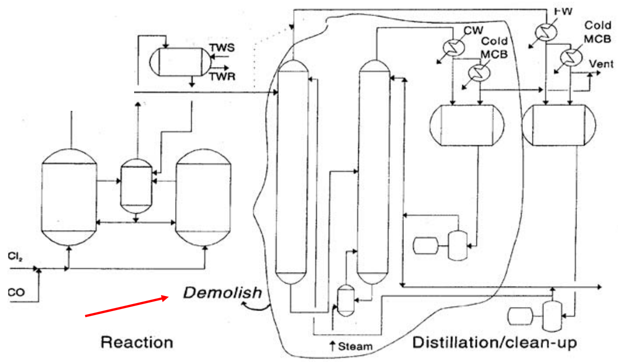
Simplify



Some ***simplification*** strategies:

- **Use simpler equipment arrangement:**
  - Gravity flow
  - Natural convection
  - Collocation of shutoff valves
- **Eliminate interconnections** to reduce the likelihood of inadvertent mixing
- **Minimize number of flanges, connections, and other potential leak locations**

Simplify



Simplification of Dow Phosgene Unit for MDI Production

R. Gowland, "Applying Inherently Safer Concepts to a Phosgene Plant Acquisition," *Process Safety Progress 15*(1), 57

DISCUSSION

- An inherent safety review recommends eliminating intermediate storage of a hazardous raw material:

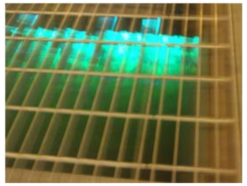
Raw Material Manufacture → Raw Material Usage

- What are the inherent safety <u>benefits</u>?
  -
  -
- What are the possible <u>drawbacks</u>?
  -
  -

Case Study: Substitution at Wastewater Plant

Chlorine alternative : *Cl_2*

- **Alternative Disinfection (UV radiation)**



Wastewater plant chlorination process– Substitute


2-25 ton Cl_2


Cl_2 Evaporators


Chlorinator

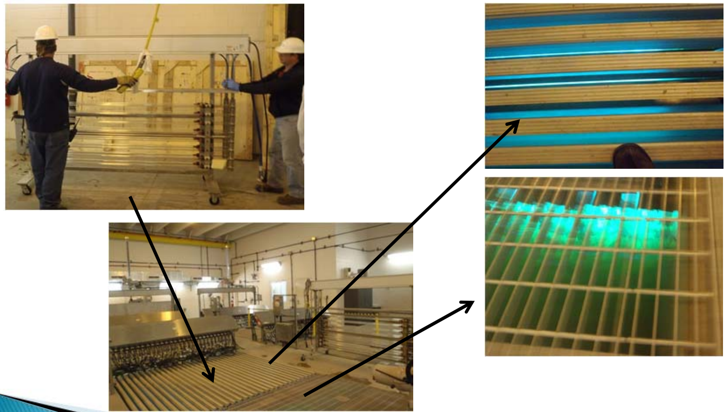

Shower/Eyewash


Chlorine contactor

SO_2 to remove excess chlorine before discharge – Substitute


Two 15 ton SO_2

Ultraviolet disinfection replaces both Cl_2 and SO_2– Substitute



453

Bulk chemical removed from process –Substitute

2-25 ton Cl_2

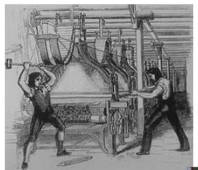
2-15 ton SO_2

454

Inherently Safer Chemistry Risks and Regulations

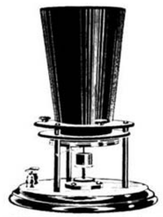
SAND No. 2012-7064C
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

The world and its inventions are always changing



Luddite loom smashing

Rapier weaving machine



1876 - Bell's original telephone

Smart phone

Photo Credits: Wikipedia – public domain

456

Chemical management is necessary to society

- New chemicals and chemical industries are part of modern life.
- Chemicals can provide an increased quality of life and an increased length of life
- Chemical hazards can also cause health and environmental damage.
- Informed chemical regulation can enhance the safety and security of chemical usage

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

457

Regulations are informed by natural science & public opinion

- Change must be managed
- Tradeoffs must be measured

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Economic trade and regulations are important factors

Discussion

- Can you give an example of unintended consequences due to trade practices?
- Can you give an example of unintended consequences due to regulations?
- What is risk transfer?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Examples of risk transfer and unintended consequences

Transboundary shipment of waste

Cement production in Europe vs North Africa

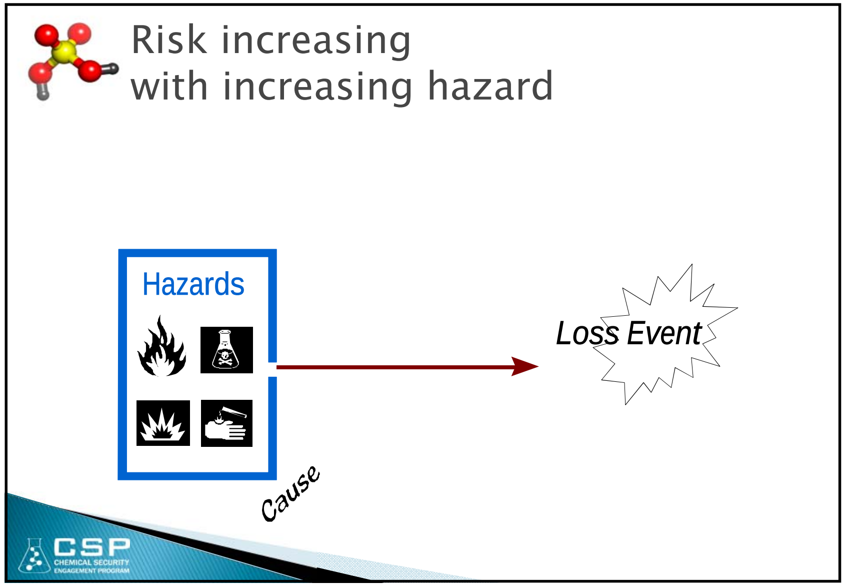
Palm oil production for transboundary biofuel

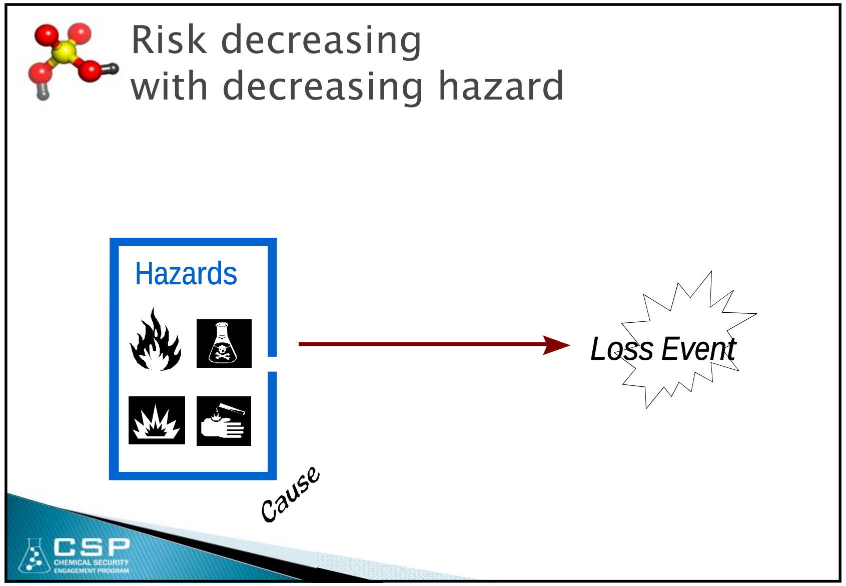
Ethanol fuel production from corn

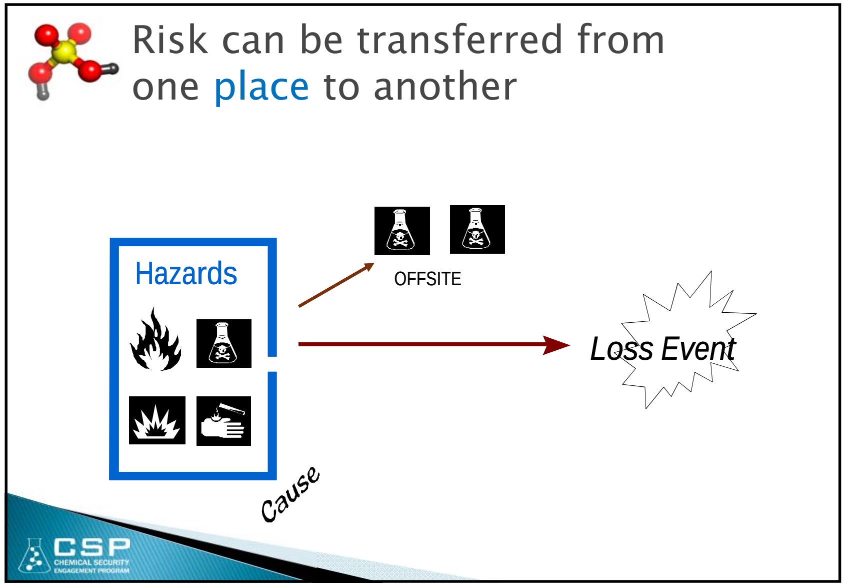
E-waste export and recycling

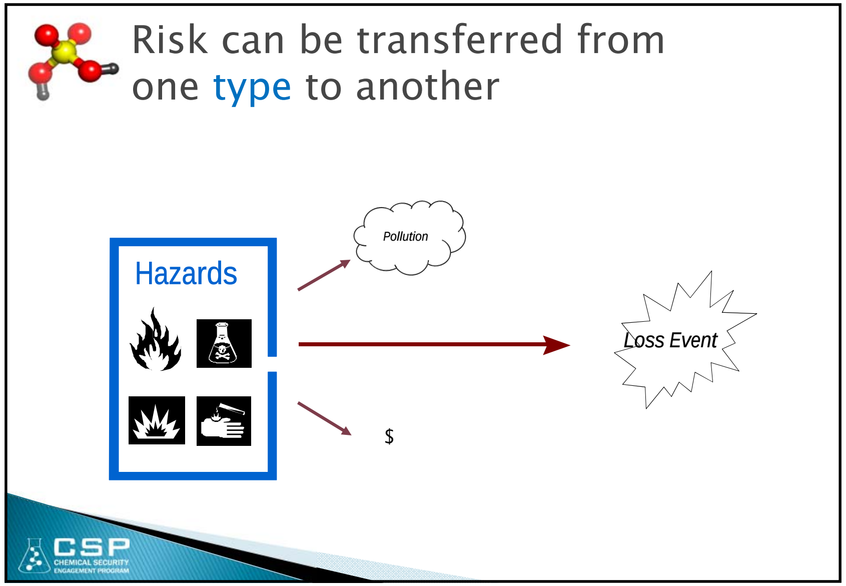
Risk can be transferred to a place where the ultimate risk increases or even decreases

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

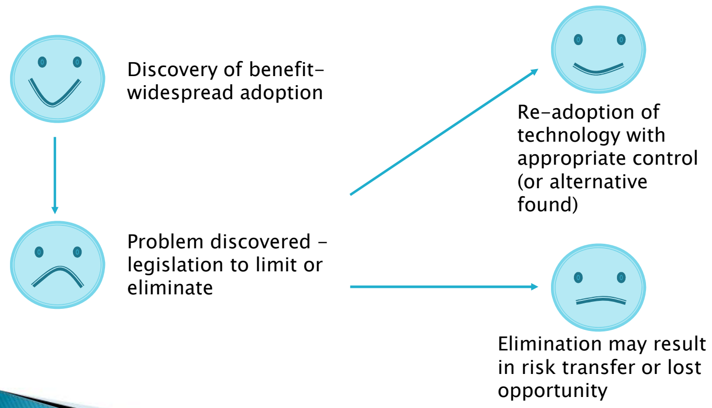

Risk increasing
with increasing hazard
Hazards
Loss Event
Cause
CSP
CHEMICAL SECURITY
ENGAGEMENT PROGRAM


Risk decreasing
with decreasing hazard
Hazards
Loss Event
Cause
CSP
CHEMICAL SECURITY
ENGAGEMENT PROGRAM


Risk can be transferred from
one place to another
OFFSITE
Hazards
Loss Event
Cause
CSP
CHEMICAL SECURITY
ENGAGEMENT PROGRAM


Risk can be transferred from
one type to another
Pollution
Hazards
Loss Event
$
CSP
CHEMICAL SECURITY
ENGAGEMENT PROGRAM

The natural history of a technology



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

465

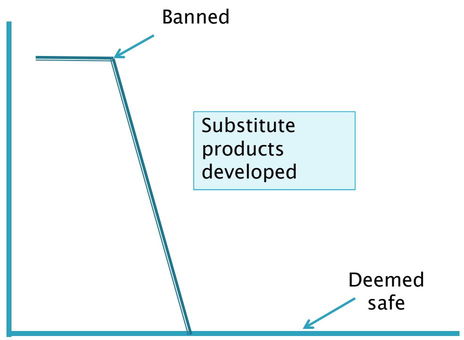
Discussion question

- Can you identify a particular chemical that was accepted by society and then determined to be hazardous ?
  -
  -
  -
- What was eventually done?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

466

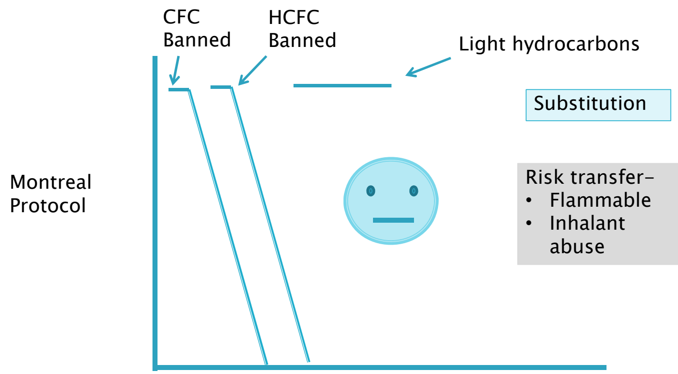
Cyclamates (artificial sweetener)



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

467

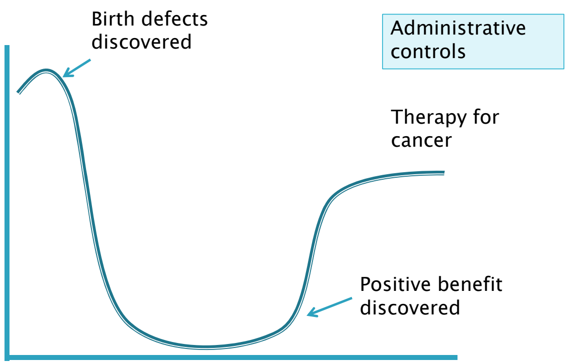
Propellants (spray cans)



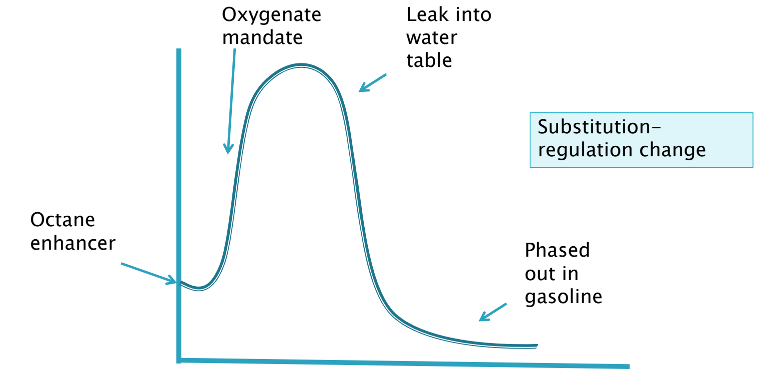
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

468

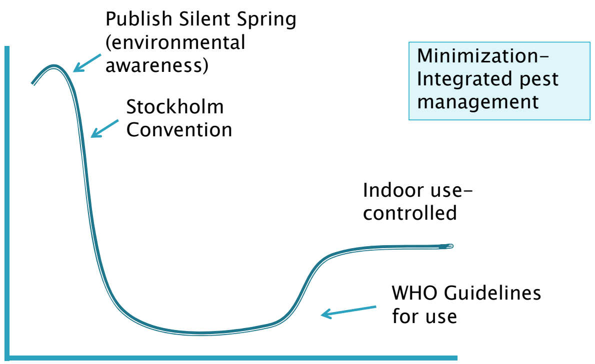
Thalidomide (therapy drug)



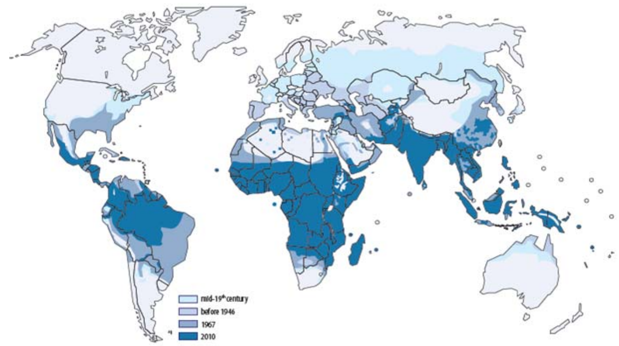
MTBE (gasoline additive)



DDT (pesticide)



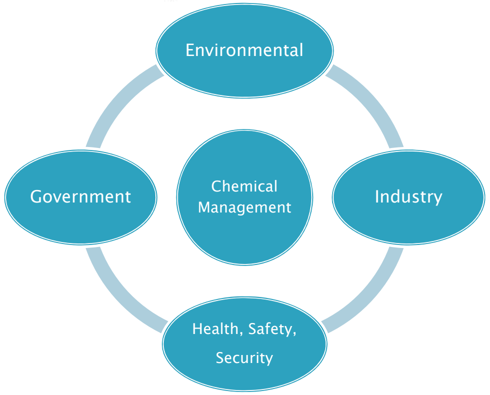
Malaria has retreated globally



Note: This compositive map does not claim to be complete. It is intended to illustrate where malaria transmission existed over the years.

Source: Mendis K, et al and WHO.

Regulation results in mandatory and voluntary improvement



Various stakeholders in the chemical enterprise

Government	Trade Associations	Professional Societies	NGO – Environmental
EPA, DHS, OSHA	ICCA, ACC, SOCMA	AIChE, ACS, RSC	Various
Legislation, implementation	Advocacy, implementation	Science, engineering	Advocacy
Compulsory – TSCA, SARA	Voluntary– Responsible Care	Voluntary	Voluntary

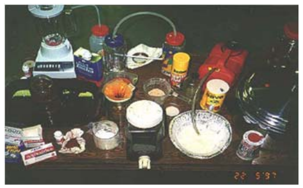
International Bodies –WHO, UNEP, FAO, OECD, ECHA

Regulation must also consider security (dual-use chemicals)

Chemical	Legitimate use	Illegitimate use
Ammonium Nitrate	Fertilizer, Explosive	Improvised Explosive
Sodium Cyanide	Mining, Jewelry	Poisoning, Coral reef fishing
Pseudoephedrine	Medicine	Drug making
Chlorine	Chemicals, disinfection	Poisoning

Dual-use chemical example: Pseudoephedrine

- Common ingredient in cold medicines
- Precursor to crystal methamphetamine
- Recipes on web



- Clandestine meth labs in US, 2002
  - -Caused 194 fires, 117 explosions, and 22 deaths
  - -Cost $23.8 million for cleanup

US DEA, http://www.deadiversion.usdoj.gov/pubs/brochures/pseudo/pseudo_trifold.htm, viewed Dec 2007

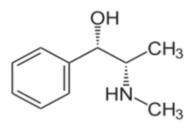
Pseudoephedrine: Regulation / Voluntary

The two key precursor chemicals used in methamphetamine production, ephedrine and pseudoephedrine are not under international controls. However, they are included in a special monitoring list of chemicals not included in the 1988 UN Convention, but for which substantial evidence exists of their use in illicit drug manufacture. – 2012 International Narcotics Control Strategy Report

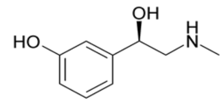
FDA continues to consider NDA-approved and over the counter monograph products containing pseudoephedrine as safe and effective for their intended uses. Measures restricting the sale of pseudoephedrine to achieve important public safety goals that would result from reduced product misuse should be balanced with the need to maintain access for legitimate use. –U.S. Senate Testimony– Dr. Charles Ganley – 2010

http://www.state.gov/j/inl/rls/nrcrpt/2012/

Pseudoephedrine – Inherently Safer Technology: Substitution



Pseudoephedrine



Phenylephedrine

The substitute is less effective because it is broken down in the stomach

Dual-use chemical example: Cyanide

Therence Koh/AFP/Getty Images

- Widely used in mining and metal plating industries, but is also a well known poison.
- Product tampering-Tylenol capsules
- Used for illegal reef fishing
- Popular with criminals and terrorists because it is relatively easy to obtain
- HCN is CW agent AC

Wikipedia

Cyanide fishing: squeeze bottle – ian.umces.edu/imagelibrary/

Cyanide Code - Voluntary

The "**International Cyanide Management Code For The Manufacture, Transport and Use of Cyanide In The Production of Gold**" is a voluntary industry program for the gold mining industry to promote:

- Responsible management of cyanide used in gold mining
- Enhance the protection of human health, and
- Reduce the potential for environmental impacts.

Signatories to the Cyanide Code must be audited by an independent third party to demonstrate their compliance with the Cyanide Code.

Audit results are made public.

http://www.cyanidecode.org/

Cyanide Mining– Regulation

European Directive 2006/21/EC on the management of waste from extractive industries. Article 13(6) requires "the concentration of weak acid dissociable cyanide in the pond is reduced to the lowest possible level using best available techniques", and at most all mines started after 1 May 2008 may not discharge waste containing over 10ppm weak acid dissociable (WAD) cyanide, mines built or permitted before that date are allowed no more than 50ppm initially, dropping to 25ppm in 2013 and 10ppm by 2018.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

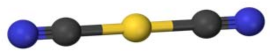
Cyanide Inherently Safer Tech. Substitution–Minimization

Gold Mining

- Thiosulfate
- Proprietary Extraction

Metal Plating

- Reduce concentration
- ZnCN with ZnCl
- CuCN with $CuSO_4$



$[Au(CN)_2]^-$

There are no easy substitutes for cyanide in mining gold or in some metal finishing applications.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Dual-use chemical example: Fertilizer bomb

Photo: US DOD

- Ammonium nitrate fertilizer and fuel oil (diesel, kerosene)
- Used to bomb building in Oklahoma City, OK, USA– April 1995
  - with nitromethane and commercial explosives
  - 168 dead, including children
- Favored by IRA, FARC, ETA, etc.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Ammonium nitrate : regulation

Proposed Rule: Ammonium Nitrate Security Program Published August 3, 2011. Under the proposed rule, the Department of Homeland Security would regulate the sale and transfer of ammonium nitrate pursuant to section 563 of the Fiscal Year 2008 Department of Homeland Security Appropriations Act with the purpose of preventing the use of ammonium nitrate in an act of terrorism.

https://www.dhs.gov/files/laws/ammonium-nitrate-regulations.shtm

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Ammonium nitrate – Inherently Safer Design: Substitution

Fertilizer substitute

- Polymer coated urea
- Sulf-N® 26 -Ammonium nitrate/sulfate

Substitutes for ammonium nitrate are not possible for explosives applications

Slow release polymer coated urea

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

485

Some resources

- E-Chemportal – Global Information on Chemical Substances
http://www.echemportal.org/echemportal/index?pageID=0&request_locale=en
- National Environmental Methods Index
https://www.nemi.gov/apex/f?p=237:1:1214478717879985
- Organisation for the Prohibition of Chemical Weapons
http://www.opcw.org/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

486

Some resources

- OECD- Environment, Health and Safety Publications
http://www.oecd.org/env/chemicalsafetyandbiosafety/environmenthealthandsafetypublications.htm
- UNEP Flexible Framework for Addressing Chemical Accident Prevention and Preparedness – A Guidance Document
http://www.unep.fr/scp/sp/saferprod/pdf/UN_Flexible_Framework_WEB_FINAL.pdf
- U.S. Chemical Safety Board
http://www.csb.gov/
- Center for Chemical Process Safety
http://www.aiche.org/ccps/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

487

Discussion topic

How can we measure tradeoffs when designing chemical legislation?

What practical legislative steps can be taken for chemical security?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Break

Process Hazard and Risk Analysis

SAND No. 2011-0991 C
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Summary of Presentation

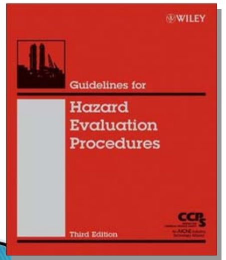
- Resources
- Acronyms
- Basic risk concepts
- Process Hazard Analysis (PHA) defined
- Experience-based versus predictive approaches
- Experience-based—Checklist
- Predictive Qualitative methods (What-If, HAZOP)
- Team meeting logistics
- Documenting PHAs
- Implementing PHA findings and recommendations

Key acronyms

PHA = process hazard analysis
HAZOP = hazard and operability [study]
RAGAGEPs = Recognized as Generally Accepted Good Engineering Practices
CCPS = Center for Chemical Process Safety
ANSI = American National Standards Institute

Hazard and risk analysis resources

CCPS 2008a. Center for Chemical Process Safety, *Guidelines for Hazard Evaluation Procedures,* Third Edition, NY: American Institute of Chemical Engineers.



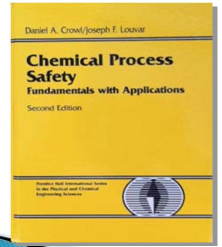
Chapter 4 • Non-Scenario-Based Hazard Evaluation Procedures
4.1 Preliminary Hazard Analysis
4.2 Safety Review
4.3 Relative Ranking
4.4 Checklist Analysis

Chapter 5 • Scenario-Based Hazard Evaluation Procedures
5.1 What-If Analysis
5.2 What-If/Checklist Analysis
5.3 Hazard and Operability Studies
5.4 Failure Modes and Effects Analysis
5.5 Fault Tree Analysis
5.6 Event Tree Analysis
5.7 Cause-Consequence Analysis and Bow-Tie Analysis
5.8 Other Techniques

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Hazard and risk analysis resources

D.A. Crowl and J.F. Louvar 2001. *Chemical Process Safety: Fundamentals with Applications,* 2nd Ed., Upper Saddle River, NJ: Prentice Hall.

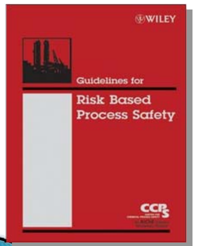


Chapter 10 • Hazards Identification
Chapter 11 • Risk Assessment

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Hazard and risk analysis resources

CCPS 2007a. Center for Chemical Process Safety, *Guidelines for Risk Based Process Safety*, NY: American Institute of Chemical Engineers.



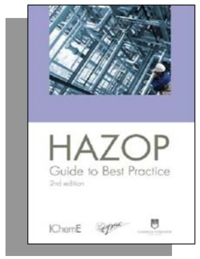
Chapter 9 • Hazard Identification and Risk Analysis
9.1 Element Overview
9.2 Key Principles and Essential Features
9.3 Possible Work Activities
9.4 Examples of Ways to Improve Effectiveness
9.5 Element Metrics
9.6 Management Review

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Hazard and risk analysis resources

B. Tyler, F. Crawley and M. Preston 2008.

HAZOP: Guide to Best Practice, 2nd Edition, Institution of Chemical Engineers, Rugby, UK.



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Hazard and Risk Analysis

- Basic risk concepts

Hazard vs. Risk

Fundamental definitions:

HAZARD
Presence of a material or condition that has the potential for causing loss or harm

RISK
A combination of the severity of consequences and the likelihood of occurrence of undesired outcomes

Source: R.W. Johnson, "Risk Management by Risk Magnitudes," *Chemical Health & Safety* 5(5), 1998

Risk

Constituents of risk:

- Likelihood and
  - Severity

  of Loss Events

$$Risk \;=\; f\,(\,Likelihood,\ Severity\,)$$

Risk

General form of risk equation:

$$Risk \;=\; Likelihood \cdot Severity^{n}$$

Most common form:

$$Risk \;=\; Likelihood \cdot Severity$$

RISK

Example units of measure:

Risk = Likelihood · Severity

$$\frac{\text{injuries}}{\text{year}} = \frac{\text{loss events}}{\text{year}} \times \frac{\text{injuries}}{\text{loss event}}$$

$$\frac{\text{\$ loss}}{\text{year}} = \frac{\text{loss events}}{\text{year}} \times \frac{\text{\$ loss}}{\text{loss event}}$$

What Is a "Process Hazard Analysis"?

A *Process Hazard Analysis* (PHA) is a structured team review of an operation involving hazardous materials/energies, to identify previously unrecognized hazards, identify opportunities to make the operation inherently safer, identify loss event scenarios, evaluate the scenario risks to identify where existing safeguards may not be adequate, and document team findings and recommendations.

What Is a "Process Hazard Analysis"?

A *Process Hazard Analysis* (PHA) is a structured team review of an operation involving hazardous materials/energies, to:

- identify previously unrecognized hazards,
- identify opportunities to make the operation inherently safer,
- identify loss event scenarios,
- evaluate the scenario risks to identify where existing safeguards may not be adequate, and
- document team findings and recommendations.

What Is a "Process Hazard Analysis"?

Process Hazard Analysis (PHA) is a structured team review of an operation involving hazardous materials/energies, to:

- identify previously unrecognized hazards,
- identify opportunities to make the operation inherently safer,
- identify loss event scenarios,
- evaluate the scenario risks to identify where existing safeguards may not be adequate, and
- document team findings and recommendations

Focus of this module

Hazard and Risk Analysis

- Basic risk concepts
- Experience-based vs predictive approaches

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Experience-based approaches

- Some PHA methods determine the adequacy of safeguards without assessing scenario risks
- This is done on the basis of collective past experience
- Compare process with recognized and generally accepted good engineering practices (RAGAGEPs)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Experience-based approaches

- Effective way to take advantage of past experience
- Concentrates on protecting against events expected during lifetime of facility
- Low-probability, high-consequence events not analyzed
- Not good for complex or unique processes

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Experience-based approaches

Examples of experience-based approaches:

- Safety Review
- Checklist Analysis

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Experience-based approaches

Example experience-based approaches:

- Safety Review
- Checklist Analysis

Experience-based approaches

- Checklist
  - Uses a written list of items to verify the status of a system
  - Commonly used in conjunction with another hazard identification method
  - May be used to familiarize inexperienced personnel with a process
  - Common basis for management review
- Addresses material, equipment, and procedures

Experience-based approaches Checklist Activity

- Checklist Activity:
  Form 4 groups
- List at least 5 questions that require a Yes/No answer about a chemical storage area at your site that would be included in a hazard analysis of the area.
  - Example: gas cylinder storage

Experience-based approaches Checklist Activity

Gas cylinders storage area: Possible Checklist Questions

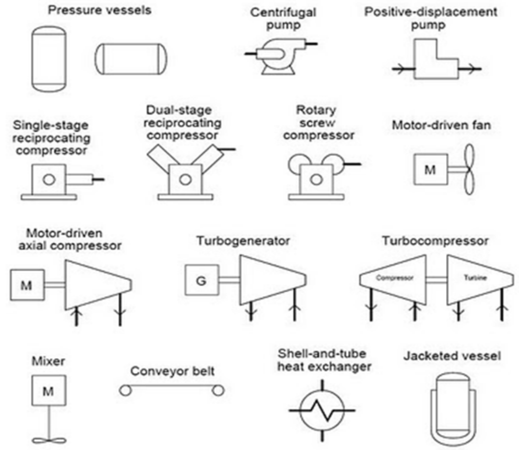
- If cylinders are stored outside, are they stored out of direct sunlight to prevent over pressure?
- Are cylinders secured by means of chocks or chains while in storage?
- Are cylinders stored away from standing water?
- Are cylinders stored so that objects cannot fall on them or strike them?
- Are cylinders stored so that a leak will not enter a lower elevation of a building or process area?
- Are cylinders stored with the valve cover or cap secured in place?

Hazard Identification Methodologies

- Many hazard identification methodologies will be aided by piping and instrumentation diagrams (P&ID) or process flow diagrams (PFD)
- P&ID and PFD present the nominal plant or system layout
  - P&ID is at an equipment and component level
  - PFD is a simplified P&ID to present process level

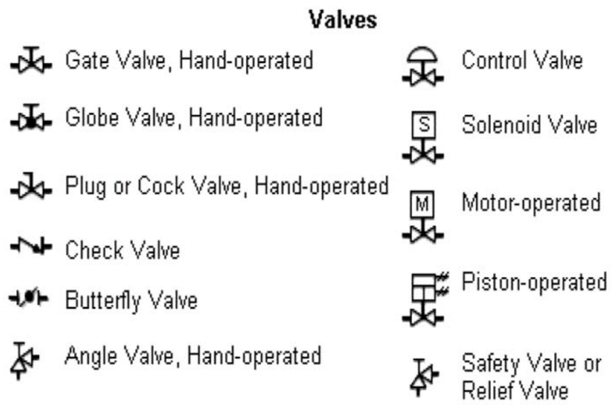
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Common P&ID Legend



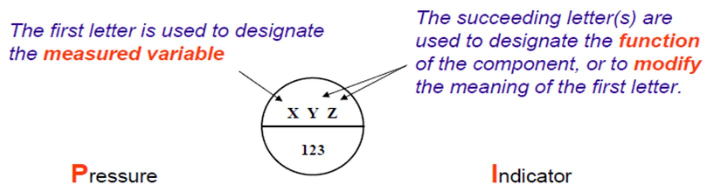
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Common P&ID Legend



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Common P&ID Legend

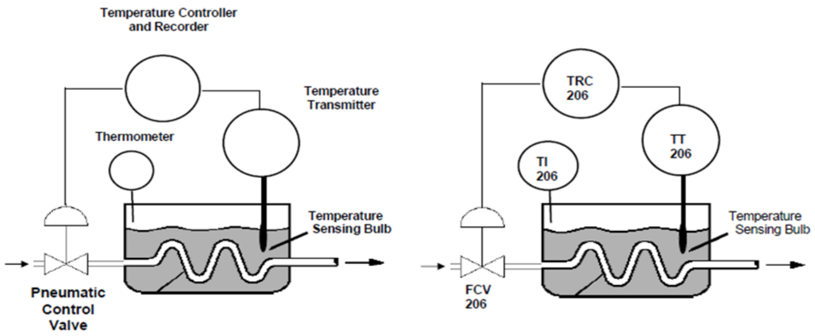


Pressure
Level
Flow
Temperature

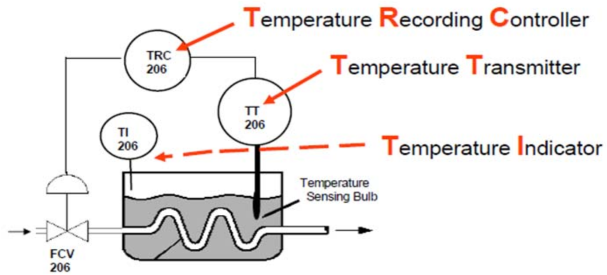
Indicator
Recorder
Controller
Transmitter

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

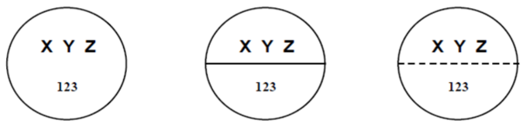
Common P&ID Legend



Common P&ID Legend



Common P&ID Legend



No Line
The instrument is mounted in the field near the process, (close to the operator)

Solid Line
The instrument is mounted in the control room (accessible to the operator)

No Line
The instrument is mounted out of sight (not accessible to the operator)

Predictive studies

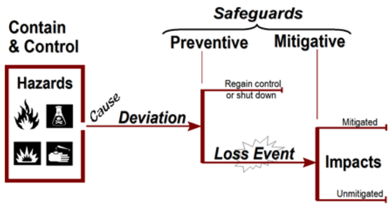
- Supplement adherence to good practice
- Qualitative or quantitative
- Able to study adequacy of safeguards against low probability / high severity scenarios
- All predictive studies are scenario-based approaches

Scenario - definition

Scenario:

An unplanned event or incident sequence that results in a loss event and its associated impacts, including the success or failure of safeguards involved in the incident sequence.

- CCPS 2008a



Scenario necessary ingredients:

- Initiating cause

  AND

- Loss event or safe outcome

<u>Example of a simple scenario:</u>

While unloading a tankcar into a caustic storage tank, the tank high level alarm sounded due to the person unloading not paying close attention to the operation.

The operator noticed and responded to the alarm right away, stopping the unloading operation. Normal production was then resumed.

•What is the *initiating cause*?

•What is the *consequence?*

Predictive studies

Objective of scenario-based approaches:

- Identify and analyze <u>all</u> failure scenarios
  - Not generally possible just by inspection
  - Systematic approach needed
  - In reality, many scenarios eliminated by common sense and experience
    - Negligible likelihood
    - Unimportant consequence

Predictive studies

Some scenario-based approaches:

- What-If Analysis
- What-If / Checklist Analysis
- Hazard and Operability (HAZOP) Study
- Failure Modes and Effects Analysis (FMEA)
- Fault Tree Analysis (FTA)
- Event Tree Analysis (ETA)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Hazard and Risk Analysis

- Basic risk concepts
- Experience-based vs predictive approaches
- Qualitative methods (What-If, HAZOP)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What-If Analysis

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What-If Analysis

Concept: Conduct thorough, systematic examination by asking questions that begin with “What if...”

- Usually conducted by a relatively small team (3-5 persons)
- Process divided up into “segments” (e.g., unit operations)
- Review from input to output of process
- Question formulation left up to the team members

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What-If Analysis

- Question usually suggests an initiating cause.

  "What if the raw material is in the wrong concentration?"

- If so, postulated response develops a scenario.

  "If the concentration of oxidant was doubled, the reaction could not be controlled and a rapid exotherm would result..."

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What-If Analysis

Answering each "What if …" question:

1 Describe potential consequences and impacts

2 If a consequence of concern, assess cause likelihood

3 Identify and evaluate intervening safeguards

4 Determine adequacy of safeguards

5 Develop findings and recommendations (as required)

6 Raise new questions

Move to next segment when no more questions are raised.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Adequacy of safeguards

- Determining the adequacy of safeguards is done on a scenario-by-scenario basis
- *Scenario risk* is a function of:
  - Initiating cause frequency
  - Loss event impact
  - Safeguards effectiveness
- If the *scenario risk* is found to be too high, safeguards are considered inadequate
- Risk based on:
  - Qualitative judgment
  - Risk matrix
  - Risk magnitude

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What-If Exercise

Get into 4 groups and develop a What-IF analysis for the following three scenarios.

List the consequences, safeguards, and recommendations on the What-If worksheet.

1. What-If a chlorine cylinder is dropped from the hoist during cylinder changes?
2. What-If a chlorine main cylinder valve develops a leak while the cylinder is in operation?
3. What-If the pressure reducing valve vent becomes stuck in the open position?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

PROCESS SEGMENT:	SCOPE:		What-If Analysis
REVIEW DATE:	INTENT:		
What If …	**Consequences**	**Safeguards**	**Finding/Recommendation** Comments
1. A chlorine cylinder is dropped from the hoist during cylinder changes?			
2. A chlorine main cylinder valve develops a leak while the cylinder is in operation?			
3. The pressure reducing valve vent becomes stuck in the open position?			

Hazard and Operability Study

HAZOP

HAZOP Study

- HAZOP study process was developed within the process industries
- Team-based approach
- Needs well-defined system parameters
- Used as hazard and/or operability study method
  - Safety issues dominate for existing process
  - Operability issues prevail for new designs
  - Many issues relate to both safety and operability

HAZOP Study

Assumptions:

- No incidents when system operates as intended ("normal operation")
- Failure scenarios occur when system deviates from intended operation ("abnormal situation")

HAZOP Study

- Establish review scope
- Identify study "nodes"
- Establish Node 1 design/operation intent
- Identify Deviation 1 from Node 1 intent
- Identify causes, loss events, safeguards
- Decide whether action is warranted
- Repeat for every node and deviation

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Study nodes

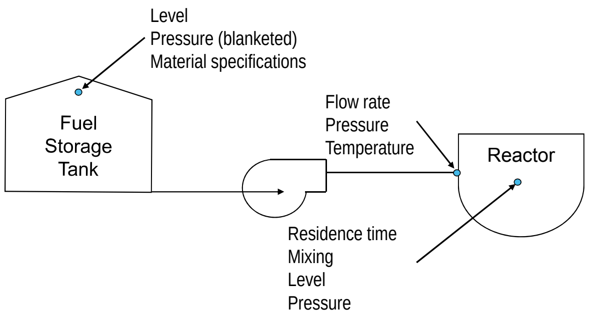
A node is a specific point in a process or procedure where deviations are studied.

Typical study nodes:

- Process vessel
- Transfer line
  - Strictly: Wherever a process parameter changes
  - At end of line (vessel interface)
  - Line may include pump, valves, filter, etc.
- Procedural step

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Study nodes



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Design/operational

INTENT

The intent describes the design/operational parameters defining normal operation.

- Functions
- Limits
- Compositions
- Procedural steps

It answers one of these questions:
"What is this part of the process designed to do?"
"What is supposed to be done at this point in time?"

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Design/operational intent

A complete design/operational intent includes:

- Equipment used
- All functions or operations intended to be achieved in this part of the process
- All intended locations/destinations
- Quantitative limits for all pertinent process parameters
- Intended stream composition limits

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Design/operational intent

Example:

The intent of a storage tank is to:

Maintain a working inventory of liquid RM-12 which is supplied by tank (rail) cars from outside suppliers. The node does not include the tank loading systems.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

HAZOP Guide Words

Guide Words are applied to the design intent to systematically identify deviations from normal operation.

- NONE
- MORE OF
- LESS OF
- PART OF
- AS WELL AS
- REVERSE
- OTHER THAN

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

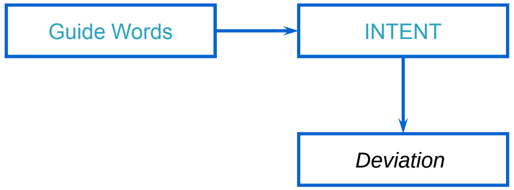
HAZOP Guide Words

Guide Word	Meaning
NONE	Negation of intent
MORE OF	Exceed intended upper limit
LESS OF	Drop below intended lower limit
PART OF	Achieve part of intent
AS WELL AS	Something in addition to intent
REVERSE	Logical opposite of intent occurs
OTHER THAN	Something different from intent

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

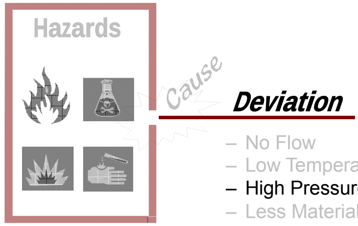
Deviations from Intent

- Do not begin developing deviations until intent is fully described, documented and agreed upon
- List of deviations can be started as soon as intent is established



Deviations

A *deviation* is an abnormal situation, outside defined design or operational parameters.



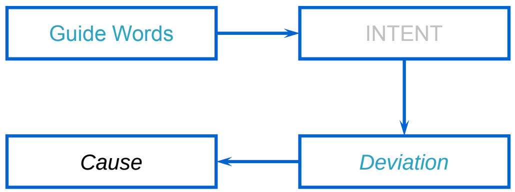
- No Flow
- Low Temperature
- High Pressure *(exceed upper limit of normal range)*
- Less Material Added
- Excess Impurities
- Transfer to Wrong Tank
- Loss of Containment
- etc.

HAZOP Deviations Guide

Design Intent Example	NO / NONE	MORE OF	LESS OF
"Contain the working inventory of liquid RM-12"	Containment lost Procedure step skipped No [function] No transfer No agitation No reaction	Procedure started too late Procedure done too long Too much [function] Too much transferred Too much agitation High [controlled variable] High reaction rate High flow rate High pressure High temperature	Procedure started too soon Procedure stopped too soon Not enough [function] Not enough transferred Not enough agitation Low [controlled variable] Low reaction rate Low flow rate Low pressure Low temperature
PART OF	AS WELL AS	REVERSE	OTHER THAN
Part of procedure step skipped Part of [function] achieved Part of [composition] Component missing Phase missing Catalyst deactivated	Extra step performed Extra [function] Transfer from more than one source Transfer to more than one destination Extra [composition] Extra phase present Impurities; dilution	Steps done in wrong order Reverse [function] Reverse flow Reverse mixing	Wrong procedure performed Wrong [function] achieved Transfer from wrong source Transfer to wrong destination Maintenance/test/sampling at wrong time/location

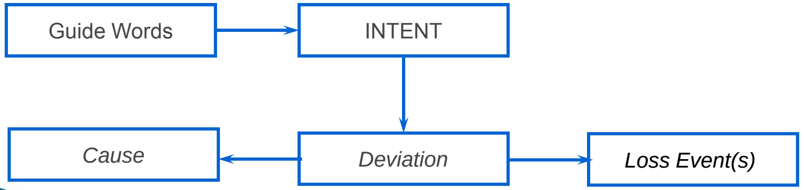
Initiating causes

- Identify deviation cause(s)
  - Must look backward in time sequence
  - Only identify local causes (i.e., in current study node)
  - Most deviations have more than one possible cause



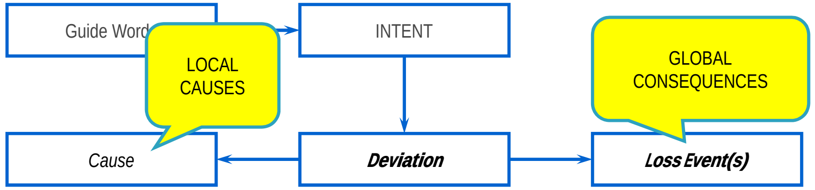
Loss events

- Determine cause and deviation consequences, assuming failure of protection safeguards
- Take scenario all the way to a loss consequence
- Consequences can be anywhere and anytime



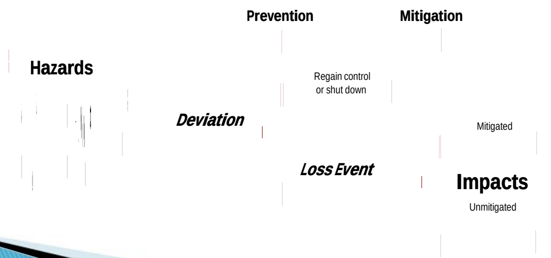
Loss events

- Determine cause and deviation consequences, assuming failure of protection safeguards
- Take scenario all the way to a loss consequence
- Consequences can be anywhere and anytime



Safeguards

- Document preventive safeguards that intervene between the specific Cause-Consequence pair
- Note that different Consequences are possible, depending on safeguard success or failure *(e.g., PRV)*



HAZOP Exercise

- Work in Groups
- Fill out the HAZOPS analysis sheet:
  - Using the Tank T-100 example, and the **Guide Words**, “LEVEL HIGH” and “LEVEL LOW”, list the following:
  - Cause
  - Consequence
  - Safeguards
  - Findings/Recommendations

REVIEW DATE

NODE:

SCOPE:

INTENT:

HAZOP Study

Guide Word	Deviation	Cause	Consequences	Safeguards	Finding/Recommendation Comments

Node 1 T-100 Storage Tank

Review Date:

SCOPE: T-100 Storage Tank

INTENT: Maintain level of Reactant A fuel in T-100 storage tank for transfer to process vessel

HAZOP Study

Guide Word, Deviation	Value	Causes	Consequences	Safeguards	Finding/Rec. # Comments
LEVEL	High	1. High flow into T-100 2. Failure of the T-100 level control system. 3. Pumps-101A and B both stop.	1. Overflow could cause injury to operator in area. 2. Overflow would be contained by secondary containment system. No environmental hazard identified.	Inlet valve, level control systems, and pumps are inspected and replaced on a regular maintenance schedule. There is a redundant level control system. Secondary containment system designed to capture 50% overflow	Increase the frequency of maintenance inspections. Test integrity of secondary containment.
LEVEL	Low		1. Possible damage to Pump, P-101A, impeller, leading to vibration and leak and personal injury.	Inlet valves, level control systems, and pumps are inspected and replaced on a regular maintenance schedule. Pump, P-101A shuts down automatically when level is too low.	Increase the frequency of maintenance inspections.

PHA method selection guide

HAZOP	What-If/Checklist	FMEA	FTA	ETA
By deviation	By checklist item	By component	By loss event	By cause
Best for process operations	*Best for relatively standard operations*	*Best for mechanical and electrical systems*	*Best for complex systems/operations*	*Best to study one or only a few causes*
Good for continuous and procedure-based operations	Good for continuous and procedure-based operations	Good for continuous operations	Good for continuous operations; possible for procedure-based	Good to analyze administrative and engineering controls
Higher level of effort	Lower level of effort	Higher level of effort	Highest level of effort	Higher level of effort
Can analyze complex processes with multiple safeguards	*Mostly appropriate for simpler operations*	*Best analyzes processes with single-point failures*	*Can analyze complex processes with multiple safeguards*	*Can analyze complex processes with multiple safeguards*
Distinguishes between causes and safeguards	Does <u>not</u> distinguish between causes and safeguards	Does <u>not</u> distinguish between causes and safeguards	Distinguishes between causes and safeguards	Distinguishes between causes and safeguards
Only looks at causes that could lead to deviations	Only studies causes from checklist and what-if questioning	Looks at all failure modes of all components	Only studies causes and safeguards related to top event	Looks at all safeguards protecting against cause

Hazard and Risk Analysis PHA Team Review

The following are common to all PHA team reviews:

- Team composition
- Preparation
- First team review meeting
- Final team review meeting

PHA Team Composition

5 to 7 team members optimum

- Team leader (facilitator) – hazard analysis expertise
- Scribe – responsible for PHA documentation
- Key members – should have process/engineering expertise, operating and maintenance experience
- Supporting members – instruments, electrical, mechanical, explosion hazards, etc.

PHA Preparation

At initial scheduling of review and designation as team leader:

- ☐Become familiar with the plant's PSM procedures
- ☐Determine exact scope of PHA
- ☐With PSM Coordinator, select one or more PHA methods that are appropriate to the complexity of the process

  (Different techniques can be used for different parts of the process)

PHA Preparation

~ 6 weeks before start date of team review:

- ❑Compile process safety information for process to be studied
- ❑Obtain procedures for all modes of operation
- ❑Gather other pertinent information
- ❑Determine missing or out-of-date information
- ❑Make action plan for updating or developing missing information prior to the start of the team reviews

PHA Preparation

~ 4 weeks before expected start date:

- ❑Confirm final selection of review team members
- ❑Give copy of PHA Procedures to scribe; emphasize the necessity for thorough documentation
- ❑Estimate the number of review-hours needed to complete PHA team review, or check previous estimate
- ❑Establish an initial schedule of review sessions, coordinated with shift schedules of team members

PHA Timing

Plan PHA team review in half-day sessions of 3 to 3½ hours duration.

- *Optimum:* 1 session/day, 4 sessions/week
- *Maximum:* 8 sessions/week

- Schedule sessions on a long-term plan
- Schedule at set time on set days
- PHA team reviews usually take one or two days to get started, then ~ ½ day per typical P&ID, unit operation or short procedure

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

PHA Preparation

~ 2 to 3 weeks before start date:

- ❑Obtain copies of all incident reports on file related to the process or the highly hazardous materials in the process
- ❑Reserve meeting room
- ❑Arrange for computer hardware and software to be used, if any
- ❑Divide up process into study nodes or segments
- ❑Develop initial design intent for each study node, with the assistance of other review team members as needed

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

PHA Preparation

During the week before the start date:

- ❑Select and notify one person to give process overview
- ❑Arrange for walk-around of facility, including any necessary training and PPE

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

First team review meeting

2 Scope and objectives

- Go over exact boundaries of system to be studied
- Explain purpose for conducting the PHA

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

First team review meeting

3 Methodology

- Familiarize team members with methodology to be used
- Explain why selected methodology is appropriate for reviewing this particular process

First team review meeting

4 Process safety information

- Review what chemical, process, equipment and procedural information is available to the team
- Ensure all required information is available before proceeding

First team review meeting

5 Process overview

- Prearrange for someone to give brief process overview, covering such details as:
  - Process, controls
  - Equipment, buildings
  - Personnel, shift schedules
  - Hazardous materials, process chemistry
  - Safety systems, emergency equipment
  - Procedures
  - What is in general vicinity of process
- Have plant layout drawings available

First team review meeting

6 Unit tour

- Prearrange for tour through entire facility to be included in team review
- Follow all safety procedures and PPE requirements
- Have team members look for items such as:
  - General plant condition
  - Possible previously unrecognized hazards
  - Human factors (valves, labeling, etc.)
  - Traffic and pedestrian patterns
  - Activities on operator rounds (gauges, etc.)
  - Emergency egress routes

First team review meeting

7 Review previous incidents

- Review all incident and near-miss reports on file for the process being studied
- Also review sister-plant and industry-wide incidents for the type of process being studied
- Identify which incidents had potential for catastrophic on-site or off-site / environmental consequences
- Make sure detailed assessment (e.g., HAZOP Study) covers all previous significant incidents

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

First team review meeting

8 Review facility siting

- Discuss issues related to whether buildings intended for occupancy are designed and arranged such that people are adequately protected against major incidents
- Various approaches are possible:
  - API Recommended Practices 752, 753
  - Topical review (e.g., CCPS 2008a page 291)
  - Checklist review (e.g., Appendix F of W.L. Frank and D.K. Whittle, *Revalidating Process Hazard Analyses*, NY: American Institute of Chemical Engineers, 2001)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

First team review meeting

9 Review human factors

- Discuss issues related to designing equipment, operations and work environments so they match human capabilities, limitations and needs
- Human factors are associated with:
  - Initiating causes (e.g., operational errors causing process upsets)
  - Preventive safeguards (e.g., operator response to deviations)
  - Mitigative safeguards (e.g., emergency response actions)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

First team review meeting

9 Review human factors (continued)

- Various approaches are possible:
  - Ergonomic studies
  - Topical review of positive and negative human factors (e.g., CCPS 2008a pages 277-279)
  - Checklist review (e.g., Appendix G of W.L. Frank and D.K. Whittle, *Revalidating Process Hazard Analyses*, NY: American Institute of Chemical Engineers, 2001)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

First team review meeting

10 Identify and document process hazards

- See earlier module on Hazards and Potential Consequences
- Also an opportunity to address inherent safety issues

First team review meeting

To do during the final team review meeting:

- Ensure entire scope of review has been covered
- Read through all findings and recommendations to
  - Ensure each finding and recommendation is understandable to those needing to review and implement them
  - Consolidate similar findings
- Ensure all previous significant incidents have been addressed in the PHA scenarios

Hazard and Risk Analysis PHA report

Goal: Record the results such that study is understandable, can be easily updated, and supports the team's decisions.

- System studied
- What was done
- By whom
- When
- Findings and recommendations
- PHA worksheets
- Information upon which the PHA was based

Report Disposition

- Draft report
  - prepared by scribe
  - reviewed by all team members
  - presented to management, preferably in a face-to-face meeting
- Management input considered by review team
- Final report
  - prepared by scribe
  - reviewed by all team members
  - accepted by management
  - kept in permanent PHA file

Implementing findings & recommendations

What is the most important product of a PHA?

1. The PHA report
2. A deeper understanding gained of the system
3. Findings and recommendations from the study

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Implementing findings & recommendations

What is the most important product of a PHA?

1. The PHA report
2. A deeper understanding gained of the system
3. Findings and recommendations from the study
4. The actions taken in response to the findings and recommendations from the study

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Implementing findings & recommendations

- Findings and recommendations are developed throughout team review
  - Analysis of hazards; inherent safety options
  - Facility siting review
  - Human factors review
  - HAZOP, What-If, etc.
- Basis for determining whether finding or recommendation is warranted:
  - CHECKLIST REVIEW: Code/standard is violated
  - PREDICTIVE ANALYSIS: Scenario risk is too high (also if code/standard is violated)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Implementing findings & recommendations

Wording of findings and recommendations:

- Be as general as possible in wording of finding, to allow flexibility in how item is resolved

Install reverse flow protection in Line 112-9 to prevent backflow of raw material to storage	instead of	Install a Cagey Model 21R swing check valve in the inlet flange connection to the reactor

- Describing the concern as part of the finding will help ensure the actual concern is addressed
- Use of words such as these warrants follow-up to ensure the team's concern was actually addressed:
  - CONSIDER…
  - STUDY…
  - INVESTIGATE…..

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

PHA risk-control actions

Example risk-control actions:

- Alter physical design or basic process control system
- Add new layer of protection or improve existing layers
- Change operating method
- Change process conditions
- Change process materials
- Modify inspection/test/maintenance frequency or method
- Reduce likely number of people and/or value of property exposed

PHA action item implementation

"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."

- OSHA PSM Standard, 29 CFR 1910.119(e)(5) and U.S. EPA RMP Rule, 40 CFR 68.67(e)

1 – Document findings & recommendations

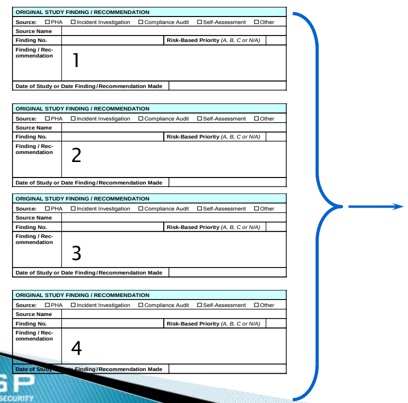
Example form:

ORIGINAL STUDY FINDING / RECOMMENDATION			
Source: ☐ PHA ☐ Incident Investigation ☐ Compliance Audit ☐ Self-Assessment ☐ Other			
Source Name			
Finding No.		**Risk-Based Priority** *(A, B, C or N/A)*	
Finding / Recommendation			
Date of Study or Date Finding / Recommendation Made			

2 – Present findings & recommendations

PHA team

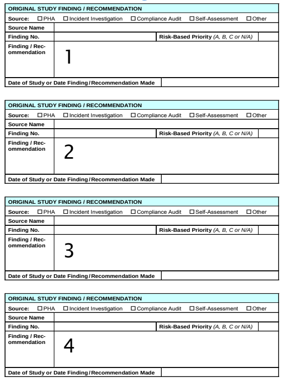
Line management



2 – Present findings & recommendations

PHA team

Line management



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

3 – Line management response

For each PHA team finding/recommendation:

ACTION COMMITTED TO BY MANAGEMENT		
Specific Action To Be Taken		
To Be Completed By		*Time extension requires management approval*
Responsible Person		

Suggestions:

- Use database or spreadsheet
- Flag imminent and overdue actions
- Periodically report overall status to top management

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Example

ORIGINAL STUDY FINDING / RECOMMENDATION			
Source:	☒ PHA ☐ Incident Investigation ☐ Compliance Audit ☐ Self-Assessment ☐ Other		
Source Name	Formaldehyde Unloading PHA		
Finding No.	PHA-UF-11-01	**Risk-Based Priority** *(A, B, C or N/A)*	B
Finding / Recommendation	*Safeguards against formaldehyde storage tank overfilling are considered to be inadequate due to the signals for the controlling level indication and the high level alarm both being taken off of the same level transmitter. Options for consideration: Take manual level reading before unloading into the tank to cross-check adequate capacity for unloading; add separate high level switch for the high level alarm.*		
Date of Study or Date Finding / Recommendation Made	1 March 2011		

ACTION COMMITTED TO BY MANAGEMENT		
Specific Action To Be Taken	The following steps are to be taken to adopt and implement finding PHA-UF-11-01: (1) Add a separate high level switch on the formaldehyde storage tank, using a different level measurement technology than the controlling level sensor. (2) Add the new level switch, in addition to the high level alarm, to the MI critical equipment list and schedule for regular functional testing. (3) Until the new level switch is installed, implement a temporary procedural change to take manual level readings before unloading into the tank to cross-check adequate capacity for unloading, ensuring proper PPE is specified and used for performing the manual level readings.	
To Be Completed By	1 September 2011	*Time extension requires management approval*
Responsible Person	I. M. Engineer	

Chemical SAFETY AND SECURITY TRAINING

4 – Document final resolution

Document how each action item was implemented.

FINAL RESOLUTION		
Resolution Details *(attach drawings, procedures, etc.)*		
Associated MOC(s)		
DATE COMPLETED		
Date Communicated		
How Communicated		*Attach documentation of the communication(s)*

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Communication of actions

Communicate actions taken in response to PHA findings and recommendations.

TO WHOM?

- To operating, maintenance and other employees whose work assignments are in the process and who may be affected by the recommendations or actions

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Communication of actions

HOW?

- Train through plant training program when needed
  - Use appropriate techniques
  - Verify understanding
- Otherwise inform, such as by
  - Safety meetings
  - Beginning-of-shift communications
  - E-mail
- Document communications

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Communication of actions

WHAT?

- Physical changes
- Personnel or responsibility/accountability updates
- Operating / maintenance procedures
- Emergency procedures; Emergency Response Plan
- Safe work practice procedures
- Control limits or practices

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

DISCUSSION

WHY?

What are two or more reasons why it is important to communicate PHA action items to affected employees?

-
-
-
-

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Final word

The task of the PHA team is to identify where action is needed, not to redesign the system.

Summary of Presentation

- Defined Process Hazard Analysis (PHA)
- Compared experience versus scenario types of analysis
- Described the use of checklists
- Gave an example of a What-If analysis
- Gave an example of a HAZOPS analysis
- Described the elements of a PHA team
- Discussed documenting and communicating PHA results

Day 3

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Safe Work Practices

SAND No. 2011-0785C

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-AC04-94AL85000.

Process Safety Management

Hazards

- •Material hazards
- •Energy hazards
- •Chemical interaction hazards

Controls

- •Job hazard analysis
- •Operating procedures (OPs)
  - •Safe Work Practices
    - •Lockout-Tagout
    - •Confined space
    - •Line breaking
- •Hot work permit

Job Hazard Analysis

Job Hazard Analysis focuses on job tasks as a way to identify hazards before they occur. It focuses on the relationship between the worker, the task, the tools, and the work environment.

Not the same as process hazard analysis.

Essential Steps in Job Hazard Analysis

- Involve your employees!
- List, rank, and set priorities for hazardous jobs
- Review your accident history/lessons learned
- Conduct a preliminary job review
- Outline the steps or tasks

What Jobs Need a Hazard Analysis ?

- Jobs with the highest injury or illness rates
- Jobs with the potential to cause severe or disabling injuries or illness
- Jobs in which one simple human error could lead to a severe accident or injury;
- Jobs that are new to your operation or have undergone changes in processes and procedures; and
- Jobs complex enough to require written instructions

The Job Hazard Analysis Asks Several Questions

- What can go wrong?
- What are the consequences?
- How could it happen?
- What are other contributing factors?
- What is the likelihood of an incident?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Job Hazard Analysis Form

Job Hazard Analysis

Date: ____________ JHA Number: ________ Steps: 1 through 5

Location of Task: ________________________________

Task Description: ________________________________

Step 1 Description	Hazards	Preventive Measure(s)
Step 2 Description	Hazards	Preventive Measure(s)
Step 3 Description	Hazards	Preventive Measure(s)
Step 4 Description	Hazards	Preventive Measure(s)
Step 5 Description	Hazards	Preventive Measure(s)
Safe Job Procedures		

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Exercise

Task Description: Worker reaches into metal box to the right of a grinding wheel machine, grasps a 15-pound casting and carries it to grinding wheel. Worker grinds 20 to 30 castings per hour.

- What are the hazards? Consider the equipment hazards, the material hazards, and ergonomic stressors.
- What controls can mitigate the hazards?

Credit: US Occupational Safety and Health Administration

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Safe Work Practices

Safe Work Practices provide for the control of hazards during work activities

Safe Work Practices required by the US Process Safety Management Standard:

- Lockout -Tagout
- Confined space entry
- Line breaking
- Control over entry by maintenance contractors

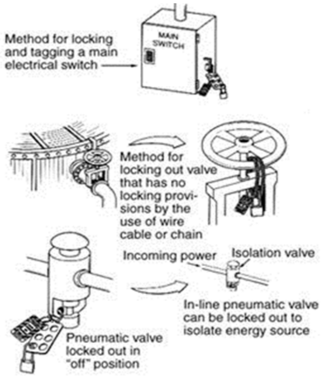
They are generally written methods outlining how to perform a task with minimum risk to people, equipment, materials, environment, and processes.

They are issued
- to specific persons
- for a specific time period
- for a specific job

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Lockout-Tagout (LOTO) Addresses *All* Forms of Hazardous Energy

- Electrical energy *from generated elec*trical power, static sources, or electrical storage devices (batteries or capacitors)
- Kinetic (mechanical) energy – *in the* moving parts of mechanical systems
- Potential energy –*stored in pressure* vessels, gas tanks, hydraulic or pneumatic systems, and springs
- Thermal energy *(high or low temperature)* resulting from mechanical work, radiation, chemical reactivity, or electrical resistance



Credit: Lawrence Berkeley Laboratory

Lockout-Tagout Definition

Lockout-Tagout (LOTO) or lock and tag is a safety procedure which is used in industry and research settings to ensure that dangerous machines are properly shut off and not started up again prior to the completion of maintenance or servicing work.

OSHA 1910.147

Lockout-Tagout (LOTO)

- U.S. Department of Labor Statistics:
  - Approximately 3 million workers are at risk of injury if lockout-Tagout is not properly implemented.
  - LOTO prevents an estimated <u>120 fatalities</u> and <u>50,000 injuries</u> each year.
  - Workers injured on the job from exposure to hazardous energy lose an average of <u>24 workdays</u> for recuperation.
  - United Auto Workers (UAW) reported that 20% of their fatalities between 1973 and 1995 were attributed to inadequate hazardous energy control procedures.

LOTO Incidents

- A worker attempted to prevent an elevator from moving by jamming the doors open with a wooden plank while the elevator was on the second floor and then turning off the outside panel switch on the main floor. Worker was killed when the elevator returned to the main floor.
- Worker turned off the power to a packaging machine and attempted to remove the jam. Residual hydraulic pressure activated the holding device and the worker's arm was caught in the packaging machine.
- A mechanic was repairing an electrically operated caustic pump and had turned off the pump toggle switch. A co-worker dragged a cable across the toggle switch and caustic liquid was sprayed on the mechanic.

Steps to Safe LOTO

- Prepare for shutdown
- Shutdown machine or piece of equipment
- Isolate or block all hazardous energy sources for the equipment
- Apply lockout or tagout devices
- Release all stored energy
- Verify energy isolation
- Perform work

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Steps to Release from LOTO

- Make the work area safe
- Check the work area to ensure individuals are clear of the hazard area
- Remove locks, tags, and devices
- Notify affected workers
- Re-energize

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

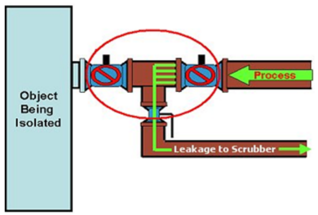
Isolation of Energy

LOTO Practices-

•Only <u>one</u> key for each lock the worker controls
•<u>Only</u> the worker who installs lock can remove it
•Shift changes- New lock added <u>before</u> old one removed
•*Authorized employee* for group lockout device
•LOTO program
  •Energy control procedures
  •Training
  •Periodic inspections
•Alternatives (US regulation)
  •Cord & plug
  •Hot tap procedures

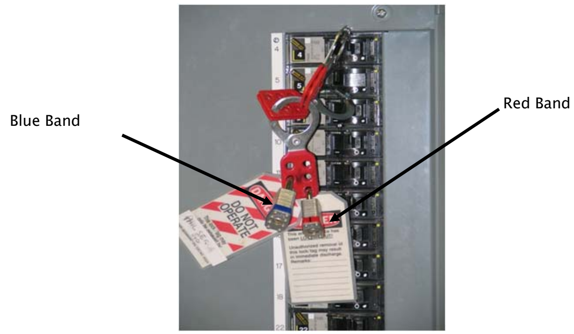
Dissipation or Control of Energy

•Blind or blank piping
  •Lock and tag inline valves
•Remove stored energy-springs, hydraulics



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Each Company Assigns Unique Locks and Tags



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

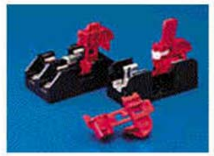
LOTO Locks and Tags

Lock Self Adhesive Band , IDEAL Part Number 34-003

Other LOTO Devices

BALL VALVE LOCKOUTS - Brady Catalog #65666 & #65669 Panduit Catalog #PSL-BV1 & #PSL-BV2 (Similar)

GATE VALVE LOCKOUT - Brady Catalog #65560 to 65564



Circuit Breaker LOCKOUT...OPEN

Circuit Breaker LOCKOUT...LOCKED

Case Study

Replacement of Nitrogen Pressure Vessel Seals

A group of employees are assigned to replace the head seals on twelve large nitrogen pressure vessels (accumulator bottles) at a manufacturing facility. Each pressure vessel has an operating pressure of about 5,000 psig. Replacement of the seals on each vessel requires that its head be opened, releasing any vessel contents to the atmosphere. The vessels lack individual gauges to indicate internal pressure levels.

Credit: US Occupational Safety and Health Administration

Case Study

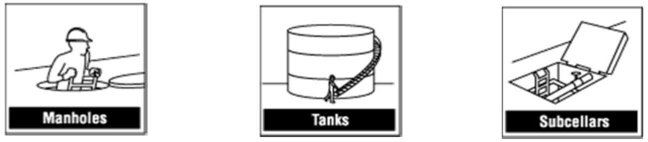
- Did the pressure within the nitrogen vessels constitute hazardous energy?
- Were the employees performing a servicing and/or maintenance operation that was subject to unexpected energization, start up, or release of hazardous energy?
- Would the group lockout or tagout provisions apply to this operation?

Confined Space

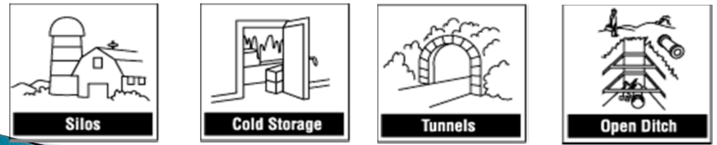
Confined space is any space that has:

- Limited or restricted means of entry or exit;
- Is large enough for a person to enter to perform tasks and is not designed or configured for continuous occupancy

Confined Space



All of these spaces constitute a confined space…



Credit: Canadian Centre for Occupational Health and Safety

Permit-Required Confined Space

- Contains or has the potential to contain a hazardous atmosphere
- Contains a material that has the potential for engulfing the entrant
- Has an internal configuration that might cause an entrant to be trapped or asphyxiated by inwardly converging walls or by a floor that slopes downward and tapers to a smaller cross section
- Contains any other recognized serious safety or health hazards
- Work activities may introduce serious health & safety hazards
  - Welding
  - Spray paintings or coatings

Confined Space Incidents

60% of fatalities are of would-be rescuers!

- 2003-City engineer killed in landfill manhole when retrieving flow meter
- 2004-Mechanic dies from lack of oxygen in transport tank
- 2005-A utility cleanup worker for a brick manufacturer suffocated in a storage silo
- 2006-Welder dies during welding repair inside of cargo tank compartment

Confined Space Permit

- Essential Elements of a CS Permit:
  - List potential hazards
  - List hazard controls
    - PPE, ventilation, barricades,
    - line blanking. LOTO
  - Communication equipment
  - Emergency & retrieval equipment
  - Pre-entry & continuous monitoring values
    - Oxygen, flammability, toxicity concentrations
  - Calibration/bump test information

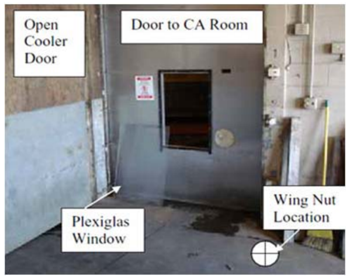
Confined Space Alternate Procedures

1. The *only* hazard posed by the space is an actual or potential atmospheric hazard controlled by mechanical ventilation.
   - Example: Underground communication vaults
2. No actual or potential atmospheric hazards, and all hazards are eliminated without entering the space.
   - Energy isolation-LOTO
   - Pipe or line isolation
   - Shielding of entrapment, mechanical hazards
   - Fall protection

Credit: Utah Safety Council

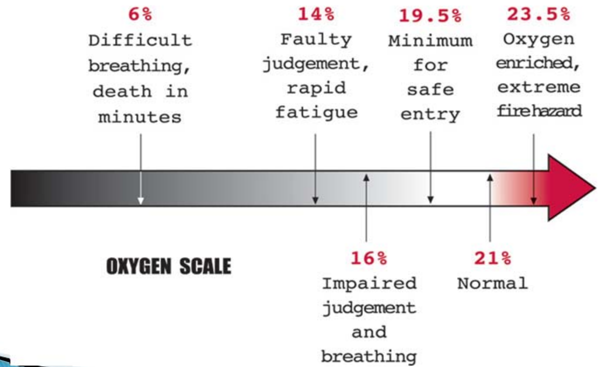
Atmospheric Hazards in Confined Spaces

- Oxygen Deficiency
- Oxygen Enrichment
- Flammable Vapors
- Flammable Gases
- Combustible Dust
- Toxic Vapors or Gases



Controlled Atmosphere Storage Room
Credit: US NIOSH

Oxygen Concentration



Atmospheric Testing of the Confined Space

1. Oxygen is tested first
   Combustible gas meters are oxygen-dependent and will not provide reliable readings when used in oxygen-deficient atmospheres.

2. Combustible gases and vapors are tested second
   The threat of fire and explosion is a more immediate acute hazard

3. Toxic atmospheres are tested last
   In most instances, the exposure limit for a toxic gas or vapor is less likely to be exceeded than the flammability limit over a short period of time.

Many modern direct-reading instruments provide simultaneous readings of multiple gases.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Example of Need to Air Sample for Toxics

- American Conference of Governmental Industrial Hygienists (ACGIH) short term exposure limit (STEL) to styrene exceeded
  - 186 parts per million (ppm) measured as STEL
  - ACGIH STEL is 40 ppm
  - Standard set to minimize the potential of irritation to the eyes and respiratory tract
- Task involved positioning and securing of uncured liner material in a sewer manhole.
- Lining expanded and off gassed styrene
- Manhole was under continuous ventilation
- Oxygen and flammable limits in acceptable range

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Confined Space Air Monitoring Poor Practices

- No monitoring checklist
- Using your senses to detect atmospheric hazards
- No training in gas detection monitoring
- No factory instrument calibration
- No daily “bump” test
- No pre-entry monitoring
- No continuous monitoring
- No attendant trained in monitoring

Credit: OC Environmental Services

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Emergency During Entry

•Entrants evacuated–entry aborts.
(Call rescuers if needed).
•Permit is *void*.
•Reevaluate program to correct/prevent prohibited condition.
•Occurrence of emergency (usually) is proof of deficient program.
•No re-entry until program (and permit) is amended.
(May require new program.)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Opening Lines and Vessels "Line Breaking" Definition

Line breaking means the intentional opening of a pipe, line, or duct that is or has been carrying flammable, corrosive, or toxic material, an inert gas, or any fluid at a volume, pressure, or temperature capable of causing injury.

US OSHA "Ammonia High Pressure Receiver Standard Operating Procedure" http://www.osha.gov/SLTC/etools/ammonia_refrigeration/receiving/receiver_sop.html

Hazards of Opening Lines and Vessels

- Hot or cold fluids
- Toxic release and exposure
    - Ammonia
    - Hydrogen Sulfide
- Fire and explosion
    - Hydrocarbons
    - Pyrophoric materials
    - Moisture sensitive materials
- Pressure release
    - Pipeline pigging
    - Steam

Credit: Reagan Safety

Line Breaking Procedures & Permitting

- Operating procedures
- Scope includes both employees *and* contractors
- Permit
    - Identify the hazard
        - SDS, process information
        - Consider cleaning agents which may be reactive
    - Establish required controls
        - Barricades-warning signs, cones, flags
        - Safety equipment-pipe supports, fall protection, fire extinguisher, monitoring equipment
        - Isolate or control system hazards
            - Cool system
            - Depressurize system
            - Flush system
            - LOTO energy sources
        - Appropriate personal protective equipment (PPE)

Line Breaking/Line Opening Procedures

- Additional considerations:
    - Replace broken, corroded and stripped bolts first
    - If transferring flammable chemical residue, bond the container to the pipe
    - Control access to area to authorized personnel
    - Log all isolation valves
    - Ensure personnel are trained and training documented
    - Prepare emergency plan

Credit: Reagan Safety

Hot Work Definition

Hot work is work involving electric or gas welding, torch cutting, grinding, brazing, or similar flame or spark-producing operations.

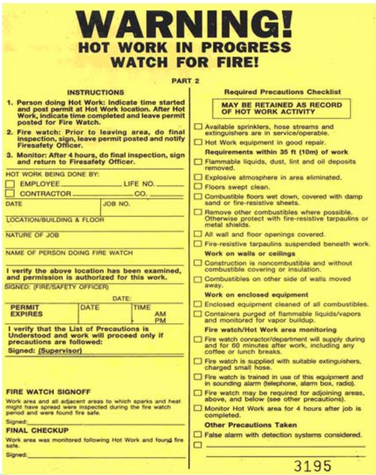
OSHA 1910.252

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

Hot Work Permit

- Fire prevention and protection requirements
- Implemented prior to beginning the hot work operati
- Date(s) authorized for hot work
- Identify the object on which hot work is to be perform
- Permit shall be kept on file until completion of the ho operations.

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM



WARNING!
HOT WORK IN PROGRESS
WATCH FOR FIRE!

PART 2

INSTRUCTIONS

1. **Person doing Hot Work: Indicate time started and post permit at Hot Work location. After Hot Work, indicate time completed and leave permit posted for Fire Watch.**
2. **Fire watch: Prior to leaving area, do final inspection, sign, leave permit posted and notify Firesafety Officer.**
3. **Monitor: After 4 hours, do final inspection, sign and return to Firesafety Officer.**

HOT WORK BEING DONE BY:
☐ EMPLOYEE ______ LIFE NO. ______
☐ CONTRACTOR ______ CO. ______

DATE | JOB NO.

LOCATION/BUILDING & FLOOR

NATURE OF JOB

NAME OF PERSON DOING FIRE WATCH

I verify the above location has been examined, and permission is authorized for this work.

SIGNED: (FIRE/SAFETY OFFICER)

DATE:

PERMIT EXPIRES | DATE | TIME AM PM

I verify that the List of Precautions is Understood and work will proceed only if precautions are followed:
Signed: (Supervisor)

FIRE WATCH SIGNOFF
Work area and all adjacent areas to which sparks and heat might have spread were inspected during the fire watch period and were found fire safe.
Signed: ______

FINAL CHECKUP
Work area was monitored following Hot Work and found fire safe.
Signed: ______

Required Precautions Checklist

MAY BE RETAINED AS RECORD OF HOT WORK ACTIVITY

☐ Available sprinklers, hose streams and extinguishers are in service/operable.
☐ Hot Work equipment in good repair.

Requirements within 35 ft (10m) of work
☐ Flammable liquids, dust, lint and oil deposits removed.
☐ Explosive atmosphere in area eliminated.
☐ Floors swept clean.
☐ Combustible floors wet down, covered with damp sand or fire-resistive sheets.
☐ Remove other combustibles where possible. Otherwise protect with fire-resistive tarpaulins or metal shields.
☐ All wall and floor openings covered.
☐ Fire-resistive tarpaulins suspended beneath work.

Work on walls or ceilings
☐ Construction is noncombustible and without combustible covering or insulation.
☐ Combustibles on other side of walls moved away.

Work on enclosed equipment
☐ Enclosed equipment cleaned of all combustibles.
☐ Containers purged of flammable liquids/vapors and monitored for vapor buildup.

Fire watch/Hot Work area monitoring
☐ Fire watch conractor/department will supply during and for 60 minutes after work, including any coffee or lunch breaks.
☐ Fire watch is supplied with suitable extinguishers, charged small hose.
☐ Fire watch is trained in use of this equipment and in sounding alarm (telephone, alarm box, radio).
☐ Fire watch may be required for adjoining areas, above, and below (see other precautions).
☐ Monitor Hot Work area for 4 hours after job is completed.

Other Precautions Taken
☐ False alarm with detection systems considered.
☐ ______

3195

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

Responsibility for Hot Work is Clearly Outlined

Permit Authorizing Individual – Inspects hot work site before starting

Hot Work Operators – Perform hot work operations

Fire Watch – is posted to monitor safe operations

Designated Area – Location approved for hot work operations.

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

Fire Protection during Hot Work

•All entrances and exits clear
•Correct poor housekeeping practices
•Use appropriate shielding of flammable surfaces
•Keep work area free of unnecessary combustible materials
•Do not use flammable degreasing agents
•Monitor the atmosphere-<10 % of Lower Explosive Limit (LEL)

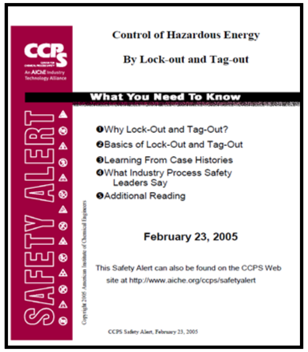
Fire Fighting Equipment and Procedures

- All workers should know the location of the fire fighting equipment in their area.
- Fire extinguishers are checked monthly
- Mark empty fire extinguisher with "empty" and never return empty extinguisher to its fire station.
- All fire extinguishers should be inspected on an annual basis by a certified company.
- All workers should receive training before using fire extinguishing equipment.
- If Fire Watch determines fire may grow beyond control-emergency services must be contacted

Hot Work Area is Controlled by Zoning

•Hot zone- inside permit space
•Warm zone – outside occupied by attendant personnel
•Cold or support zone – equipment and supplies
•Barricades and barriers
•Shields and railings

Resources: LOTO



CCPS

SAFETY ALERT

Control of Hazardous Energy

By Lock-out and Tag-out

What You Need To Know

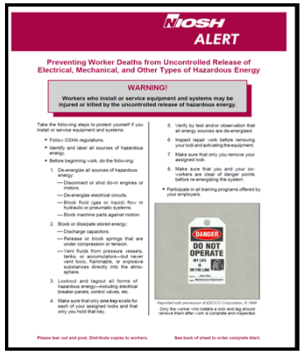
❶Why Lock-Out and Tag-Out?
❷Basics of Lock-Out and Tag-Out
❸Learning From Case Histories
❹What Industry Process Safety Leaders Say
❺Additional Reading

February 23, 2005

This Safety Alert can also be found on the CCPS Web site at http://www.aiche.org/ccps/safetyalert

CCPS Safety Alert, February 23, 2005

http://www.osha.gov/SLTC/controlhazardousenergy/index.html



NIOSH ALERT

Preventing Worker Deaths from Uncontrolled Release of Electrical, Mechanical, and Other Types of Hazardous Energy

WARNING!

Workers who install or service equipment and systems may be injured or killed by the uncontrolled release of hazardous energy.

DANGER

DO NOT OPERATE

http://www.cdc.gov/niosh/docs/99-110/pdfs/99-110sum.pdf

Chemical Hazard Controls
Personal Protective Equipment

SAND No. 2012-1421C
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation,
a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under
contract DE-AC04-94AL85000

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Personal Protective Equipment (PPE)

- Hierarchy of controls
- Limitations of PPE
- Hazard assessment
- Training
- Characteristics of PPE
- Protective clothing
- Gloves
- Eyewear
- Respirators
- Exercise

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

64
2

Hierarchy of Controls

- Limiting exposure to chemical hazards should follow the *Hierarchy of Controls*

1. Eliminate
2. Substitute
3. Engineering control
4. Administrative control
5. Personal Protective Equipment

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

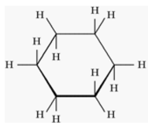
64
3

Hierarchy of Controls

Change the process

eliminate the hazard

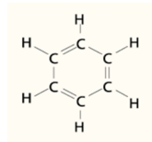
(e.g. Lower process temperature)



Substitution

less-hazardous substance

(e.g. – cyclohexane for benzene)



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

644

Engineering Controls

Enclose the hazard,

- Use a barrier or
- Ventilate
  - Dilution ventilation
  - Local exhaust ventilation (LEV)

645

Administrative Controls

Organizational safety policies,
Standard operating procedures,
Task-specific procedures

646

Personal Protective Equipment (PPE)

- PPE is the *least* desired control
- Does not eliminate the hazard
- Depends on worker compliance
- May create heat stress

647

Personal Protective Equipment (PPE)

- However, PPE may be necessary when:
  - Engineering controls are being installed
  - During emergency response
  - Non-routine equipment maintenance
  - When engineering controls are not feasible
  - To supplement other control methods

Can exposure be controlled by other means?

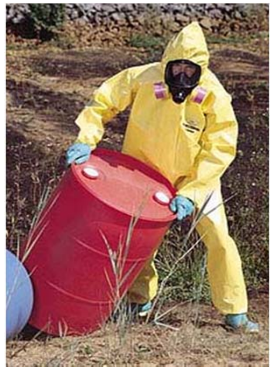
648

PPE Hazard Assessment (Required by US regulations)

- Identify the hazard(s)
  - Chemical
  - Mechanical
  - Electrical
  - Light energy (lasers, welding)
  - Fire response
  - Hot processes
- Identify the potential exposure route
  - Inhalation
  - Skin contact
  - Eye contact
- Select the PPE

PPE Hazard Assessment

- Identify the type of skin contact
  - Immersion
  - Spray
  - Splash
  - Mist
  - Vapor (gaseous)
- Consider the exposure time
  - Incidental contact
  - Continuous immersion
  - Unknown/emergency response



PPE Exercise

- List one work activity in your laboratory or facility that uses PPE
- What is the hazard?
- What is the route of exposure? Inhalation, skin, eyes, or ?
- Are there ways to control exposure to this hazard other than PPE?
- What other ways?

PPE Training

Employees should be trained to know:

- When PPE is necessary
- What PPE is necessary
- How to properly don, doff, adjust and wear PPE
- Limitations of PPE
- Proper care, maintenance, useful life and disposal
- Involve workers in selection

http://www.free-training.com/OSHA/ppe/Ppemenu.htm

PPE Training

Retraining is necessary when there is:

- A change in the hazards
- A change in the PPE required
- Inadequate worker knowledge or use of PPE

http://www.free-training.com/OSHA/ppe/Ppemenu.htm

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

653

General characteristics of PPE

Protective clothing and gloves:
–Act as a barrier to prevent contact with the skin
–Protect against
Toxics
Corrosives
Irritants
Sensitizers (allergens)
Thermal injury (burns)
Physical Trauma

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

654

General characteristics of PPE

Protective clothing and gloves

- When selecting consider:
  - Permeation
    - Breakthrough time
    - ASTM F739 Standard
  - Penetration
  - Degradation
  - Comfort
  - Heat stress
  - Ergonomics
  - Cost

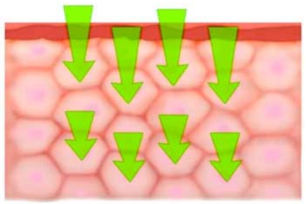


Photo credit: Permeation, http://www.cdc.gov/niosh/topics/skin/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

655

Permeation Rate (PR)	Permeation Breakthrough (PB)	Permeation Degradation rate (DR)
E- Excellent; permeation rate of less than 0.9 mg/cm²/min	>Greater than (time - minutes)	E - Excellent; fluid has very little degrading effect.
VG - Very Good; permeation rate of less than 9 mg/cm²/min	< Less than (time - minutes)	G - Good; fluid has minor degrading effect.
G - Good; permeation rate of less than 90 mg/cm²/min		F - Fair; fluid has moderate degrading effect.
F - Fair; permeation rate of less than 900 mg/cm²/min		P - Poor; fluid has pronounced degrading effect.
P - Poor; permeation rate of less than 9000 mg/cm²/min		NR - Fluid is not recommended with this material.
NR - Not recommended; permeation rate greater than 9000 mg/cm²/min		† Not tested, but breakthrough time > 480 min DR expected to be Good to Excellent
		†† Not tested, but expected to be Good to Excellent based on similar tested materials

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

656

Protective Clothing

- Special Applications
  - Hot processes
  - High voltage/arc flash
    - NFPA 70E
  - Foundries/molten metal
  - Refineries
- Select flame resistant clothing
- Chemical resistant coating may be added to flame resistant clothing

Gloves

- **Evaluate the work task**
  - **Chemical immersion or incidental contact?**
  - **Consider ergonomics/dexterity required**
- **Use glove charts**
  - **Charts recommend gloves for specific chemicals**
    - **Evaluate permeation rates and breakthrough time of selected glove for the specific task**
  - **Consider several glove manufactures data before final selection.**
    - http://www.mapaglove.com
    - http://www.ansellpro.com
    - http://www.bestglove.com/site/chemrest/

The first square in each column for each glove type is color coded. This is an easy-to-read indication of how we rate this type of glove in relation to its applicability for each chemical listed. The color represents an overall rating for both degradation and permeation. The letter in each square is for Degradation alone…

GREEN: The glove is very well suited for application with that chemical.

YELLOW: The glove is suitable for that application under careful control of its use.

RED: Avoid use of the glove with this chemical.

CHEMICAL	LAMINATE FILM BARRIER			NITRILE SOL-VEX			UNSUPPORTED NEOPRENE 29-865			SUPPORTED POLYVINYL ALCOHOL PVA			POLYVINYL CHLORIDE (Vinyl) SNORKEL			NATURAL RUBBER CANNERS AND HANDLERS*			NEOPRENE/ NATURAL RUBBER BLEND CHEMI-PRO*		
	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate
1. Acetaldehyde	■	380	E	P	—	—	E	10	F	NR	—	—	NR	—	—	E	7	F	E	10	F
2. Acetic Acid	■	150	—	G	270	—	E	60	—	NR	—	—	F	180	—	E	110	—	E	260	—
3. Acetone	▲	>480	E	NR	—	—	E	10	F	P	—	—	NR	—	—	E	10	F	G	10	G
4. Acetonitrile	▲	>480	E	F	30	F	E	20	G	■	150	G	NR	—	—	E	4	VG	E	10	VG
5. Acrylic Acid	—	—	—	G	120	—	E	390	—	NR	—	—	NR	—	—	E	80	—	E	65	—
6. Acrylonitrile	E	>480	E	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
7. Allyl Alcohol	▲	>480	E	F	140	F	E	140	VG	P	—	—	P	60	G	E	>10	VG	E	20	VG
8. Ammonia Gas	■	19	E	▲	>480	—	▲	>480	—	—	—	—	■	6	VG	—	—	—	■	27	VG
9. Ammonium Fluoride, 40%	—	—	—	E	>360	—	E	>480	—	NR	—	—	E	>360	—	E	>360	—	E	>360	—
10. Ammonium Hydroxide	E	30	—	E	>360	—	E	250	—	NR	—	—	E	240	—	E	90	—	E	240	—
11. Amyl Acetate	▲	>480	E	E	60	G	NR	—	—	G	>360	E	P	—	—	NR	—	—	P	—	—
12. Amyl Alcohol	—	—	—	E	30	E	E	290	VG	G	180	G	G	12	E	E	25	VG	E	45	VG
13. Aniline	▲	>480	E	NR	—	—	E	100	P	F	>360	E	F	180	VG	E	25	VG	E	50	G
14. Aqua Regia	—	—	—	F	>360	—	G	>480	—	NR	—	—	G	120	—	NR	—	—	G	180	—
15. Benzaldehyde	▲	>480	E	NR	—	—	NR	—	—	G	>360	E	NR	—	—	G	10	VG	G	25	F
16. Benzene, Benzol	▲	>480	E	P	—	—	NR	—	—	E	>360	E	NR	—	—	NR	—	—	NR	—	—
17. Benzotrichloride	—	—	—	E	>480	E	NR	—	—	—	—	—	—	—	—	NR	—	—	NR	—	—
18. Benzotrifluoride	—	—	—	E	170	G	F	—	—	E	—	—	G	<10	F	P	50	G	—	—	—
19. Bromine Water	—	—	—	E	>480	E	E	>480	E	—	—	—	—	—	—	—	—	—	—	—	—
20. 1-Bromopropane	▲	>480	E	■	23	F	■	<10	P	▲	>480	E	■	<10	F	■	<10	P	■	<10	P

General types of Glove materials

Laminated Gloves: 4H®, Silver Shield®

- Useful for a wide range of chemicals.

  NOT HYDROGEN FLUORIDE!
- Can use with a nitrile over glove to improve dexterity.

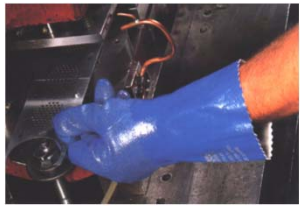
Butyl Rubber

- Highest permeation resistance to gas or water vapors.
- Uses: acids, formaldehyde, phenol, alcohols.

General types of Glove materials

Neoprene
- Protects against acids, caustics.
- Resists alcohols, glycols.

Nitrile
- Good replacement for latex
- Protects against acids, bases, oils, aliphatic hydrocarbon solvents and esters, grease, fats
- NOT ketones
- Resists cuts, snags, punctures and abrasions



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

661

Latex Allergy

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

662

Proper steps to remove Gloves

1 2 3

4 5 6

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

663

Eye & Face Protection

- Each day, 2000 U.S. workers have a job-related eye injury that requires medical treatment.
- Nearly *three out of five* U.S. workers are injured while failing to wear eye and face protection.

NIOSH. (2010). http://www.cdc.gov/niosh/topics/eye/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

664

Types of Eye Hazards

Hazard Type	Common related tasks	Protective Eyewear
Impact	Chipping, grinding, machining, abrasive blasting, sawing, drilling, riveting, sanding,…	Safety glasses with sideshields Goggles
Heat	Furnace operations, smelting, pouring, casting, hot dipping, welding, …	Face shield with infrared protection
Chemicals	Pouring, spraying, transferring, dipping acids, solvents or other injurious chemicals	Goggles Faceshield
Particles/ Dust	Woodworking, metal working, and general dusty conditions	Safety glasses with sideshields
Optical Radiation	Welding, torch-cutting, brazing, and laser work	Welding helmet Laser glasses -Must protect for specific wavelength of ultraviolet or infrared radiation.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

665

Examples: Eye & Face Protection

- Goggles
- Face shield
- Safety glasses
- Welding helmet
- Hooded faceshield

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

666

Respiratory Protection

- U.S. Respirator Requirements
  - Written program
  - Hazard assessment
    - Air monitoring
  - Medical clearance
  - Fit testing
  - Respirator selection
  - Procedures
    - Cleaning, maintenance, repairing
  - Training (annual refresher)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

667

Basic Types of Respirators

- Air purifying (APR)
  - Half Face
  - Full Face
  - Powered APR (PAPR)
- Air supply
  - Air line
  - SCBA

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

668

Air purifying respirators (APR)

- Work area must have at least 19.5% oxygen
- The contaminant must have adequate warning properties. Ex. ammonia
  - Never use APR in oxygen deficient atmospheres
- APRs work by filtering, absorbing, adsorbing the contaminant or chemical reaction.
  - Filters, cartridges, canisters
- The contaminant concentration must NOT exceed the maximum use concentration.
- Some cartridges have "end of service life" indicators or can use change schedules

669

Types of APR cartridges

Cartridge	Description
	**Organic Vapor**
	**Organic Vapor and acid gases**
	**Ammonia, methylamine and P100 particulates filter**

670

End of Service Life Indicators (ESLI)

There are very few NIOSH-approved ESLI's:

- ammonia
- carbon monoxide
- ethylene oxide
- hydrogen chloride
- hydrogen fluoride
- hydrogen sulfide
- mercury
- sulfur dioxide
- toluene-2,4-diisocyanate
- vinyl chloride

671

APR filter efficiency

National Institute of Occupational Safety and Health

Filter Efficiencies

Filter Class	
N95	Filters at least 95% of airborne particles. Not resistant to oil.
N99	Filters at least 99% of airborne particles. Not resistant to oil.
N100	Filters at least 99.97% of airborne particles. Not resistant to oil.
R95	Filters at least 95% of airborne particles. Somewhat resistant to oil.
P95	Filters at least 95% of airborne particles. Strongly resistant to oil.
P99	Filters at least 99% of airborne particles. Strongly resistant to oil.
P100	Filters at least 99.97% of airborne particles. Strongly resistant to oil

672

Assigned Protection Factors (APF)

- Level of workplace respiratory protection that a respirator or class of respirators is expected to provide.
- Each specific *type* of respirator has an Assigned Protection Factor (APF).
- Select respirator based on the exposure limit of a contaminant and the level in the workplace.

Maximum Use Concentration (MUC)
= APF x Occupational Exposure Limit
(e.g. PEL, TLV)

673

Assigned Protection Factors (APF)

Type of Respirator	Half Face Mask	Full Facepiece	Helmet/ Hood	Loose-Fitting Facepiece
Air-Purifying	**10**	**50**	**-**	**-**
PAPR	**50**	**1,000**	**25/1,000**	**25**
Supplied-Air or Airline				
– Demand	**10**	**50**	**-**	**-**
– Continuous flow	**50**	**1,000**	**25/1000**	**25**
– Pressure demand	**50**	**1,000**	**-**	**-**
SCBA				
– Demand	**10**	**50**	**50**	**-**
– Pressure Demand	**-**	**10,000**	**10,000**	**-**

674

Assigned Protection Factors (APF)

Workplace air sampling indicates the exposure to benzene is 15 parts per million (ppm). The exposure limit is 0.5 ppm (ACGIH TLV).

What respirator should you choose?

Maximum Use Concentration (MUC) = APF x OEL
Half Face Mask: MUC = 10 x 0.5 ppm = 5 ppm
PAPR (LFF): MUC = 25 x 0.5 ppm = 12.5 ppm
Full Face Respirator: MUC = 50 x 0.5 ppm = 25 ppm

675

Filtering Facepieces

676

Filtering Facepieces: Inappropriate use

Respirator Fit Testing

- Qualitative
  - Irritant smoke
    - stannic chloride
  - Isoamyl acetate
    - banana oil
  - Saccharin
  - Bitrex
- Quantitative
  - Portacount

Respirator Fit Test

Positive / Negative pressure fit test

Supplied Air

- Supplies breathing air to worker
  - SCBA
  - Airline
- Must use Grade D Air
- Many limitations

Breathing air quality & use

- Compressed breathing air must be at least Type 1 – Grade D [ANSI/CGA G-7.1-1989]:
  - Oxygen content = 19.5 – 23.5%
  - Hydrocarbon (condensed) = 5 milligrams/cubic meter or less
  - CO ≤ 10 parts per million (ppm) or less
  - CO_2 of 1,000 parts per million (ppm) or less
  - Lack of noticeable odor
- Compressors may be equipped with in-line air-purifying sorbent beds and filters.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

681

Maintenance & Storage

- Disposable filtering face-piece:
  - Dispose after use
- Air purifying respirators:
  - Discard cartridges based on expiration date, end-of-service life indicator or calculated service life
  - Clean
  - Dry
  - Place in sealable bag (write your name on bag)
  - Contact Safety Office for repairs
- SCBA:
  - Inspected monthly
  - Accessible and clearly marked

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

682

Discussion

- A contractor has been hired to sweep out a work area that contains lead dust. The plant safety officer has recommended that the worker don a full-face air purifying respirator with a HEPA filter (P100) during this activity.
- Later that week the plant safety officer observes the worker sweeping without wearing the respirator. When asked why he is not wearing the respirator, the worker states “it is too uncomfortable to wear.”
- What approach should the safety officer take to ensure the worker wears a respirator?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

683

PPE Exercise

- Worker A needs to transfer 10 liters of acetone into a hazardous waste drum.
- The safety officer has determined that due to the use of ventilation, the air concentration of acetone is below the exposure limit.
- The worker may have incidental skin contact with the acetone during pouring.
- Prolonged skin exposure to acetone causes dry and cracked skin, but acetone is not normally absorbed through the skin.
- There is also a possibility that the acetone may splash in the worker’s face during pouring.

What PPE should Worker A wear?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

684

PPE Exercise

- Worker B is walking back from the break room when he notices a yellow cloud of chlorine coming towards him from the chlorine storage area. He also notices that some of the chlorine has come into contact with water under one of the tanks and formed chlorine hydrate.
- He alerts the emergency response team who arrive at the emergency staging area.
  - Chlorine is a corrosive and toxic gas by inhalation.
  - Chlorine hydrate is corrosive to the skin and eyes.
  - The airborne concentration of chlorine is unknown in this situation.

What PPE should the emergency response team use?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

PPE Exercise

- Worker C is tasked with adding zinc oxide pigment into a mixing bath by hand.
- This task will take 15 minutes.
- Worker C performs this task once every day.
- The safety officer has determined that the airborne concentration during this task is 20 milligrams/cubic meter.
- The short term exposure limit (15 minutes) for zinc oxide is 10 milligrams/cubic meter.
- Zinc oxide powder is mildly irritating to the skin and eyes, but not toxic or corrosive.

What PPE should Worker C wear?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Break

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Security Considerations with Industrial Fire Protection

SAND No. 2012-1755C
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-AC04-94AL85000.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Primary Course Objectives

- Provide a broad overview of industrial fire protection
- Apply engineering principles to generic industrial fire protection issues
- Discuss historical examples of industrial fire protection hazards
- Develop security related scenarios which may be compromised by fire, explosion, or inadvertent chemical release

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

689

Key Terms

- Siting – fix or build something in a particular place
- Egress – pathways for entering and exiting
- Suppression – extinguishing or containing of fire
- Extinguishability – ability to completely disrupt fire process
- Compartmentation – ability to isolate particular areas from other area

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

690

Course Structure

- Introduction
- Perspectives and statistical overview
- Facility/Plant siting and location
- Construction considerations
  - Fire resistant construction
  - Smoke control
  - Fire suppression systems
- Storage of flammable liquids
- Ignition Sources
- Security considerations and scenarios

http://www.draegerdive.com

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

691

Introduction to Industrial Fire Protection

For common workplace conditions, fire safety may be achieved by simple methods

- Enforcement of approved fire codes and standards
  - National Fire Protection Association (NFPA)
    - http://www.nfpa.org/index.asp
  - International Building Codes (IBC)
    - http://www.iccsafe.org/Pages/default.aspx
- Local or national fire officials and chiefs

NFPA National Fire Protection Association The authority on fire, electrical, and building safety

ICC INTERNATIONAL CODE COUNCIL People Helping People Build a Safer World™

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

692

Introduction to Industrial Fire Protection

- Industrial facilities have unique hazards
  - Chemical production or use
  - Storage of flammable or volatile materials
  - Access controls or personnel restrictions
- Unique operations require additional considerations included with simpler methods


superstock.com


news.thomasnet.com


kellerfencenorth.com


www.archiexpo.com

Introduction to Industrial Fire Protection

- Additional considerations require the use of an engineering approach
- Steps for an engineering approach include
  - Identification of possible accident scenarios
  - Analysis of consequences resulting in accidents
  - Evaluation of alternative protection methods

Introduction to Industrial Fire Protection

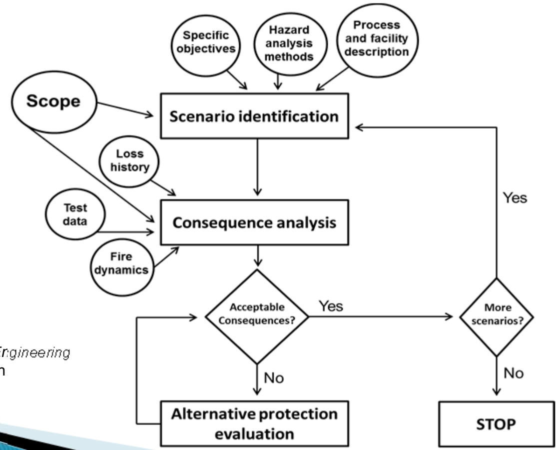
Scenario Identification

- Pre-incident situations (start-up, maintenance, shutdown)
- Ignition source
- Ignited material
- Flaming or smoldering combustion
- Fire spread and heat release rates of ignited material
- Fire spread to secondary combustibles

Introduction to Industrial Fire Protection

- Consequence Analysis
  - Property damage or loss
  - Personnel injury or fatality
  - Interruption of operation continuity
  - Explosion damage (i.e., surrounding community)
- Evaluation of alternative protection methods
  - Effectiveness (e.g., prevention of life/property loss)
  - Benefits (e.g., financial, continuity of operation, environmental)

Introduction to Industrial Fire Protection



Industrial Fire Protection Engineering
Robert G. Zalosh

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

697

Perspectives and Statistical Overview

- Types of facilities involved in large monetary loss fires
  - US industrial fires with >$30M US property damage
  - European large-loss fires
- Types of fires and explosions in large industrial losses
- Industrial fires with most fatalities

http://www.safety-s2s.eu

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

698

Perspectives and Statistical Overview

- Ignition sources in large loss fires
- Time of fire initiation
- Presence of automatic detection and suppressions systems
- Effectiveness of detection and suppression systems

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

699

Perspectives and Statistical Overview

Type of Facility	Number of >$30M Losses	% of U.S. Large Loss Fires
Warehouses	17	27%
Petroleum Refineries	12	19%
Power Plants	5	8%
Chemical Plants	5	8%
Grain Elevators	3	
Textile Plants	2	
Telephone Exchanges	2	
Ink Manufacturing	2	
Aluminum Plants	2	

Historic data on US fires prior to 2003

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

700

Perspectives and Statistical Overview

Type of Fire/Explosion	% of Incidents	Example
Flammable Liquid	17%	GM Livonia, Sandoz Basel
Plastic Storage	12.5%	Ford Cologne Warehouse
Dust Explosion	9%	Malden Mills
Vapor Cloud Explosion	8%	Phillips Petroleum
Gas Explosion	5%	Ford Rouge Powerhouse
Electrical Cable	5%	Ameritech Hinsdale
Aerosol Products	5%	K Mart
Gas Fires	5%	Gas Turbine Fire, VA

Historic data on US fires prior to 2003

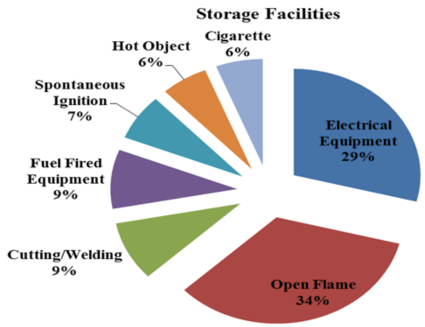
Perspectives and Statistical Overview

Type of Facility	# of Incidents	# of Fatalities	Example
Petrochemical Plant	10	726 – 967	Pemex, Mexico City
Factories	9	549 – 606	Garment Factory in Bangladesh
Offshore Oil/Gas Platforms	2	203	Piper Alpha, North Sea
Fireworks Facility	5	145	Jennings, Oklahoma USA

- Multiple Fatality (>20)
- Industrial fires and explosions between 1981 - 2000

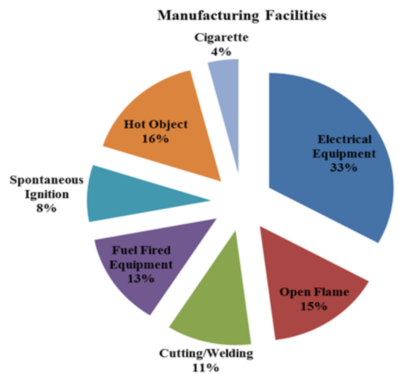
Perspectives and Statistical Overview

Ignition sources in large loss fires



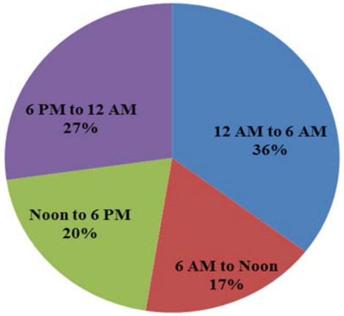
Perspectives and Statistical Overview

Ignition sources in large loss fires



Perspectives and Statistical Overview

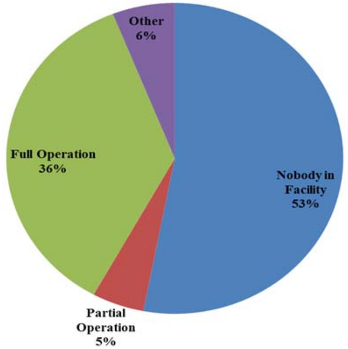
Time Distribution of large loss fires from NFPA data on 338 Fires in 1985



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Perspectives and Statistical Overview

Operational status of facilities in large loss fires



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Perspectives and Statistical Overview

Automatic Sprinkler System Status	Number of Fires
Not Installed	14
Overpowered by Fire	7
System Shut Off Before Fire	2
Not in Area of Fire Origin	3
Damaged by Explosion	1
Unknown	1
Total	**28**

Status of automatic suppression systems in 1987 large loss fires (NFPA Journal, 1988)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Perspectives and Statistical Overview

Automatic Detection System Status	Number of Fires
Not Installed	19
Functioned as Designed	4
Not in Area of Fire Origin	1
Installation Incomplete	1
Unknown	3
Total	**28**

Status of automatic detection systems in 1987 large loss fires (NFPA Journal, 1988)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Facility Siting and Location

- Safe separation distances
  - Flame radiation
  - Toxic and/or flammable vapor clouds
  - Blast waves
- Water supply access and reliability
  - Susceptibility to drought
  - Robust supply of water

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

709

Facility Siting and Location

- Safe egress, rescue, and manual fire fighting
  - Egress to adjacent protected building or designated area
  - Distance from fire department
  - Site accessibility
- Hazard segregation and isolation
  - Grouping similar hazardous chemicals
  - Isolating and protection special or targeted dual use chemicals
  - Isolation and elimination of ignition sources

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

710

Facility Siting and Location

Miscellaneous considerations

- Environmental (e.g., flooding, drought)
- Naturally occurring hazards (e.g., earthquake)
- Water run-off with the possibility of contamination
  - Waterways such as rivers, lakes, ponds
  - Underground aquifer
  - Food supplies

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

711

Facility Siting incident

- Sandoz Basel Fire, 1986 in Switzerland
- Textile and agrochemical manufacturing facility
- Structural steel framed building that was 90m long, 50m wide with two 12m high peaks. 12cm brick wall in the middle to create two separate buildings

http://www.swissinfo.ch/eng

http://www.novaquatis.eawag.ch/media/2006/20061101/index_EN

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

712

Facility Siting incident

- Original use was for machinery storage, converted over to flammable liquids storage
  - Explosion-proof electrical fixtures
  - Sealed sewer drains
  - Installed three water curtains to be operated by plant fire brigade
- No automatic sprinklers or smoke detectors
- Chemicals stored in plastic bags, plastic and steel drums
- Materials stacked to maximum height of 8m

Facility Siting incident

- Storage at the time of incident
  - 859 metric tons of organophosphate insecticide
  - 12 metric tons of a phenyl-urea derivative used for weed control
  - 73 metric tons of di-nitrocresol derivative herbicide
  - 26 metric tons of fungicide
  - 11 metric tons of water soluble organic mercury compounds
  - 5.6 metric tons of misc. agrochemicals
  - 364 metric tons of various formulating agents
- Most have flash points of 30°C and higher

Facility Siting incident

- Incident occurred on October 31, 1986
- Key points to the incident
  - Palletized chemicals were plastic shrink wrapped and then finished by using a blow torch
  - Plastic wrap could ignite if exposed for sufficient duration
  - Chemicals in the warehouse (e.g., Prussian Blue dye) could burn flamelessly, smokelessly, and slowly thus eluding early detection by workers
  - No automatic suppression or smoke detection

Facility Siting incident

- Initial fire responders determined that fire spread was too rapid to control
  - Fire foam was used, but proved to be ineffective
  - Responders directed to cool surrounding buildings
  - Limited success as steel drums were propelled from the building of fire origin to adjacent structures
- Water was applied at 30 cubic meters per minute
- Containment basins filled quickly and toxic chemicals flowed into the Rhine River

http://www.rockwool.com

http://www.swissinfo.ch/eng

Facility Siting incident

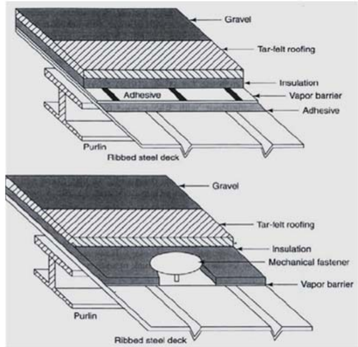
- Extensive environmental impacts
  - Most fish were killed by mercury poisoning in a 250km section of the Rhine downstream of Basel
  - Subsoil water levels had to be pumped away to preserve the municipal underground water supply
  - Wind carried the smoke produced by the fire over residential communities causing eye and respiratory issues
- Extensive financial impacts
  - $60M US in settle charges
  - Figure does NOT include environmental clean-up and restoration efforts

http://www.novaquatis.eawag.ch/media/2006/20061101/index_EN

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Construction Considerations

- Fire resistant construction
  - Fire walls – hour rating
  - Fire doors – prevents smoke form passing under
  - Roofing – connecting areas, fastened to fire walls
- Smoke control
  - Isolation
  - Ventilation
- Fire suppression systems
  - Not only water but could include foams, dry chemical, carbon dioxide, halon, etc.

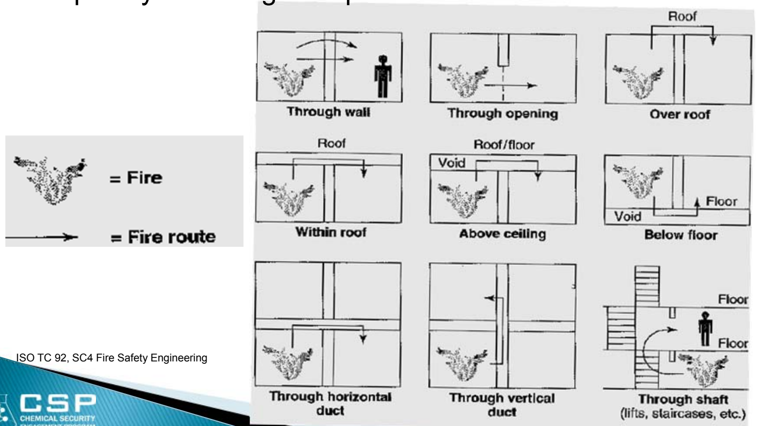


Industrial Fire Protection Engineering
Robert G. Zalosh

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Construction Considerations

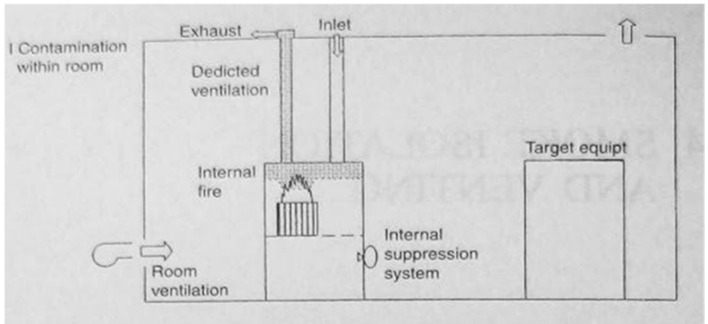
Frequency occurring fire spread routes



ISO TC 92, SC4 Fire Safety Engineering

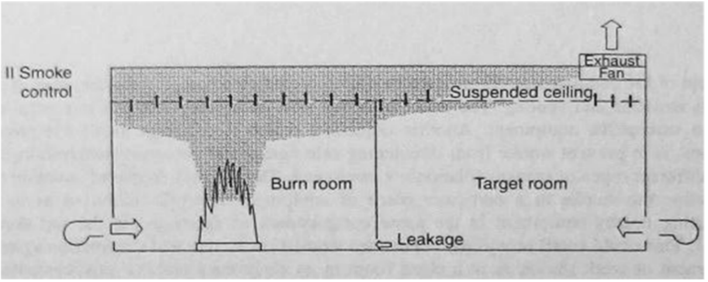
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Ventilation System

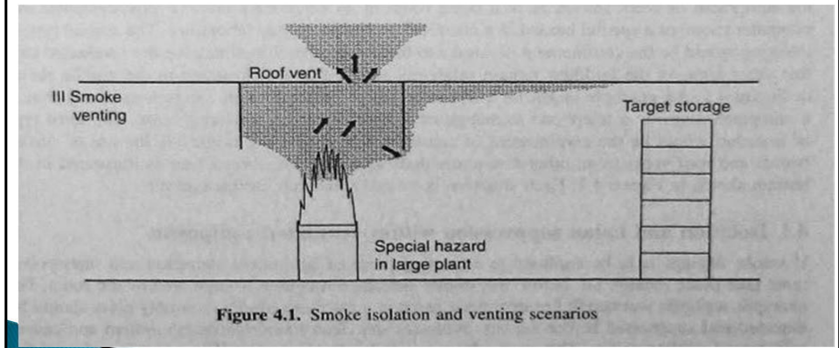


CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Ventilation System



Ventilation System



Construction Considerations

- Structural and thermal properties of construction material
- Fire resistance analytical calculations
- Fire resistance testing for listing
- Fire wall design and loss experience
- Insulated metal deck roofing
- Water spray protection of structural steel
- Protective insulation materials on structural steel

Protective spray insulation material for structural steel
www.barrierst.com

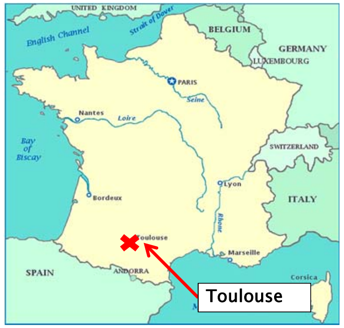
Storage: Flammable Chemicals

- Chemical properties must be considered
  - Flash point
  - Auto-ignition temperatures
  - Extinguishability
- Storage tanks
  - Capacity
  - Tank spacing
  - Emergency ventilation
  - Fire suppression
  - General designs should be approved to meet specifications (such as FM Global – Factory Mutual)

FM APPROVED

Storage Incident

- Toulouse, France (September 2001)
  - AZote Fertilisant (AZF)
  - Manufactured fertilizer
  - 300 tons of ammonium nitrate stored onsite (2,000 ton capacity)



www.yourchildlearns.com

Storage Incident

- Explosion left a crater 70m long, 40m wide, 6m deep
- Poor maintenance contributed to the incident
- Mislabeled 500 kg container sodium dichlorisocynate accidently stored with ammonium nitrate
- Reacted in humid weather to form nitrate trichloride
- 29 fatalities
- 2,500 seriously wounded
- ~60 – 70% of the city's windows shattered, causing injuries
- $2Billion USD damages paid

http://oliaklodvenitiens.files.wordpress.com/2011/09/azf002.jpg

Storage Incident

- Toulouse Video (1 minute, 30 seconds)

Storage Incident

- Toulouse Video (3 minutes)

Storage Incident

- Ammonium Nitrate Video (3 minutes, 30 seconds)

Storage Considerations

- Combustible materials
  - Quantity (e.g., rolls, drums)
  - Type (e.g., liquids, powders, gases)
  - Mixed commodities
- Effective measures to protect against fires
  - Suppression systems
    - Water
    - Dry-chemical
  - Spacing of discharge points (e.g., sprinkler heads)
  - Limit ignition sources
  - Remove unnecessary combustibles

Ignition Sources

- Sparks produced during welding or maintenance
  - General Motors Livonia Fire, 1953
  - 6 fatalities, $35M US property loss
- Discarded cigarette
  - Ford Cologne Fire, 1977
  - $100M US property loss
- Open flame
  - Sandoz Basel Fire, 1986
  - $60M US property loss,
  - Thousands experienced health issues
- Electrical arc in wiring
  - Hinsdale Telephone Office Fire, 1988
  - Between $40 – 60M US property loss

73
1

Ignition Sources

- High Energy Arcing Fault (30 seconds)

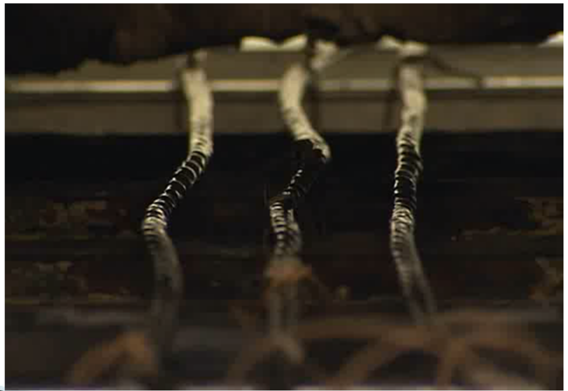
732

Fires in Cabling

- Electrical arcing
- Spurious actuation
- System inoperability
- Reliability of systems

Fires in Cabling

- Arcing video (2 minutes)



Security Considerations

- Access of fire fighting personnel into secured areas
- Cable fire affecting security system reliability
  - Effects pumps, lights, cameras, security gates, etc.
- Occupant load of security personnel in spaces with insufficient exits
- Fire as a means of distraction
  - Pulls resources away

735

Lessons Learned

- Need for fire walls and other passive barriers
- Need for roof deck fire spread tests
- Need to regularly test sprinkler water flow rates and to fixed known impairments
- Need for fire resistant electrical cables
- Need for containment of contaminated water run-off

736

Lessons Learned

- Need to upgrade warehouse sprinkler protection to accommodate storage of more combustible commodities
- Need for smoke control in facilities with equipment vulnerable to damage from smoke and corrosive combustion products
- Need for adequate emergency egress provisions for large number of workers
- Need for improved protection of flammable liquid warehouse

Areas needing improvement

- Need for automatic detection and suppression systems in areas containing large quantities of electrical equipment and cables
- Need for adequate emergency egress provisions for large numbers of workers
- Effective sprinkler protection for flammable liquids in plastic containers

Areas needing improvement

- Need for compartmentation via reliable fire walls and doors in large manufacturing facilities
- Need to restrict storage of special hazard commodities in general purpose warehouses
- Problems caused by residue of flammable liquids on building walls, ceilings, and floors

Summary of key points

- Broad overview of industrial fire protection
- Engineering based methodology to identify potential fire hazards
- Context of historic fires
- Security considerations which may be compromised by fire or explosion

Questions?

References and Additional Resources

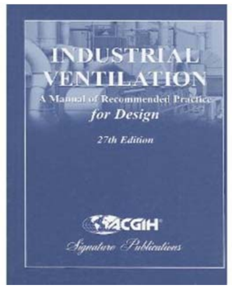
- *Industrial Fire Protection*, Robert Zalosh
- *SFPE Handbook of Fire Protection Engineering*
- *Fire Dynamics*, Dougal Drysdale
- *Principles of Smoke Management*, John Klote and James Milke
- *Ignition Handbook*, Vytenis Babrauskas

Controlling Chemical Hazards
Laboratory and Industrial Ventilation

SAND No. 2012-1603C
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-AC04-94AL85000.

Ventilation

- Definitions
- Common Terminology
- Purpose
- Hazard Assessment
- General Ventilation
- Local Exhaust Ventilation
- Ventilation Evaluation
- Troubleshooting
- Exercises



American Conference of Governmental Industrial Hygienists (ACGIH) Ventilation Manual 27th Edition
http://www.acgih.org/store/ProductDetail.cfm?id=1905

Definitions

- **Heating, ventilating and air conditioning** (HVAC): refers to the distribution system for heating, ventilating, cooling, dehumidifying and cleansing air.
- **Replacement/Supply air**: refers to replacement air for HVAC and local exhaust ventilation.
- **General ventilation**: refers to ventilation that controls the air environment by removing and replacing contaminated air before chemical concentrations reach unacceptable levels.
- **Local exhaust ventilation (LEV)**: refers to systems designed to enclose, or capture and remove contaminated air at the source.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Common Terms

Q = volume of air in cubic meters

V = velocity of air in meters per second

- Duct velocity–velocity required to transport the contaminant
- Face velocity–velocity on the front of an enclosing hood
- Capture velocity–velocity required to capture contaminant at point of generation

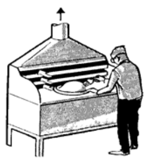
A = cross sectional area of hood opening in square meters

X = distance of ventilation from the source in meters

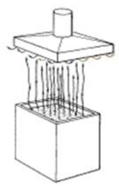
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Purposes of Ventilation

- Protect workers from health hazards
  - *Dilute, capture, or contain* contaminants
- Protect workers from hot processes
  - *Ovens, foundries*
- Protect the product
  - *Semiconductor*
  - *Electronics*
  - *Pharmaceuticals*



Slot Hood



Canopy Hood

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Purposes of Ventilation

- Emergency ventilation
  - Standalone fans
  - Detectors connected to ventilation or scrubber systems
  - Safe room
    - Positive pressure
- Enclosed vented rooms or cabinets
  - Gas cabinets
- Comply with health and safety regulations

Photo credit: Advanced Specialty Gas Equipment

Photo credit: Emergency Responder Products

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Hazard Assessment

- What are the airborne contaminants?
  - Particles
  - Solvent vapors
  - Acid mists
  - Metal fumes
- How do to the workers interact wi source contaminant?
- Are workers exposed to air contaminants in concentrations over an exposure limit?
  *Requires air monitoring of the task
- Dilution or local exhaust ventilation?

Picture Credit : International Labor Organization

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

749

General Ventilation

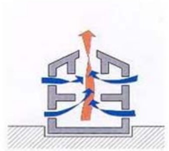
- Natural Ventilation:
  - Useful for hot processes
  - Chimney effect
  - Windows and doors kept open
- Example: a warehouse opens the w create natural ventilation

  Q = 0.2 AV

  A = square meters (area of open doors)

  V = wind speed in kilometers/hour

  Q = estimates the volumetric flow rate through the building (m^3/s)



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

750

General Ventilation

Dilution Ventilation

-Heat control

-Dilution of odors, flammables

<u>-Not</u> for control of toxics

Principles

-Contaminant emissions must be widely dispersed

-Exhaust openings must be near contaminant source

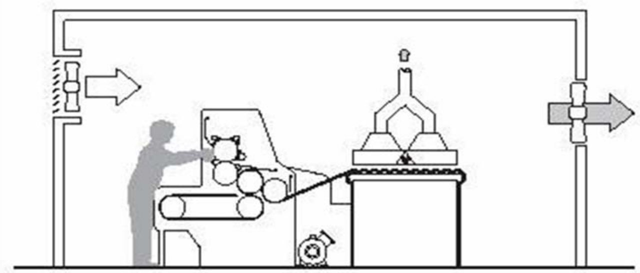
-The worker must not be downstream of contaminant

-Air flow over worker should not exceed 3.5 meters/sec

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

751

General Ventilation



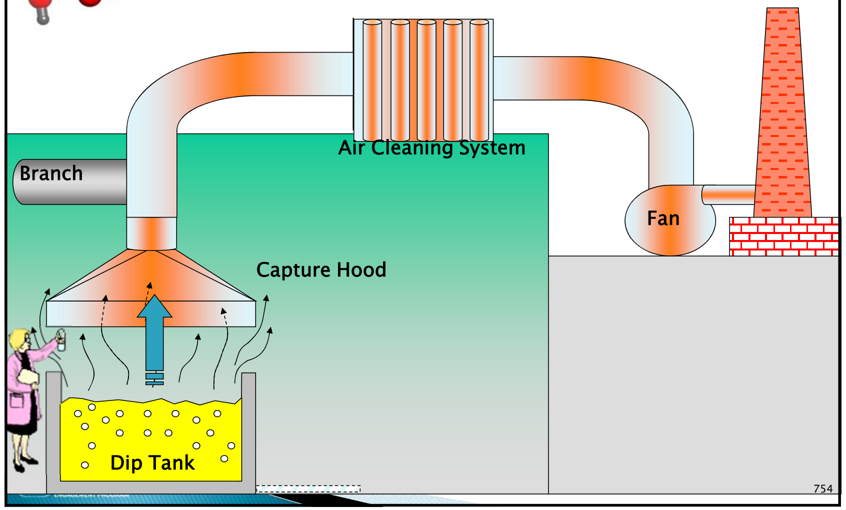
General ventilation for cleaning a printing press

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Local Exhaust Ventilation (LEV)

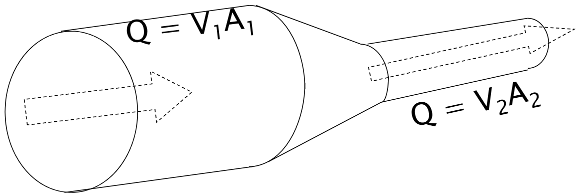
- Use when contaminant concentration cannot be controlled by dilution ventilation or other controls
- Select the type of LEV from hazard assessment
  - Which type is best to capture the contaminant?
    - Enclosed or capture hood?
    - Consider worker's needs
  - What duct transport velocity is required to carry the contaminant? Heavy particles?
  - What face or capture velocity is required?
- Select duct material for the contaminant
- Ensure enough replacement air/adequate fan size

Local Exhaust Ventilation (LEV)



Local Exhaust Ventilation (LEV)

Volumetric Flow Rate, Q = VA [**Circular Opening**]

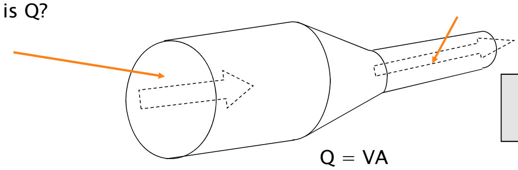


Q = Volumetric flow rate, in cubic meters/second
V = Average velocity, in meters/second
A = Cross-sectional area in square meters

Local Exhaust Ventilation (LEV)

Duct diameter = 1 meter
V = 600 meters/second
What is Q?

Duct diameter = 0.5 meter
What is the duct velocity (V)?



For circular ducts
$A = \pi d^2/4$

Q = VA

Q = (600 m/s)(π[1 m]^2/4)

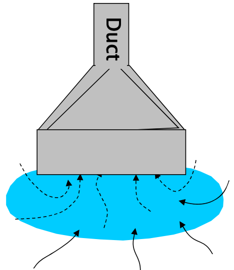
Q = 471 meters^3/second

Q = VA

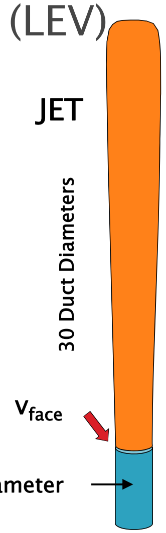
471 meters^3/s = V (π[0.5m]^2/4)

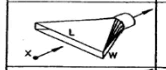
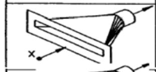
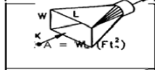
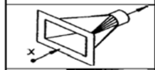
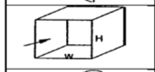
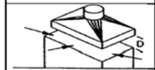
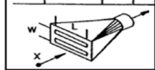
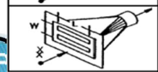
V = 2400 meters/second

Local Exhaust Ventilation (LEV)



Capture of contaminant is only effective within <u>one</u> <u>(1) duct diameter</u>

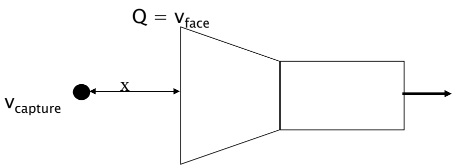


HOOD TYPE	DESCRIPTION	ASPECT RATIO, W/L	AIR FLOW
	SLOT	0.2 OR LESS	$Q = 3.7\ LVX$
	FLANGED SLOT	0.2 OR LESS	$Q = 2.6\ LVX$
	PLAIN OPENING	0.2 OR GREATER AND ROUND	$Q = V(10X^2 + A)$
	FLANGED OPENING	0.2 OR GREATER AND ROUND	$Q = 0.75V(10X^2 + A)$
	BOOTH	TO SUIT WORK	$Q = VA = VWH$
	CANOPY	TO SUIT WORK	$Q = 1.4\ PVD$ SEE FIG. VS-99-03 P = PERIMETER D = HEIGHT ABOVE WORK
	PLAIN MULTIPLE SLOT OPENING 2 OR MORE SLOTS	0.2 OR GREATER	$Q = V(10X^2 + A)$
	FLANGED MULTIPLE SLOT OPENING 2 OR MORE SLOTS	0.2 OR GREATER	$Q = 0.75V(10X^2 + A)$

ACGIH Ventilation Manual

Local Exhaust Ventilation (LEV)

<u>Capture Velocity (V_c)</u>: [Plain Opening]



$Q = V_c\,(10x^2 + A)$

X = distance of source from hood face

Recommended Capture Velocities

CONDITION	EXAMPLES	CAPTURE VELOCITY Range in meters/second
No velocity, Quiet air	Evaporation from tanks, degreasers	0.25 – 0.5
Low velocity, moderately still air	Spray booths, container filling, welding, plating	0.5 – 1.0
Active generation into rapid air motion	Spray painting (shallow booths), crushers	1.0 – 2.5
High initial velocity into very rapid air motion	Grinding, abrasive blasting, tumbling	2.5 – 10.1

ACGIH Ventilation Manual

Recommended Duct Velocities

CONTAMINANT	EXAMPLES	DUCT VELOCITY Meters/second
Vapors, gases, smoke	Vapors, gases, smoke	5.0 – 10.1
Fumes	Welding	10.1 – 12.7
Very fine dust	Cotton lint	12.7 – 15.2
Dry dusts & powders	Cotton dust	15.2 – 20.3
Industrial dust	Grinding dust, limestone dust	17.8 – 20.3
Heavy dust	Sawdust, metal turnings	20.3 – 22.9
Heavy/moist dusts	Lead dusts, cement dust	> 22.9

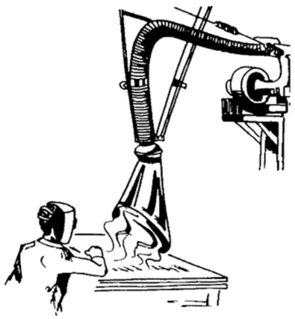
ACGIH Ventilation Manual

Local Exhaust Ventilation (LEV)

- Canopy hood:
  - Best for controlling hot processes
  - Not good for capturing dusts, or vapors
  - Not good where cross-drafts exist
  - Worker must not put head under canopy

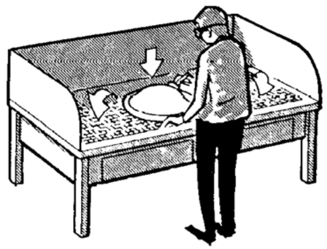
Local Exhaust Ventilation (LEV)

- "Elephant trunk":
  - Good for welding fumes, small process tasks, machining, disconnecting process lines
  - Place close to contaminant
  - Ensure adequate capture velocity at distance from contaminant
  - *Flanged* opening captures contaminant better



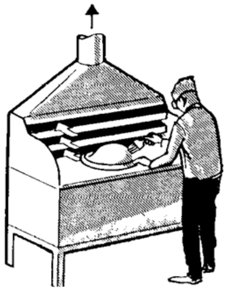
Local Exhaust Ventilation (LEV)

- Downdraft hood:
  - Vapors pulled down through grill
  - Capture velocity depends on source distance from grill
  - Not for hot operations



Local Exhaust Ventilation (LEV)

- Slot ventilation:
  - Best for liquid open surface tanks
    - Acid baths
    - Plating tanks
  - Pulls air across the tank away from worker
  - Side enclosures prevent cross drafts
  - Push-Pull design is optional (push jet)



Local Exhaust Ventilation (LEV)

- Fume hood:
  - Laboratory use
  - Best for small amounts of chemicals
  - Sash must be kept at set level
  - NO storage of equipment in the hood!

Local Exhaust Ventilation (LEV)

- Enclosures:
  - Example:
    - Paint booths
  - Control of exposure to liquid aerosols and vapors
  - Flammability hazard
  - Must have scheduled filter changeout
  - Operator must be upstream

Local Exhaust Ventilation (LEV)

- Other vented enclosures
  - Glove boxes
  - Furnaces/ovens
  - Abrasive blasting

Photo credit: Borel Furnaces and Ovens

Photo credit: U. S. Department of Labor. OSHA

Local Exhaust Ventilation (LEV)

Exhaust Systems:

- Do not place exhaust stack near air intakes
  - Re-entrains contaminants into the building
- Do not use rain caps
- Stack height depends on:
  - Contaminant temperature
  - Building height
  - Atmospheric conditions
  - Discharge velocity
  - Ideal discharge velocity is <u>15 meters per second</u>

Ventilation Systems Evaluation

- **Evaluate capture velocity**
  - **Quantitatively-anemometers, velometers**
  - **Qualitatively-smoke tubes,**
    - **Visualizes air movement**
    - **Use water vapor for clean rooms**

Photo Credit: All Products Inc.

770

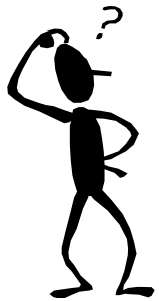
Ventilation Systems Evaluation

- Air velocity measurements
  - Measure air velocities (meter/sec) at a number of points
  - Average the results and determine volumetric flow rate: Q = VA
  - All instruments must be calibrated periodically
  - Types:
    - Swinging vane velometer
    - Hot-wire anemometer

771

Troubleshooting

- Wrong hood for process
  - Example: canopy hood for toxics
- Insufficient capture velocity
- Insufficient duct velocity
  - ~14 meters/second for vapors
  - ~18 meters/second for dust
- Too much air flow = turbulence
- Traffic or competing air currents
- Insufficient make up air
  - Negative pressure
  - Can't open doors



772

Exercise

- What is the preferred ventilation system for the following situation?
  - Dilute non-toxic odors in the warehouse

A) General ventilation
B) Local exhaust ventilation

Exercise

- What is the preferred ventilation system for the following situation?
  - Acid processing bath with open surface area

A) Lab fume hood
B) Slot ventilation
C) Elephant trunk
D) Canopy hood
E) Paint booth

Exercise

- What is the preferred ventilation system for the following situation?
  - Welding table

A) Lab fume hood
B) Slot ventilation
C) Elephant trunk
D) Canopy hood
E) Paint booth

Exercise

- What is the preferred ventilation system for the following situation?
  - Chemical analysis of small samples for quality control

A) Lab fume hood
B) Slot ventilation
C) Elephant trunk
D) Canopy hood
E) Paint booth

Exercise

- What is the preferred ventilation system for the following situation?
  - Spray painting a large piece of equipment

A) Lab fume hood
B) Slot ventilation
C) Elephant trunk
D) Canopy hood
E) Paint booth

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

777

US Standards & Guidelines

ACGIH
American Conference of Governmental Industrial Hygienists
Industrial Ventilation, A Manual of Recommended Practice

AIHA
American Industrial Hygiene Association
Standard Z9.2, Fundamentals Governing the Design and Operation of Local Exhaust Ventilation Systems

ASHRAE
American Society of Heating, Refrigeration and Air Conditioning Engineers
Standard 62.1-2010, Ventilation for Acceptable Indoor Air Quality

OSHA
Occupational Safety and Health Administration
Ventilation, 29 Code of Federal Regulations 1910.94
http://osha.gov/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

778

Summary of Presentation

- Provided ventilation definitions and terminology
- Summarized the purpose of ventilation
- Described general exhaust ventilation
- Described local exhaust ventilation
- Demonstrated volumetric flow rate and capture velocity calculations
- Described how to evaluate a ventilation system
- Provided examples of ventilation problems (troubleshooting)
- Listed ventilation standards and guidelines

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

779

Lunch

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Chemical Inventory System Demonstration

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Behavior Based Safety (BBS)

SAND No.. 2011-0487C

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

What is Behavior Based Safety?

Behavior is "the manner of conducting oneself."*

Therefore, behaviors are <u>observable</u> acts.

Behavior Based Safety focuses on behaviors that promote safety.

* Merriam-Webster dictionary

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Behavior Based Safety is NOT…

- A fully-developed safety program.
  - It is a process designed to eliminate behaviors that put workers at risk and enhance existing safety protocols.
- A process used to enforce safety rules, nor to correct hazardous conditions.
  - Safety rule violations and hazardous workplace conditions must be corrected outside of the BBS process.
- A process for assigning blame or criticizing workers.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

How does BBS Differ From Traditional Safety?

Traditional Safety…

- Is *reactive* – focuses on correcting problems only after they have occurred.
- Searches for "root cause" of accidents
  - Using incident/accident data from investigations
    - e.g. Incident and Severity rate: TRCR/DART
- Focuses on making the working environment less hazardous.
- Sometimes assigns blame to individuals.
  - Emphasis on negative reinforcement.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

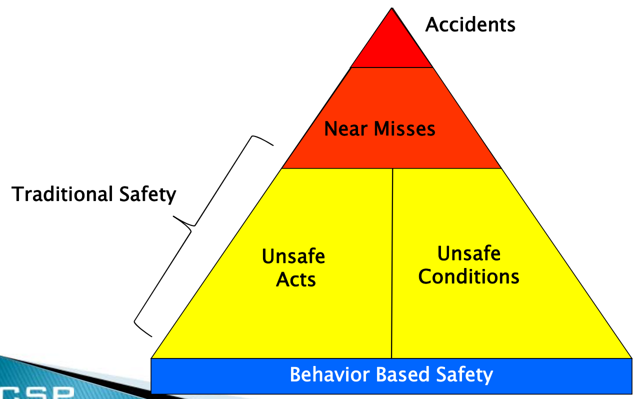
How does BBS Differ From Traditional Safety?

Behavior Based Safety…

- Is proactive – discourages 'at-risk' behaviors.
- Focuses on observing worker behavior.
  - Common behaviors that place employees at risk are noted and adjustments are made.
  - Data come from behavioral observations.
- Has a holistic understanding of worker behavior.
  - Notes the environment in which behavior occurs, the behavior itself, and consequences of this behavior.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Behavior Based Safety Underlies and Benefits Traditional Safety



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Always keep in mind…

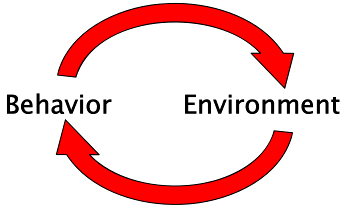
BBS is focused on two concepts:

- BEHAVIOR
  - What is behavior?
  - What are the factors influencing "at-risk" behavior?
  - How can this behavior be discouraged?
- RISK
  - What is risk?
  - Why do people take risks?
  - What are the consequences of taking these risks?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Behavior is "the manner of conducting oneself"

Behaviors cannot be isolated from the environment in which they occur.

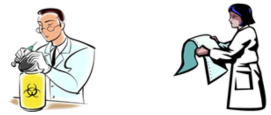


Therefore, if employees are expected to promote safe practices the working environment must encourage this behavior.

Risk = exposure x probability

Exposure – extent a person is involved in an activity.

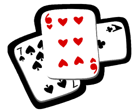
Direct



Indirect

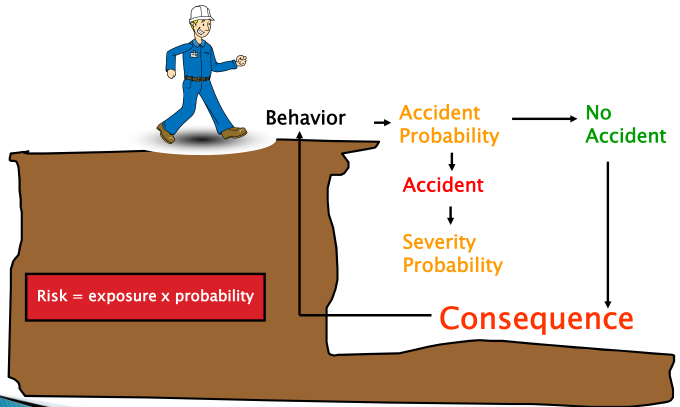
Probability – the chances of an accident occurring during activity.

1 in 6



1 in 52

How do Consequences Affect At-Risk Behavior?



Positive Consequences Influence At-Risk Behavior

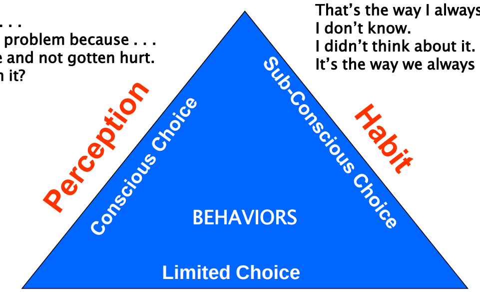
- Convenience
- Time savings
- Increased productivity
- Getting away with it
- Feeling bullet-proof

How does cheaper/better/faster influence taking risks?

Worker's reasons for taking a risk:

In my opinion . . .
In my experience . . .
I don't think it's a problem because . . .
I've done it before and not gotten hurt.
What's wrong with it?

That's the way I always do it!
I don't know.
I didn't think about it.
It's the way we always do it around here.



Obstacle

I can't do it any other way because . . .
It would be difficult to do it that way because . . .
If I do it that way, (this would happen).

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Implementing Behavior Based Safety

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM
Sandia National Laboratories

Prior to Implementation

Important to develop a BBS Committee and working structure that persists after implementation:

- Designs the BBS process.
- Develops the implementation strategy.
- Implements the BBS process.
- Steers the BBS process.
  - Assures observation and data quality through a Quality Assurance Plan.
  - Champions worker involvement and completion of observations.
  - Analyzes observation data to identify the causes of at-risk behaviors and develops recommendations.
  - Facilitates removal of barriers to workers being able to easily perform work safely.
  - Reports the results of data analysis.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Responsibilities of Managers & Supervisors

- Understand the process (receive training)
- Establish BBS as a part of the job
- Help identify and correct systems issues
- Remove barriers
- Support:
  - Time for:
    - Training
    - BBS Committee duties and meetings
    - Observations
- Encourage and provide positive reinforcement: workers, observers, BBS Committee members

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

4 Steps of Implementation

The BBS implementation process consists of four steps we will discuss in further detail:

1. Establish Feasible Goals
2. Develop Observation Checklists
3. Take observations
4. Provide Feedback

Step 1: Establish Feasible Goals

The overall purpose of BBS is to establish a culture of safety in the working environment. However, attainable goals need to exist in working toward this.

Make goals SMART:

Specific – Motivational – Attainable – Relevant – Trackable

e.g. A goal of "zero-injuries" is NOT SMART, but a goal of 80% participation in appropriate safety training is SMART.

Goals should focus on outcomes, NOT behaviors.

Step 1: Establish Feasible Goals

Employee participation in the goal-setting process is important, and must continue throughout the BBS process to ensure success. There are two broad reasons for this:

1. "Employee buy-in" – verbal and nonverbal support for change from those directly affected.
2. Interpersonal trust – trust among employees, and trust between employees and management.

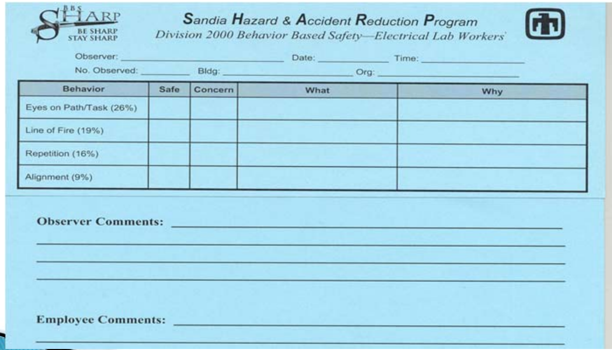
Step 2: Develop Observation Checklists

In looking for behaviors that encourage safe practice, there are several options:

- Review past accident/incident reports to identify behavior that could have prevented them.
  - Focus on those that could have prevented the largest number of accidents.
- Consult with employees and managers.
  - It is important for employees to take responsibility for their actions.
  - Beneficial for developing trust.
- Observe workers for a period of time.

Step 2: Develop Observation Checklists

Remember in developing the list that positive reinforcement is better for employee participation (i.e. specify criteria for good performance).



BBS SHARP
BE SHARP STAY SHARP

Sandia Hazard & Accident Reduction Program
Division 2000 Behavior Based Safety—Electrical Lab Workers

Observer: ______ Date: ______ Time: ______
No. Observed: ______ Bldg: ______ Org: ______

Behavior	Safe	Concern	What	Why
Eyes on Path/Task (26%)				
Line of Fire (19%)				
Repetition (16%)				
Alignment (9%)				

Observer Comments: ______

Employee Comments: ______

Step 3: Observing

There are several decisions to be made when selecting an observation method or methods:

- Who will observe?
  - Self-observation
  - Peer-to-peer
  - Top-down
  - Working groups
- Frequency of observations?
  - Daily, bi-weekly, monthly
- How will feedback be given?
  - Immediately
  - Within a week

Observers have…

Three main responsibilities:

- Gather data
  - Observation data (Safe/Concern)
  - Discussion data (What/Why)
- Give feedback
  - Positive reinforcement for safe behaviors
  - Provide coaching on concerns
- To remain objective/unbiased

Step 3: Observing

As an example, Sandia's method of observation is:

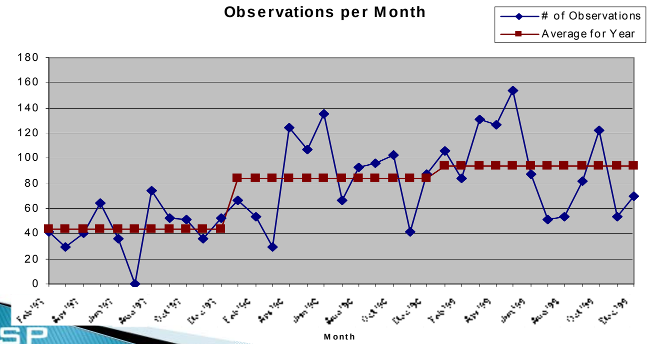
- Peer-to-peer
- Anonymous (No Names/No Blame)
- Announced
- 5 minutes or less
- Provide feedback:
  - Positive reinforcement for safe behaviors
  - Coaching for behaviors of concern
- Identify obstacles
- Foster safety communication

An Observer's Job is NOT:

- Ambush or spy on workers,
- "Catch" people doing activities unsafely,
- Criticize worker performance,
- "Safety cop" (risks vs. rules; right vs. wrong; safe vs. unsafe),
- Watch a whole task or job,
- Force people to change,
- Turn people in for discipline,
- Identify conditions that don't directly impact critical behaviors.

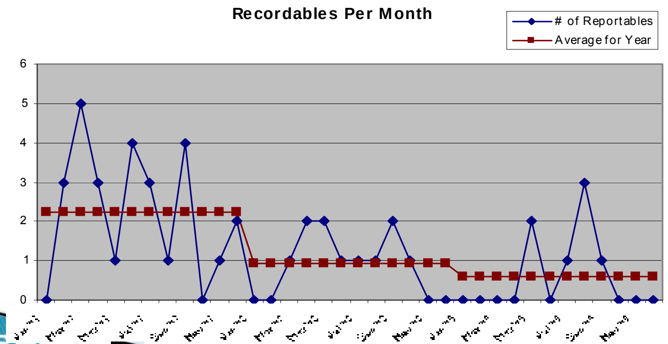
What happens with more observations?

Feedback Changes Behaviors



Fewer injuries !

Changed Behaviors Reduce Accidents



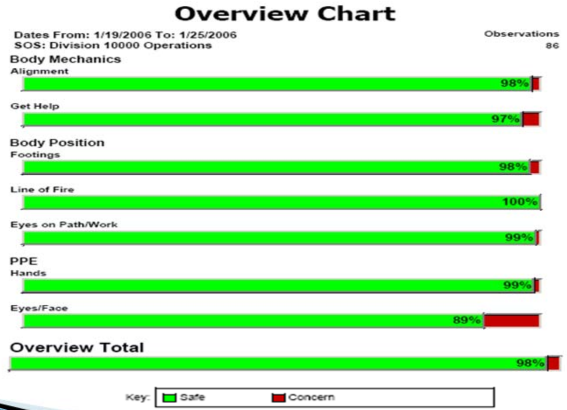
Step 4: Providing feedback

Providing feedback to workers in a timely manner is important. Using multiple methods has proven beneficial:

- Verbal – Immediate feedback during observations.
- Through reports written after observation data collected.
- Posting graphs/charts where all can see.
- Having celebrations for milestones or providing other incentives.

NOTE: It is important that workers are allowed time to adjust their performance before being observed again.

Example of a "Green/Red" Chart from Observations of a Division at Sandia



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Why Implement Behavior Based Safety?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

The BBS Process Closes the Gap to "Nobody Gets Hurt"

- Focuses on the critical few precautions that would prevent the most injuries
- Prioritizes actions to remove barriers
- Generates actionable data
- Provides positive reinforcement of safe behaviors
- Engages workers and management:

Worker driven and Management supported

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

BBS is proven to reduce injuries

- At 850+ companies injuries were reduced by an average of:
  - 37% after 1 year
  - 66% after 2 years
  - 87% after 3 years
- Multisite Success – See case study of BP's Fabrics and Fibers Business Unit (FFBU) included in your extra materials.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

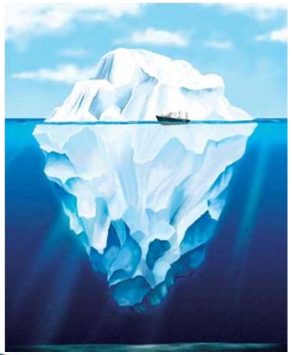
Benefits Outweigh the Costs

What is the Return on Investment for BBS?

- Saves time, money, energy, and can improve morale among employees and between employees and managers.
- Costs of accidents/incidents are both direct and indirect:
  - Direct costs: investigation, production downtime, medical expenses, damage to equipment or product, repairs, legal costs, fines, etc.
  - Indirect costs: employer/public liability, business interruption, training replacements, loss of goodwill/employee morale, negative public image.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Why Implement Behavior Based Safety?



Remember:

The Iceberg Theory

For every accident, there are many "near misses" that go unnoticed.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sources

- M. Dominic Cooper. "Behavioral Safety Interventions: A review of process design factors." *Safety Management*. Feb 2009.
- Thomas E. Boyce and Horacio R. Roman. "Institutionalizing behavior-based safety: Theories, concepts, and practical suggestions." *The Behavior Analyst Today*. Vol 3, No 1. April 2002.
- Jason DePasquale and E. Scott Geller. "Critical success factors for behavior-based safety: A study of twenty industry-wide applications." *Journal of Safety Research*. Vol 30, No 4. 1999.
- Beth Sulzer-Azaroff and John Austin. "Does BBS Work? Behavior-Based Safety & Injurty Reduction: A Survey of the Evidence." *Professional Safety*. July 2000.
- E. Scott Geller. "How to Get More People Involved in Behavior-Based Safety: Selling an Effective Process." Cambridge Center for Behavioral Studies. Accessed 12/2010. <http://www.behavior.org/resource.php?id=332>.
- "Introduction to BBS." Cambridge Center for Behavioral Studies. Accessed 12/2010. <http://www.behavior.org/resource.php?id=330>.
- Byron Chandler and Thomas A. Huntebrinker. "Multisite Success with Systematic BBS." *Professional Safety*. June 2003.
- D. Cooper. "The return on investment of the B-BS process." *Giornale Italiano di Medicina del Lavoro ed Ergonoima*. Vol 32, No 1. 2010.
- M. D. Cooper Ph.D. "Towards a model of safety culture." *Safety Science*. Vol 36. 2000.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Break

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Process Equipment Inspection and Testing

SAND No. 2011-0798C
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation,
a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM
Sandia National Laboratories

Topics

- Resources
- Mechanical Integrity – Design/Build, Inspect/Test/Maintain, Correct
- Maintaining Control of Processes
- Loss of Containment Description
- Safeguards
- Maintenance of Equipment
- Summary

Key acronyms

MI = *mechanical (asset) integrity*

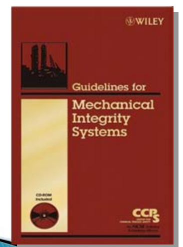
ITM = *inspections, testing, maintenance*

PM = *preventive maintenance*

MMS = *maintenance management system*

Resource

CCPS 2006. Center for Chemical Process Safety, *Guidelines for Mechanical Integrity Systems*, NY: AIChE.



Chapter
1 Introduction
2 Management responsibility
3 Equipment selection
4 Inspection, testing and preventive maintenance
5 MI training program
6 MI program procedures
7 Quality assurance
8 Equipment deficiency management
9 Equipment-specific integrity management
10 MI program implementation
11 Risk management tools
12 Continuous improvement of MI programs
Resource CD included

Process Safety Beacon

CCPS Center for Chemical Process Safety 20 Years — An AIChE Industry Technology Alliance

http: //www.aiche.org/ccps/safetybeacon.htm

Messages for Manufacturing Personnel

Sponsored by CCPS Supporters

April 2006

Mechanical Integrity

BEFORE

The flange on the left is badly corroded and the bolts are in very poor condition - a leak waiting to happen. Fortunately, the poor condition was noted during a plant inspection and the flange was replaced (as shown on the right).

The picture on the left shows a corroded control valve. Could you count on this valve to operate when you need it? The picture on the right shows the replacement valve, which, if properly maintained and tested, is much more likely to function correctly when needed.

AFTER

This picture shows an improvised pipe support made from scaffolding, springs and clamps.

Did you know?

- In 2004, process safety incidents reported to the Canadian Chemical Producers Association indicate that 25% were caused by problems with process equipment mechanical integrity.
- Further analysis of the same data shows that mechanical integrity failure is a cause of up to 50% of the incidents in several years between 1998 and 2003.
- ALL OF US are the first line of defense for plant integrity issues like the ones shown here. We are in the plant every day and have the opportunity to see and report these problems.

What You Can Do

- Plan regular plant tours to look for mechanical integrity problems – such as corroded equipment, piping and valves, inadequate piping support, small drips or wet spots around flanges.
- Listen as well as look! For example, does that pump sound different? If so, perhaps maintenance should check it in case there is something wrong.
- But, don't wait for "official" plant safety tours and inspections. Be constantly aware of visual and other signs of equipment mechanical integrity problems.
- If you see or hear something that concerns you, report it promptly and follow-up to make sure steps are taken to correct the situation.

"You can see a lot just by looking!" (Yogi Berra, New York Yankees)

Three basic MI activities

1. Design and build reliability into process equipment and controls
2. Inspect / test / maintain the integrity of the equipment and controls
3. Successfully correct failures and performance degradations as they occur

Three basic MI activities: By whom?

1. Design and build reliability into process equipment, controls [ENGINEERING/CONSTRUCTION]
2. Inspect / test / maintain the integrity of the equipment and controls [PLANT MAINTENANCE]
3. Successfully correct failures and performance degradations as they occur [PLANT MAINTENANCE]

Three basic MI activities

1. Design and build reliability into process equipment, controls
2. Inspect / test / maintain the integrity of the equipment and controls
3. Successfully correct failures and performance degradations as they occur

Focus of this module (items 2 and 3)

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained
4. Determine how often tasks need to be performed
5. Equip with maintenance procedures and training
6. Document ITMs
7. Correct identified deficiencies

---

8. Equipment-specific issues

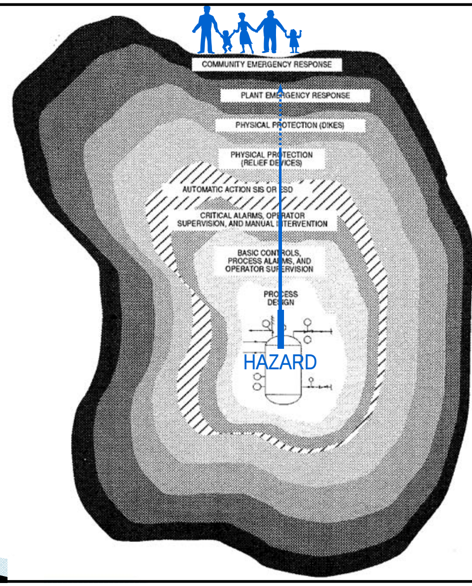
Equipment Inspections and Testing

1. Understand the importance of plant equipment PM

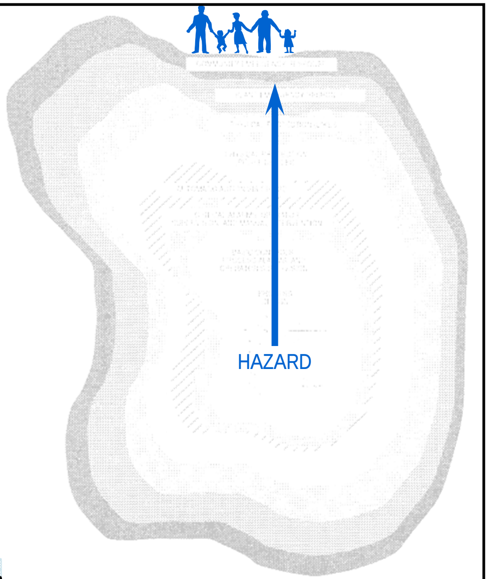
"Layers of Protection" between hazards and receptors

=

"Defense In Depth"



"Layers of Protection" between hazards and receptors MUST BE MAINTAINED TO BE EFFECTIVE



CCPS Center for Chemical Process Safety

Process Safety Beacon

http://www.aiche.org/CCPS/Publications/Beacon/index.aspx

Messages for Manufacturing Personnel

Sponsored by CCPS Process Safety Incident Database (PSID)

Mechanical Integrity

May 2009

A compressed air tank failed, blowing the bottom off of the tank (1) and sending fragments flying into a concrete wall, puncturing the wall (2). Investigation following the incident revealed several serious problems with the condition of the tank, including severe corrosion and rust at the bottom of the tank (3), where it failed, and an improper weld repair (4) which had been made to the tank at some time in the past. Although the weld repair did not contribute to this incident, it is a symptom of improper maintenance and inspection, and could have caused a tank failure. Fortunately, nobody was in the area when the tank failed, and there were no injuries.

What can you do?

- Look at vessels, piping, and other equipment as you walk through your plant, and report anything which appears to be corroded or improperly maintained. Include visual inspection of piping, vessels, compressed gas cylinders, and other equipment in routine safety inspections. Follow up and make sure that problems are corrected.
- Understand the equipment inspection and maintenance program in your plant, and understand your role in ensuring that all activities are completed as required.
- When you do mechanical work that requires removal of insulation from equipment, take the opportunity to look at the condition of the equipment and report any corrosion or other problems that you observe. Corrosion under insulation may be hidden, but mechanical work which requires removal of the insulation provides an opportunity to observe problems.
- Make sure that all welds and other repairs follow all required standards, and meet the original design specifications for the equipment.
- Assure that all pressure vessels in your plant, including portable tanks and tanks which are a part of "packaged systems" (for example, compressors, refrigeration units, compressed air systems, etc.), are included in the plant mechanical integrity inspection program and are being inspected by qualified pressure vessel inspectors. This may include inspection for internal corrosion at an appropriate frequency.
- Make sure that compressed air tanks and other portable compressed gas cylinders are stored in dry locations to prevent external rust and corrosion.

Watch out for damaged or corroded equipment!

Maintain contain and control measures

Contain & Control

Operational Mode: Normal operation

Objective: Maintain normal operation; keep hazards contained and controlled

Examples of *Contain & Control*:

- Basic process control system
- Inspections, tests, maintenance
- Operator training
  - How to conduct a procedure or operate a process correctly and consistently
  - How to keep process within established limits
- Guards, barriers against external forces
- Management of change

"Swiss cheese model"

Contain & control measure failures result in a <u>higher frequency of initiating causes</u> and a proportionally higher risk of a major incident.

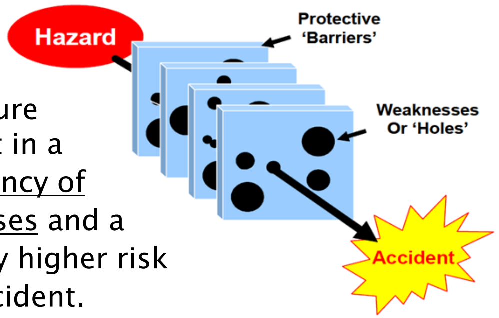
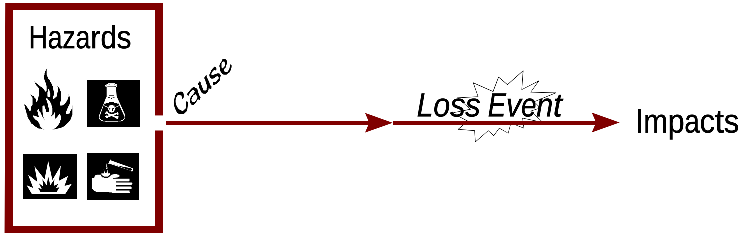
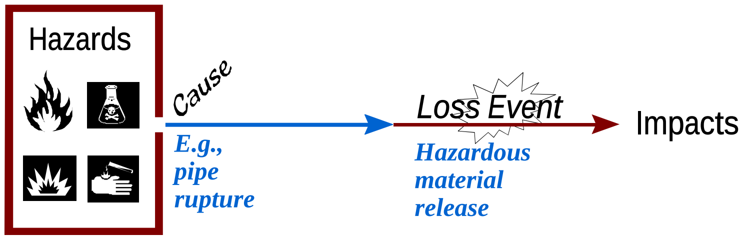


Image credit: CCPS, "Process Safety Leading and Lagging Indicators," New York: American Institute of Chemical Engineers, January 2011, www.aiche.org/ccps.
"Swiss cheese model" originally proposed by James Reason, U. Manchester, 1990.

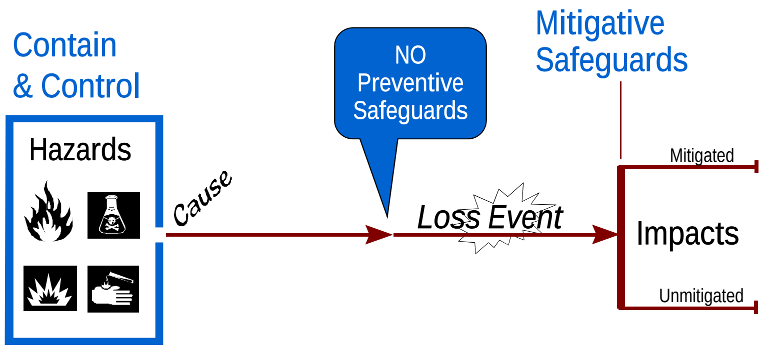
Typical loss-of-containment incident



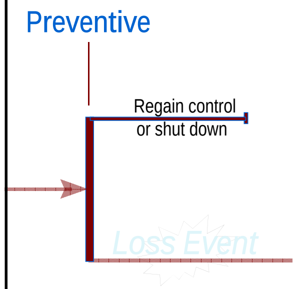
Typical loss-of-containment incident



Vitally important: Integrity of primary containment system!



Maintain preventive safeguards



Operational Mode: Abnormal operation

Objective: Regain control or shut down; keep loss events from happening

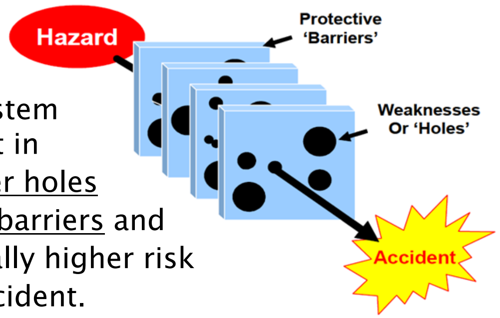
Examples of Preventive Safeguards:

- Operator response to alarm
- Safety Instrumented System
- Hardwired interlock
- Last-resort dump, quench, blowdown
- Emergency relief system

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

"Swiss cheese model" revisited

Preventive safeguard system failures result in more or larger holes in protective barriers and *a* proportionally higher risk of a major incident.



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Quantification of safeguard reliability

Probability of Failure on Demand (PFD)

$$PFD_{Total} = PFD_{Sensor} + PFD_{LogicSolver} + PFD_{FinalElement}$$

$$PFD_{Sensor} = 1 - \exp(-\lambda \cdot \tau)$$

where λ = *failure frequency*

τ = *failure duration*

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Quantification of safeguard reliability

For random failures of repairable components:

failure duration = 1/2 (*inspection interval*)

$$PFD_{Sensor} = 1 - \exp(-\lambda \cdot \tau)$$

where λ = *failure frequency*

τ = *failure duration*

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

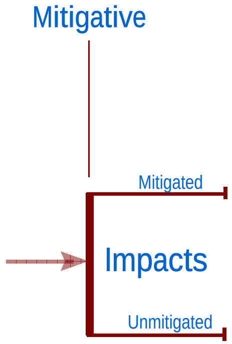
Quantification of safeguard reliability

For a sensor with a failure frequency $\lambda = 0.1$ / yr:

Test interval	Failure duration	Sensor PFD
Monthly	0.04 yr	0.004
Annually	0.5 yr	0.05
Every 5 years	2.5 yr	0.22
Never	½ (plant lifetime)	0.9 to 1.0

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Maintain mitigative safeguards



Operational Mode: Emergency

Objective: Minimize impacts

Examples of Mitigative Safeguards:

- Sprinklers, monitors, deluge
- Emergency warning systems
- Emergency response
- Secondary containment; diking/curbing
- Discharge scrubbing, flaring, treatment
- Shielding, building reinforcement, haven
- Escape respirator, PPE

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What equipment needs to be maintained?

From a *hazard* perspective:

all equipment that contains or controls MAJOR HAZARDS, or safeguards against loss events if their loss of containment or control does occur.

- Toxic/corrosive/asphyxiating materials
- Flammable/combustible materials
- Reactive/thermally sensitive materials
- Intentional chemical reactions
- Potential chemical incompatibilities
- Physical hazards (high pressure, liquefied gas…)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What equipment needs to be maintained?

From a *consequence* perspective:

all equipment that, if it failed, would result in MAJOR LOSS OR INJURY, or would eliminate a safeguard against the major loss or injury consequence.

- Severe personnel injury or fatality
- Significant environmental damage
- Significant community impact
- (Major property damage or product loss)
- (Major business interruption)

What equipment needs to be maintained?

Typical examples:

- Fixed equipment
  - Process tanks / vessels
  - Process piping + piping system components (valves, check valves…)
  - Relief and vent systems
- Rotating equipment
  - Pumps
  - Compressors
- Instruments & electrical
  - Controls
  - Shutdown systems
  - Power systems
- Emergency equipment
  - Detection, suppression, fire protection systems
  - Diking and drainage
  - etc.

What equipment needs to be maintained?

What about utilities?
(steam, cooling water, nitrogen, compressed air, etc.)

- Include all utilities that, if system components (including piping) fail, could cause a major incident or is used to protect against a major incident.
- Examples:
  - Water used to cool an exothermic chemical reaction
  - Nitrogen used to exclude oxygen from the head space of a tank containing a flammable liquid
  - Compressed air used to close a safety shutdown valve
  - Steam / process heat exchanger

What equipment needs to be maintained?

Aids in determining what must be inspected / tested / maintained:

- Codes and standards
  - E.g., all pressure vessels, all emergency reliefs
  - E.g., combustion safeguards
- Manufacturers' recommendations
- Process hazard analyses
  - Look at all equipment-failure initiating causes
  - Look at all safeguards credited as being in place, including e.g. check valves, sensors / alarms

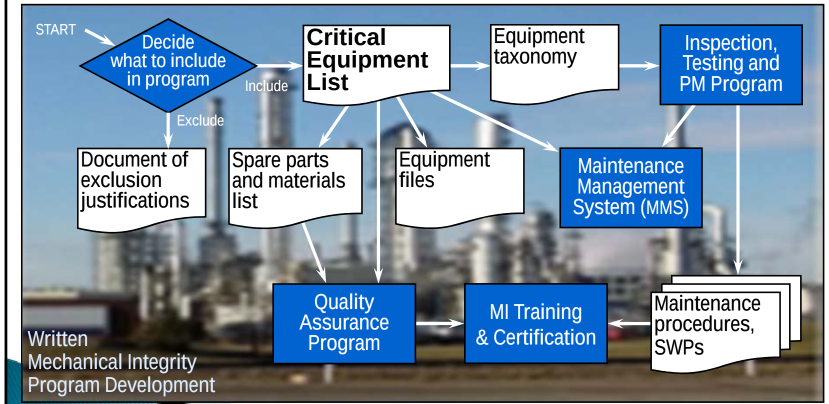
What equipment needs to be maintained?

Outcome of this step:

"Critical Equipment List"

- Inventory of all equipment and controls to be included in the mechanical integrity program
- Grouped by equipment type
- Listed using unique identifiers e.g. serial numbers and specific process / location
- Computerize in a database (or spreadsheet)

Centrality of critical equipment list to MI



Equipment Inspections and Testing

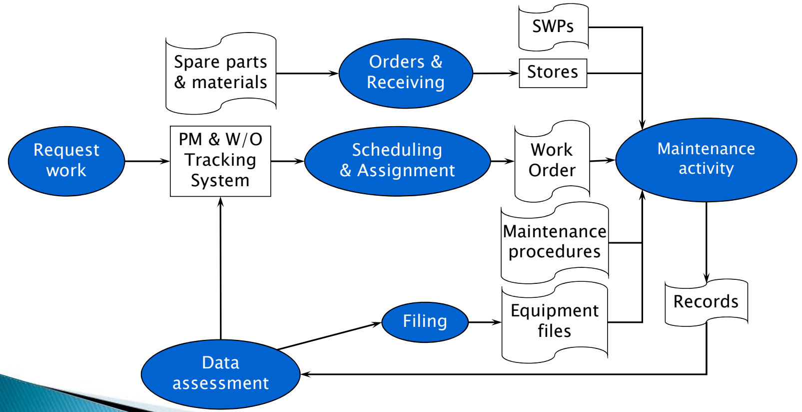
1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained

How will it be maintained?

NECESSARY INGREDIENTS

- True management commitment
- Documented program description
  - What is to be maintained
  - Who is to do it (qualifications, responsibilities)
  - How it is to be done (requirements, procedures)
  - How often it is to be done (frequencies, changes)
- Maintenance management system
  - Work order system
  - Activity scheduling
  - Spare parts inventory, quality control

MI program implementation overview



Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained
4. Determine how often tasks need to be performed

How often must ITMs be performed?

PRINCIPLES:

- ITM frequencies must be pre-established
- Some frequencies are experience-adjusted
- ITMs must be performed according to schedule

How often must ITMs be performed?

PRINCIPLES:

- ITM frequencies must be pre-established
  - Frequencies will vary by equipment type
  - Initial frequencies come from various sources
    - Authority having jurisdiction
    - Codes and standards
    - Manufacturers' recommendations
    - Calculated values to meet reliability requirements

How often must ITMs be performed?

PRINCIPLES:

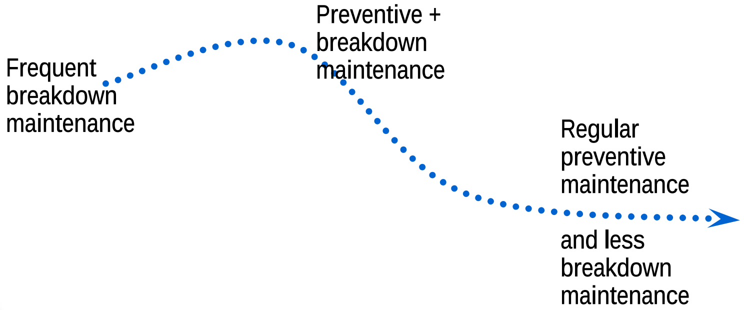
- ITM frequencies must be pre-established
- Some frequencies are experience-adjusted
  - Problems found: Do ITMs <u>more often</u>
  - Good experience: Do ITMs <u>less often</u> if allowed

How often must ITMs be performed?

PRINCIPLES:

- ITM frequencies must be pre-established
- Some frequencies are experience-adjusted
- ITMs must be performed according to schedule
  - System to schedule and execute ITMs is needed
  - Adequate resources must be available
  - *Management commitment and priority is required!*

Getting over the hump



DISCUSSION

What are some advantages in having less breakdown maintenance and more regular preventive maintenance?

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained
4. Determine how often tasks need to be performed
5. Equip with maintenance procedures and training

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Maintenance procedures and training

PRINCIPLES:

- Prepare written procedures to maintain equipment
  - Basic craft skills are assumed
  - Unique activities may require one-time procedures
  - Make procedures consistent with RAGAGEPs
  - Use standardized procedure format

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Maintenance procedures and training

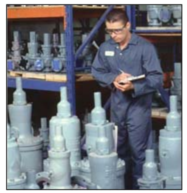
PRINCIPLES:

- Prepare written procedures to maintain equipment
- Train maintenance personnel to safely perform ITMs
  - Ensure basic craft skills by hiring, testing and training
  - Include safety procedures and safe work practices
  - Include awareness of process hazards and potential consequences
  - Establish necessary qualifications to perform critical and specialized tasks
  - Train and re-train in consistently performing tasks according to the written procedures

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained
4. Determine how often tasks need to be performed
5. Equip with maintenance procedures and training
6. Document ITMs



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Document ITMs

ITM documentation will be equipment-specific.

Examples:

- Storage tank external visual inspection checklist
- Piping system thickness measurement locations (TMLs), test description and measurement results
- Compressor vibration monitoring charts, results

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Document ITMs

ITM documentation will be equipment-specific.

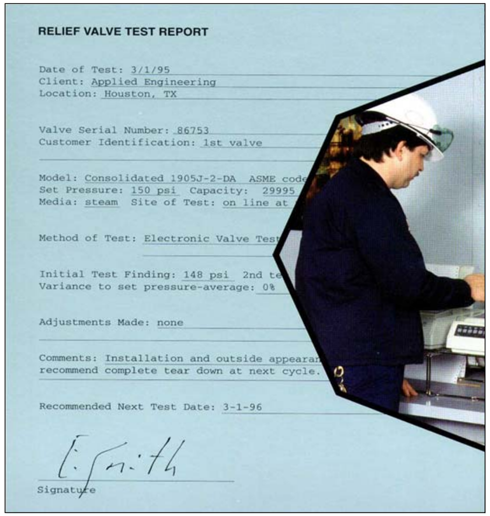
COMMON ELEMENTS:

- Date of the ITM activity
- Person's name who performed it
- Serial number or other unique equipment identifier
- Description of the ITM activity
- ITM results
  - "As-found" condition
  - "As-left" condition

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Additionally:

- Document any incipient problems
- Provide sufficient detail to inform any decision on increasing or decreasing ITM frequency



RELIEF VALVE TEST REPORT

Date of Test: 3/1/95
Client: Applied Engineering
Location: Houston, TX

Valve Serial Number: 86753
Customer Identification: 1st valve

Model: Consolidated 1905J-2-DA ASME code
Set Pressure: 150 psi Capacity: 29995
Media: steam Site of Test: on line at

Method of Test: Electronic Valve Test

Initial Test Finding: 148 psi 2nd te
Variance to set pressure-average: 0%

Adjustments Made: none

Comments: Installation and outside appearan
recommend complete tear down at next cycle.

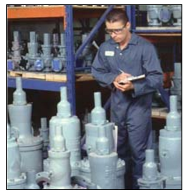
Recommended Next Test Date: 3-1-96

Signature

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained
4. Determine how often tasks need to be performed
5. Equip with maintenance procedures and training
6. Document ITMs
7. Correct identified deficiencies



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Working Definitions

Deficiency

= departure outside predetermined acceptable limit

Failure

= no longer performing intended function

Working Definitions

Deficiency

= departure outside predetermined acceptable limit

Example:

- A restricting orifice is taken out and inspected once every 6 months
- The predetermined acceptable limit for orifice enlargement due to erosion is that the orifice diameter must be no larger than 10 mm
- If the orifice diameter is > 10 mm, a deficiency exists

Working Definitions

Deficiency

Failure

Example:

- A spring-operated relief valve can fail to open due to corrosion or inlet blockage
- The same relief valve can fail to hold pressure and open prematurely due to a broken spring

(One component, two different *failure modes*)

Working Definitions

Deficiency

= departure outside predetermined acceptable limit

Failure

= no longer performing intended function

Note: All failures are deficiencies, but not all deficiencies are failures

Deficiency Corrections

OPTIONS:

- **BEST**: Correct deficiency before re-starting while system is shut down (e.g., replace corroded pipe)
- **OK**: Correct deficiency right away while system is in operation, <u>if</u> it can be done safely (e.g., switch over to on-line spare pump, fix bad pump, switch back)
- **OK**: Wait to correct deficiency until next scheduled shutdown AND put extra control measures in place (e.g., exclude personnel from area; do extra level checks)
- <u>NOT</u> OK: Operate with deficient equipment

Deficiency Corrections

ALL TOO COMMON:

- Hire an inspector
- Receive the inspection report
- The report documents equipment deficiencies and the inspector's recommended actions
- The report gets filed without any action taken

Make sure your MI program 'closes the loop' on ***<u>correcting identified deficiencies</u>****!*

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained
4. Determine how often tasks need to be performed
5. Equip with maintenance procedures and training
6. Document ITMs
7. Correct identified deficiencies

8. Equipment-specific issues

CCPS Center for Chemical Process Safety

Process Safety Beacon

http://www.aiche.org/CCPS/Publications/Beacon/index.aspx

Messages for Manufacturing Personnel

CCPS Sponsors, the Beacon Committee, and volunteer Beacon translators wish all Beacon readers a happy, prosperous *<u>and safe</u>* New Year 2010.

Corrosion and Erosion

January 2010

Mechanical integrity is one of the biggest challenges for an effective process safety management program. Think about it – in your plant, there may be hundreds of vessels, thousands of feet of pipe, and hundreds of pumps, compressors, instruments, and other equipment. All of it must be kept in good operating condition to ensure safe, reliable, and profitable operation. Management of corrosion and erosion of process piping and equipment must be a major component of any effective mechanical integrity program.

The pictures show some examples of corrosion and erosion problems which were identified in plant inspections. (1) and (2) – external corrosion of pipes in a plant; (3) – close up of erosion damage to the face of a flange; (4) – close up of eroded body and seat of a gate valve; (5) – erosion damage on the body of a valve.

Do you know?

• ***Corrosion*** is the deterioration of metal by electro-chemical reaction with substances or microbes in its environment. These substances can be process materials contained in a vessel, pipe, or other equipment, or materials in the outside environment – for example, water, salt, or contaminants in the atmosphere. The rusting of steel is an example of corrosion.
• ***Erosion Corrosion*** is the degradation of material surface due to mechanical action, often by impinging liquid, abrasion by a slurry, or particles, bubbles, or droplets suspended in fast flowing liquid or gas.
• Corrosion has been responsible for major losses in the process industries. For example, in 2006, part of a major oil field had to be shut down for several months because of multiple oil spills resulting from severe pipeline corrosion.

What can you do?

• Understand mechanical integrity programs in your plant, and your role in ensuring that these programs are effective.
• Observe pipes, vessels, and other equipment when you are working in the plant. Look for stains on the outside of insulated lines and other signs of damaged or corroded equipment. Follow up to make sure that repairs are made.
• If you are taking equipment or piping apart, look for evidence of corrosion damage – for example, corrosion under insulation, internal corrosion in pipes or other equipment, damage to flanges or valves.
• When replacing pipes, valves, or other equipment, be careful to use the same material of construction.
• Understand the corrosion and erosion corrosion properties of the materials in your plant, and what you must do to minimize corrosion problems.

Watch out for corrosion and keep the chemicals inside the equipment!

Equipment – specific issues

- Fixed equipment
- Relief and vent systems
- Rotating equipment
- Instruments & electrical
- Emergency systems

See CCPS 2006 for more details

Fixed equipment

Primary objective:

Detect weaknesses in, or deterioration of, primary containment system integrity

(tanks, vessels, piping, heat exchangers, etc.)

- Internal / external corrosion
- Erosion
- Pitting
- Embrittlement
- Fatigue
- Etc.

Fixed equipment

- Mechanisms often chemical-dependent
  - Hydrogen embrittlement
  - Stress-corrosion cracking
  - Etc.
- Mechanisms also may be process-specific
  - Pressure-dependent
  - Temperature-dependent

Fixed equipment

- Inspections and tests generally require specialized equipment and techniques
  - Thickness measurements
  - Weld inspections
  - etc.
- Trained and certified inspectors
- Codes, standards usually apply

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Fixed equipment

Important considerations:
- Corrosion under insulation
- Internal inspections
- Connected utilities
- Deficiency corrections

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Fixed equipment

Some types of equipment imperfections to detect:

- **Imperfections arising prior to commissioning and not detected before startup**
  - Equipment inadequately designed for proposed duty
    - Wrong materials specified,
    - Pressure ratings of vessel or pipework inadequate,
    - Temperature ratings inadequate, etc.
  - Defects arising during manufacture
  - Equipment damage or deterioration in transit or during storage
  - Defects arising during construction
    - Welding defects, misalignment, wrong gaskets fitted, etc.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Fixed equipment

(continued)

- **Imperfections due to equipment deterioration in service**
  - Normal wear and tear on pump or agitator seals, valve packing, flange gaskets, etc.
  - Internal and/or external corrosion, including stress corrosion cracking
  - Erosion or thinning
  - Metal fatigue or vibration effects
  - Previous periods of gross maloperation; e.g., furnace operation at above the design tube skin temperature (“creep”)
  - Hydrogen embrittlement

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Fixed equipment

(continued)

- **Imperfections arising from routine maintenance or minor modifications not carried out correctly**
  - Poor workmanship
  - Wrong materials
  - Etc.

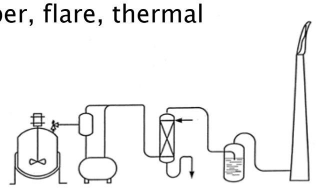
Reference: *Guidelines for Vapor Release Mitigation* (New York: American Institute of Chemical Engineers, 1988)

Relief and vent systems

Primary objectives:

Ensure relief and vent system will work when called upon to relieve excess internal pressure or vacuum; treat relief effluent

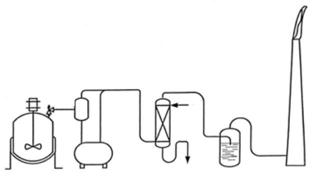
(relief valve, rupture disk, vent valve, header, cyclone separator, knockout pot, scrubber, flare, thermal oxidizer, etc.)



Relief and vent systems

Important considerations:

- Always maintain relief capability while operating
- Detect plugging
- Maintain scrubber/quench fluid levels, potency
- Verify correct reinstallation



Rotating equipment

Primary objectives:

Maintain continuous operation of rotating equipment; ensure availability of standby rotating equipment

(pumps, compressors, etc.)

Rotating equipment

Primary ITM activities:

- Vendor-specified PMs (lube, oil level checks, etc.)
- Routine visual inspections
- Incipient failure detection (vibration analysis, oil analysis, etc.)
- Periodic switchover to standby systems

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Instruments & electrical

Primary objectives:

Maintain continuous operation of controls and power systems; ensure availability of standby and emergency shutdown systems

(valves, sensors, controllers, power supplies, etc.)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Instruments & electrical

Primary ITM activities:

- Vendor-specified PMs (valve stroking, etc.)
- Routine inspections and readings (voltages, etc.)
- Scheduled functional tests
  - Safety shutdown systems: Ensure full functional tests, from sensor to final control element
  - May require testing part of the system at a time

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Emergency equipment

Primary objectives:

Ensure availability of emergency systems and integrity of passive mitigation systems

(detection, suppression, fire protection systems; diking and drainage; etc.)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Emergency equipment

Primary ITM activities:

- Routine inspections (diking integrity, drain valve closed and locked, fire extinguisher checks, etc.)
- Scheduled functional tests
  - Firewater system flow tests
  - Deluge system tests
  - Detectors and suppression system tests
  - Etc.

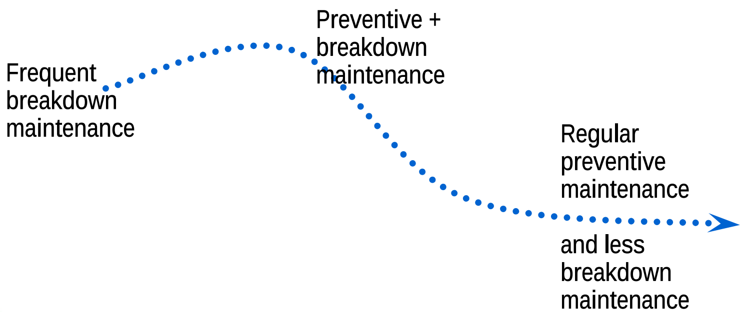
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

DISCUSSION

- What are some major challenges to having a proper inspection and testing program?
- How can these be overcome?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Getting over the hump



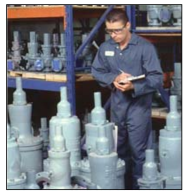
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained
4. Determine how often tasks need to be performed
5. Equip with maintenance procedures and training
6. Document ITMs
7. Correct identified deficiencies

---

8. Equipment-specific issues



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Summary

- Mechanical Integrity
  - Design/Build,
  - Inspect/Test/Maintain,
  - Correction and improvement of equipment
- Maintaining Control of Processes
- Loss of Containment Description
- Safeguards
- Maintenance of Equipment

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Day 4

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sandia National Laboratories

Chemical Transportation Safety and Security

SAND No: 2012-2778C
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Introduction

- Chemical Transportation
- Case Study Involving the Shipment of Lithium Batteries
- Chemical Transportation Risk Management - Safety
  - Resources to help manage risks
  - Identify, analyze and reduce risks
  - Safety risks
- Chemical Transportation Risk Management - Security
  - Resources and Regulations
  - Identify, analyze and reduce security risks
- Summary

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

900

Types of chemical transportation

- Chemical transportation:
  - Inside the plant
    - trucks, forklifts, pipelines, etc.
  - Local
    - Vehicles - company owned, contract services
    - pipelines
  - In-country
    - Similar to local
    - Trains
    - Ships
    - Air transport
  - International transport
    - Trucks (company owned or contract services), pipelines
    - Trains
    - Ships
    - Air transport

Chemical transportation

- It is an essential element in the chemical supply chain and
- Globalization has resulted in:
  - Increased volume
  - Increased speed
  - Strain on transportation infrastructure

Chemical transportation safety risks

- Transporting hazardous chemicals and hazardous waste

  Risks to *people, facilities, communities* and the *environment*

- Transport vehicle may carry both people and product

- Transport companies may outsource and consolidate hazardous materials
  - Package incompatible materials
  - Insecure packaging & improper labeling

Current Complexity in Chemical Transportation Increases Risk

- Thousands of regulated hazardous materials
- Differences in regulations by country
- Use of different hazard classes
- Different modes of transportation

  Road, rail, air, marine, pipeline
- Multiple packaging types

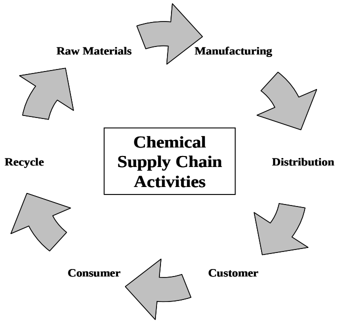
90
4

Transportation risk management

Due to the complexity of many supply chains, transportation risk management is a shared responsibility.

Roles and responsibilities may differ for each stakeholder.

Individual activities and actions can impact the risk to the overall *chemical supply chain.*



A Case Study Involving Lithium Batteries and Improper Packaging

Accident No. DCA04MZ001U.S. National Transportation Safety Board. http://www.ntsb.gov/

Lithium Batteries and Improper Packaging

Transportation mode: Air

Date: 7 Aug. 2004

Hazardous Material: Lithium-ion batteries

Type of accident: Cargo fire at the terminal

Carrier: Air freight line (non-passenger carrier)

Result: Damage to cargo unit load device ~$20,000 USD.

No injuries.

Accident No. DCA04MZ001U.S. National Transportation Safety Board. http://www.ntsb.gov/

Lithium Batteries and Improper Packaging

Background Information:

- Lithium batteries are described as Class 9 goods [miscellaneous dangerous goods – international term is hazardous materials].
- This was a prototype battery pack manufactured by a US firm.
- Battery pack was to be shipped to France for electric car research.
- Because it was a prototype battery pack special approval was required for this shipment.

U.S. National Transportation Safety Board. http://www.ntsb.gov/

Lithium Batteries and Improper Packaging

Shipping Requirements as specified by the US Department of Transportation –

- Battery pack
  - Size - 157 x 43 x 23 cm
  - Weight = 159 Kg
- Package specifications –
  - Insulating fiber glass case
  - Inside a wooden box
  - Fiberglass case bolted to the wooden box
  - Total weight = 240 Kg

U.S. National Transportation Safety Board. http://www.ntsb.gov/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

909

Lithium Batteries and Improper Packaging

This is what the packaging was supposed to look like.

U.S. National Transportation Safety Board. http://www.ntsb.gov/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

910

Lithium Batteries and Improper Packaging

How did the company prepare the lithium battery pack for packaging?

- Type of Package –
  - Cardboard box
- The package contained –
  - Battery pack with exposed terminals
  - Metal wrenches with a plastic bag of nuts and bolts.

U.S. National Transportation Safety Board. http://www.ntsb.gov/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

911

A Case Study Involving Lithium Batteries and Improper Packaging…

This is how the battery packs were packaged.

Cardboard box with battery packs

Metal tools inside the same box.

U.S. National Transportation Safety Board. http://www.ntsb.gov/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

912

A Case Study Involving Lithium Batteries and Improper Packaging…

What Happened?

- It was determined that the metal tools shifted during transportation and short circuited the positive and negative terminals of the battery pack causing localized heating.
- This heating caused the packaging to burn and ruptured of some of the other lithium ion battery cells.

U.S. National Transportation Safety Board. http://www.ntsb.gov/

A Case Study Involving Lithium Batteries and Improper Packaging…

Why did this accident happen?

A Case Study Involving Lithium Batteries and Improper Packaging…

There were guidelines detailing the proper packaging of the lithium-ion batteries.

These guidelines were not followed.

A Case Study Involving Lithium Batteries and Improper Packaging…

What could have been the outcome?

This fire could have occurred during the flight, resulting in the loss of the airplane and possibly the loss of life.

The freight box containing the battery pack was being loaded into the airplane when the worker smelled smoke.

Transportation Risk Management

Center for Chemical Process Safety (CCPS) Risk Management Publication

CCPS (2008). Guidelines for Chemical Transportation Safety, Security, and Risk Management

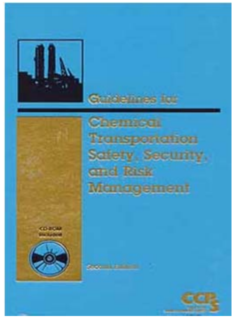
Covers transportation safety, security and risk management

Provides tools and methods to assist transportation professionals and other stakeholders

Presents a comprehensive framework for managing transportation risks

Introduces practical techniques for screening, identifying, and managing higher-level risks

Emphasizes the need to balance safety with security



918

Transportation risk management

To help calculate risks –

- *CCPS Guidelines* gives estimates for the likelihood of incidents involving:
  - Pipelines
  - Rail
  - Trucks
  - Barges
  - Ocean-going vessels
  - Intermodal transport

CCPS Transportation risk management (TRM)

The CCPS TRM process includes the following elements:

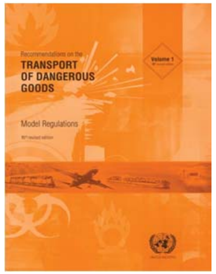
- Primary Management System
- Identification and prioritization of hazards
- Risk Analysis
- Risk Reduction
- Program Sustainability

Transportation risk management Primary management system

Primary Management Systems

Management systems should adhere to regulations and accepted international transportation standards.

- UN Model Regulations
  - http://www.unece.org/trans/danger/publi/unrec/12_e.html
- International Maritime Organization (IMDG Code)
  - http://www.imdgsupport.com/
- International Air Transport Association (IATA)
  - Dangerous Goods Regulation, 52nd Ed.



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation risk management Primary management system

A Primary Management System Should Also Include:

- Management Commitment
  - "Risk Reduction Culture"
- Policies, procedures & practices
- Emergency preparedness & response procedures
- Incident reporting system
- Management of change
- Periodic auditing of the system

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

92
2

Transportation risk management Model

Risk = f(scenario, consequence, likelihood)

Transportation risk management follows a general risk management model -

1. **Identification and Prioritization:** screen to identify and escalate issues/scenarios for more detailed risk analysis.
2. **Analysis:** the process of evaluating and estimating the overall level of risk associated with the selected scenarios.
3. **Evaluation:** compare the results against evaluation criteria used for making decisions to set the level of risk mitigation.
4. **Reduce:** develop, compare and select ways to reduce the risks to a target level if needed or as needed.

CCPS Guidelines for Chemical Transportation Safety, Security, and Risk Management

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

92
3

Transportation risk management: Identify Risks

What are the hazardous materials that will be transported?

- What are the physical and chemical properties of the materials?
  - Flammable, toxic, corrosive, reactive?
  - Gas or liquid?
- (How are they packaged?)

Photos: U.S. Department of Transportation

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation risk management: Analyze Risks

External (Accidents)

- Collisions-road, rail
- Cargo shift-road, air
- Derailment-rail
- Crash-air
- External impact-pipeline

Internal Events

- Release or spill that is not due to an external impact
- Example: equipment or containment failure

Photos: US National Transportation Safety Board

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation risk management: Analyze Risks

Potential Causes of Incidents

- Human factors
- Equipment defects
  - Corrosion
  - Overpressure
- Overfilling
- Improper packaging
- Vehicle impact
- Transportation infrastructure

Photo: US National Transportation Safety Board

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation risk management: Analyze Risks

Risk = f(scenario, consequence, likelihood)

Consequence

- Fatalities/injuries
- Property damage
- Environmental damage
- Business impact/fines
- Negative media
- Distribution system disrupted

Likelihood

- Expected probability and frequency

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation risk management: Evaluate Risks

- After analyzing the risks with respect to possible
  - Scenarios,
  - Consequences and
  - Likelihood.
- Compare the results against evaluation criteria that was used and
- Make decisions to set the level of risk mitigation.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation risk management: Risk Reduction

Address highest priority safety hazards first by:

- Written procedures
- Personnel training
- Hazard communication
- Packaging
- Spill containment
- Equipment inspection
- Personnel protection (PPE)
- Emergency response and reporting

Transportation risk management: Risk Reduction

Written procedures –

Written procedures outlining different steps and procedures associated with shipping and receiving chemicals for your company.

Transportation risk management: Risk Reduction

Personnel Training –

- Train personnel on the handling, packaging, shipping and receiving of chemicals.
- They need to know local transportation as well as international regulations for the shipment of hazardous chemicals.
- Make sure that more than one person has the training.
- Make sure training is up-to-date.

Transportation risk management: Risk Reduction

Hazard Communication

- Safety data sheets
- Shipping papers
- Labeling
- Placards (information signs)

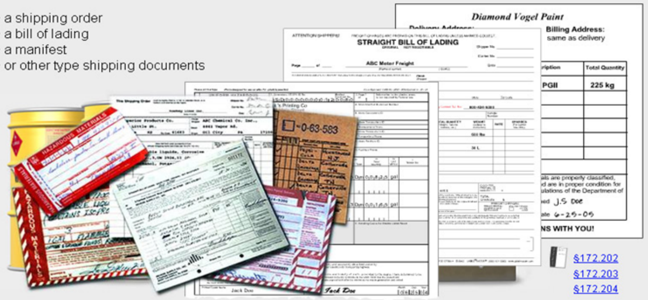
93
2

Transportation risk management: Risk Reduction

Definition of Shipping Papers

As used in the HMR, a shipping paper for hazardous materials transportation is any document that contains the information required to describe the hazardous material being transported. It may include:

- a shipping order
- a bill of lading
- a manifest
- or other type shipping documents



§172.202
§172.203
§172.204

US Department of Transportation. http://www.dot.gov/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation risk management: Risk Reduction

Closure Requirements

Closure requirements for containers of liquid hazardous materials include:

- Close tightly and securely
- Inner packaging must remain upright
- Provide cushioning when needed
- Closed in a consistent and repeatable manner
- Closed as required by the manufacturer's closure instructions, if applicable

US Department of Transportation. http://www.dot.gov/

§173.24(a)
§173.24(e)(5)
§173.24(f)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation risk management: Risk Reduction

UN Standard Packagings

Packagings tested to meet the Part 178 performance requirements are called "UN Standard Packagings."

- Standards
- Package Marking Requirements

§171.8

US Department of Transportation. http://www.dot.gov/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation risk management: Risk Reduction

Lab Packs Outer Packaging

For lab packs, the outside packaging must be a:

- UN1A2 or UN1B2 metal drum;
- UN1D plywood drum;
- UN1G fiber drum; or
- UN1H2 plastic drum tested and marked at least for Packing Group III materials.

Metal **Fiber** **Polyethylene**

§173.12(b)(1-2)

US Department of Transportation. http://www.dot.gov/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation risk management: Risk Reduction

Leaking or Damaged HM Packages

Repackage leaking or damaged HM packages in metal or plastic salvage drums. The drums must have a removable head. The drums must be compatible with the material.

- Standards
- Markings
- Shipping Papers
- Overpack Requirements

US Department of Transportation. http://www.dot.gov/ §173.3(c)

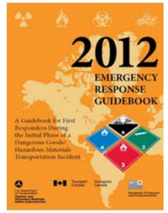
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

937

Transportation risk management: Risk Reduction

Emergency Response Guidebook (ERG)

- Interactive internet version:
  http://wwwapps.tc.gc.ca/saf-sec-sur/3/erg-gmu/erg/ergmenu.aspx
- Developed jointly by:
  US DOT, Transport Canada, Secretariat of Communications and Transportation Mexico
- For first responders to transportation incident
- Guide to quickly identify material classification
- Protect initial responders and public



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

938

Chemical Transportation Security Risks

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

939

Chemical Transportation Security Risks

- In-plant threat
  - Sabotage shipments
  - Intentional release
  - Theft
- In-transit threats
  - Hijacking
  - Theft of materials
  - Sabotage
- Attacks on pipelines

http://www.phmsa.dot.gov/hazmat/security

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

940

Transportation risk management: Security risks

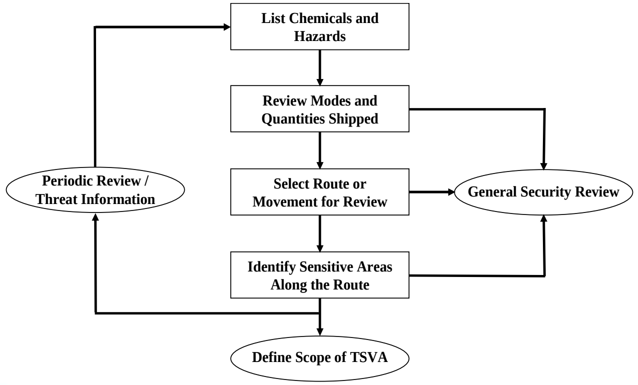
Security Risk = *f*(consequence, vulnerability, threat)

Is similar to safety risks

Safety Risk = f(scenario, consequence, likelihood)

- For security risks the initiating event is a direct attack.
- The magnitude of the incident could be greater.
  - Larger releases of hazardous material are possible,
  - Populations would be most likely the target.

Transportation Security Vulnerability Analysis



CCPS (2008). Guidelines for Chemical Transportation Safety, Security, and Risk Management

Transportation Security Risk Management: Risk Reduction

Plant Security

- Include internal transfers in plant security plan
- Limit access to facilities and shipping information
- Secure transportation equipment
- Keep an inventory of hazardous materials
  - Use tamper resistant seals
- Personnel Security
  - Background checks
  - Identification cards or badges

Transportation Security Risk Management: Risk Reduction

In transit security threats

- Vehicle travels on unprotected public roads, rail or sea
- Surroundings are constantly changing
- Sabotage or theft is not detected until in progress
- One person responsible for transport
- Typically there are no security personnel accompanying shipment

Photo: U. S. Transportation Security Administration

Transportation Security Risk Management: Risk Reduction

Potentially sensitive materials that are shipped by highway

- Depends on quantity and packaging
- ~ ≥ 3000 liters in single container
  - Explosives
  - Flammable Gases
  - Anhydrous Ammonia
  - Toxic Gases
  - Flammable Liquids & Solids
  - Oxidizers
  - Water reactive
  - Corrosives
  - Radioactive, infectious substances

Credit: US TSA Highway Security Sensitive Materials

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation Security Risk Management: Risk Reduction

High risk shipments require *high-level* controls:

Increase possibility of detecting an attack

- Provide for additional security personnel
- Alarm the shipment
- Use communication systems

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation Security Risk Management: Risk Reduction

Increase the possibility of delaying an attack

- Cargo secured to vehicle
- Immobilize vehicle
- Hazardous material in vault
- Locks, barriers, entanglements

Drum Cage

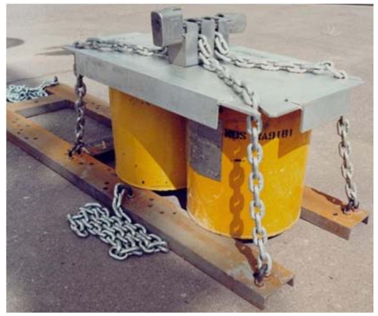
Photo credit: DOE NNSA Presentation, October 17-November 5, 2010

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation Security Risk Management: Risk Reduction

Metal Grating

Smoke Obscurant



Container Tie Down

Photo credit: DOE NNSA Presentation, October 17-November 5, 2010

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Transportation Security Risk Management: Risk Reduction

Photos: TSA User's Guide on Security Seals for Domestic Cargo

Transportation Risk Management: Selection of Transportation Contractor

- Evaluation of accident history and transportation safety plans
- Safety training of personnel
- Certifications/licensing
- Condition of equipment
- Confirm the following:
  - Secure packaging
  - Shipping documentation/bill of lading
  - Labelling
  - Safety data sheets
  - Appropriate PPE for spill response
  - Spill containment kits on board
  - Emergency Contact Information on board

US Federal Motor Carrier Safety Regulations

The US FMCSA regulates:
- Driver qualifications
- Years of service
- Equipment standards
- Driving and parking rules
- Alcohol and controlled substances
- Financial responsibility
- Operational requirements

HAZMAT training required for:
- Personnel who prepare, load/unload, or transport hazardous materials.

Balancing Transportation Security with Safety

Issue	Safety	Security
Placards	Commodity information needed by emergency responders to react appropriately to an accident and minimize any impact.	Commodity information could be used by terrorists to target specific chemicals.
Rerouting	May result in more accidents if there are longer transits or the infrastructure along an alternate route may be less well maintained or contain undesirable features (uncontrolled intersections, no shoulders, etc.).	Eliminating a shipment near a specific location (most likely a highly populated or critical area) may inadvertently transfer the risk from one community to another.

CCPS (2008). *Guidelines for Chemical Transportation Safety, Security, and Risk Management*

Balancing Transportation Security with Safety

Issue	Safety	Security
Working with supply chain partners (implementing security countermeasures)	Technology can be used for both safety and security (e.g., GPS to indicate location en route, emergency response to accident, and monitoring time-sensitive chemicals/materials).	Technologies focused on security should not distract the main function of the carriers (e.g., the safe transport of chemicals from point A to B).
Risk Analysis Methods	• Rational and structured results lead to recommendations • Participation and engagement by individuals with different perspectives, roles, and backgrounds/skill sets for safety, security, and transportation • Similar methodology • Same decision metrics (guidelines)	

CCPS (2008). *Guidelines for Chemical Transportation Safety, Security, and Risk Management*

Transportation Risk Management: Evaluate risk

Example -

- A company ships a hazardous chemical from Factory A to Factory B.
- There are two different roads that connect Factory A and B.
- One road (Route 1) is in very poor condition and goes through a heavily populated part of City, but the distance to Factory B is shorter.
- The other road (Route 2) is in better condition, does not go through any populated areas, but the distance to Factory B is longer and takes more time.

Photo: US National Transportation Safety Board

Transportation Risk Management: Evaluate risk

Example….

- A review of the transport logs shows that trucks traveling along Route 1 experience a breakdown or minor accident one time in about every 20 trips. However, no major chemical spill has resulted yet.
- The company has done a analysis and has concluded that 1 in every 50 accidents a truck will overturn and its hazardous cargo could spill.
- The company has decided that this is an unacceptable risk based on their evaluation criteria.

Transportation Risk Management: Risk reduction

Example….

The company has decided that Route 1 is an unacceptable risk to the local population and will begin using Route 2 even though the distance is longer and takes more time.

Summary

- Chemical Transportation
- Case Study Involving the Shipment of Lithium Batteries
- Chemical Transportation Risk Management - Safety
  - Resources to help manage risks
  - Identify, analyze and reduce risks
- Chemical Transportation Risk Management - Security
  - Resources and Regulations
  - Identify, analyze and reduce security risks

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

957

Principles of Security

SAND No. 2012-1606C
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-AC04-94AL85000

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

958

Objectives

- Review the Definition and Objective of Security
- First Steps - Security Awareness
- Describe four Principles of Security
- Impart the importance of Performance-Based Security
- Provide a Model for a Systematic Approach to Security

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What is security?





CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

960

Security objective

Security intends to prevent *intentional acts* which could result in unacceptable consequences

- Death/Severe Injury
- Chemical contamination
  - People
  - Environment
- Political Instability
- Economic Loss
- Industrial capacity loss
- Negative public psychological effect
- Adverse media coverage

First Steps in Chemical Security: Low Cost Principles

Chemical Security Awareness

- Property-Vehicles-Information-Personnel
- Work Area - Changes
- Behavior - Suspicious
- Procedures - Followed

Access Controls

Have (credential), Know (PIN), Are (biometric*)

Manual (guards), Automated (machines)

* Can be expensive

Basic Security Awareness

- Work area changes
  - Hole in fence
  - Suspicious packages
  - Inventory discrepancy
  - Door unlocked
- Symptoms of others behavior who are attempting to compromise security
  - Elicitation
  - Surveillance
  - Ordering supplies

Security awareness is the first step to making your facility safe from malevolent acts

Source: DHS Chemical Security Awareness Training

Awareness– Suspicious Behaviors

- Testing security – walking into, wait for discovery
- Mapping, loitering, staging vehicles
- Taking pictures of security system
- Looking in dumpster
- Trying to enter on your credential
- Asking for user name over the phone or by email
- Asking about plant layout – workers names – schedules

Source: DHS Chemical Security Awareness Training

Security Involves Systematic Diligence– even Small Things

- Missing badge
- Leaving workstation unsecured - fire alarm
- Leaving sensitive document
- Bypassing security

Know what to do - who to call

Communicate anything unusual to supervisor

Remember - YOU are the first responder

Source: DHS Chemical Security Awareness Training

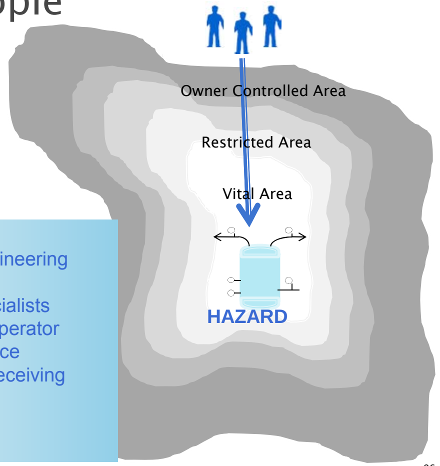
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

96 5

Access Control Integrated with Areas and People

Plant locations
- Administration
- Control rooms
- Server rooms
- Switchgear
- Process Units
- Rail / truck yards
- Stores

Plant employees
- Administration /Engineering
- Operations
  - Computer specialists
  - Control room operator
  - Process interface
  - Shipping and receiving
- Maintenance
- Security / Safety
- Special employees



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

96 6

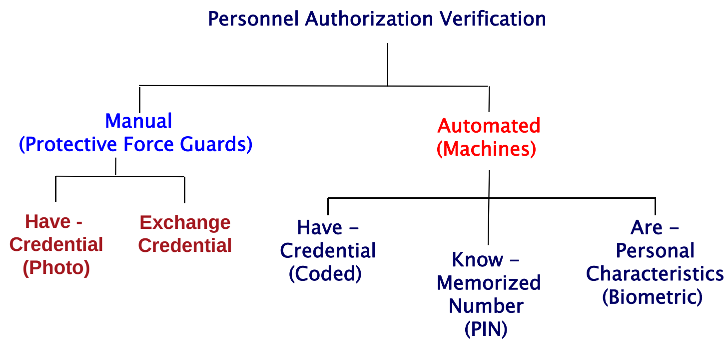
Features of a Good Entry Control System

- Integration with boundary
  - Cannot be bypassed
  - Block individuals until access authorization verified
  - Interfaces with the alarm system
- Integration with the guards/response force
  - Protects guard
  - Area is under surveillance
- Personnel integrate with system
  - Easy to use for entry and exit
  - Accommodates peak throughput (loads)
  - Accommodates special cases

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

96 7

Types of Personnel Entry Control



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

96 8

What Kinds of Chemical Facilities Need Security?

Potential consequence severity will determine which facilities need to be secured

- Small-scale research laboratories
  - Many different chemicals used in small amounts
- Large-scale manufacturing plants
  - Limited types of chemicals used in large amounts

Chemical Industry Security Based on Theft, Release, and Sabotage

- Risk to public health & safety release
  - In-situ release of toxic chemicals
  - In-situ release and ignition of flammable chemicals
  - In-situ release/detonation of explosives chemicals
- Potential targets for theft or diversion
  - Chemical weapons and precursors
  - Weapons of mass effect (toxic inhalation hazards)
  - IED precursors
- Reactive and stored in transportation containers
  - Chemicals that react with water to generate toxic gases

Source: DHS Chemical Security

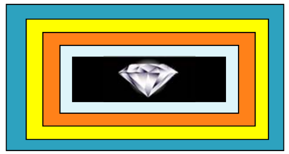
Principles of Physical Security

General Principles followed to help ensure effective, appropriate security

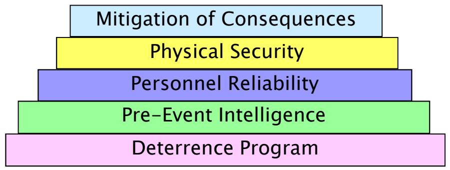
1. Defense in Depth
2. Balanced Security
3. Integrated Security
4. Managed Risk

Principle 1: Defense in Depth

- Layers
  - Physical

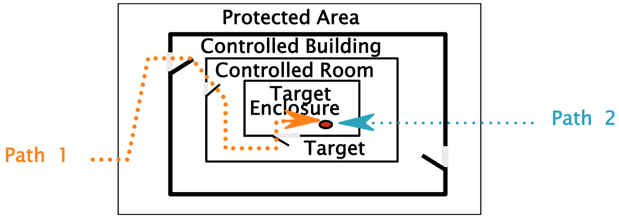


  - Administrative and Programmatic



Principle 2: Balanced Protection

- Physical Layers
- Adversary Scenarios
  - Adversary paths (physical)



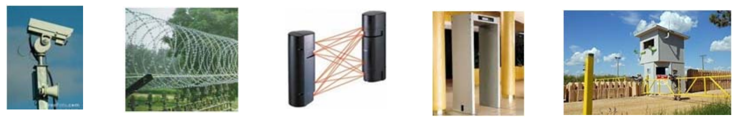
Balanced Protection

- Each Path is composed on many protection elements
  - Walls, fences, sensors, cameras, access controls, etc…
- Protection elements each possess delay and detection components
  - For example:
    - Fence delays adversaries *20* seconds, and provides 50% likelihood that adversary is detected
    - Wall delays adversary 120 seconds and provides a 10% likelihood of detection
    - Guard delays adversary 20 seconds and provides a 30% likelihood of detection
- Balanced protection objective:
  - for every possible adversary path
  - cumulative detection and delay encountered along path will be the similar
  - regardless of adversary path
  - NO WEAK PATH

Principle 3: System Integration

- Detection alerts Response
- Access Delay slows the adversary to provide time for Response
- Response prevents the consequence

Integrated Security



- Contribution to security system of each can be reduced to its contribution to:
  - Detection of adversary or malevolent event
  - Delay of adversary
  - Response to adversary
- Integrated security evaluates composite contribution of all components to these three elements
  - Assures that overall detection is sufficient and precedes delay
  - Assures that adversary delay time exceeds expected response time
  - Assures that response capability is greater than expected adversary

Principle 4: Managed Risk

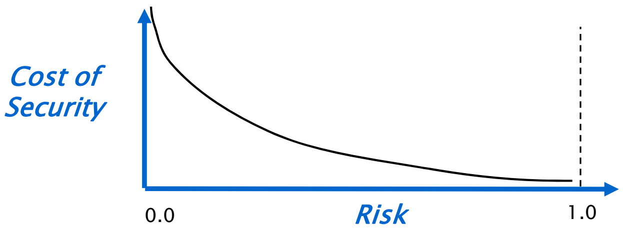
- How much Security is enough ???

Managed Risk

- Benefits of Security is Reduced Risk
- What is Risk?
  - Risk = Consequence Severity * Probability of Consequence
- What is Security Risk?
  - Probability of Consequence Occurrence ⇒
    - Frequency of attempted event

      X
    - Probability of successful attempt
  - Probability of successful attempt is
    - 1 - Probability of security system effectiveness

Managed Risk



- The benefit (risk reduction) increases with increased security investment (cost)
- However, there is a point where the increased benefit does not justify the increased cost

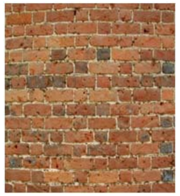
Objectives

- Review the Definition and Objective of Security
- First Steps – Security Awareness
- Describe Four Principles of Security
- Impart the Importance of Performance-Based Security
- Provide a Model for a Systematic Approach to Security

980

Requirements-Driven Security

- Design Constraints
  - Understand Operational Conditions
- Design Requirements
  - Consequences to be prevented
    - Identify Targets to be protected
  - Define Threats against which targets will be protected



981

Target Identification

What are possible sources of unacceptable consequences?

- Dispersal
  - Identify areas to protect
- Theft
  - Identify material to protect

982

Target Identification

Characterize Types of Targets

- Form
- Storage manner and location
- Flow of chemicals
- Vulnerability of Chemicals
  - Flammable
  - Explosive
  - Caustic

- **Criticality / Effect**
- **Access / Vulnerability**
- **Recoverability / Redundancy**
- **Vulnerability**

983

The Physical Protection System Must Have a Basis for Design

Threat Assessment: An evaluation of the threats- based on available intelligence, law enforcement, and open source information that describes the motivations, intentions, and capabilities of these threats

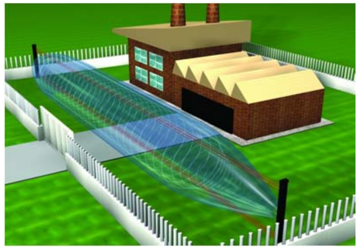
Design Basis Threat: A policy document used to establish performance criteria for a physical protection system (PPS). It is based on the results of threat assessments as well as other policy considerations

984

Define the Threats

In physical security:

- Knowing adversary permits customizing security to maximize effectiveness
- As adversary not known, develop hypothetical adversary to customize security
- Hypothetical adversary description should be influenced by actual threat data



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

985

Design Basis Threat

- A Design Basis Threat (DBT) is a formalized approach to develop a threat-based design criteria
- DBT consists of the attributes and characteristics of potential adversaries. These attributes and characteristics are used as criteria to develop a customized security system design.
- The DBT is typically defined at a national level for a State.
- At the facility level, also:
  - Consider local threats
    - Local criminals, terrorists, protestors
  - Consider insider threats
    - Employees and others with access

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

986

Objectives

- Review the Definition and Objective of Security
- First Steps – Security Awareness
- Describe the Principles of Security
- Impart the Importance of Performance-Based Security
- Provide a Model for a Systematic Approach to Security

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

987

Model: Design and Evaluation Process Outline (DEPO)

Define PPS Requirements → **Characterize PPS** → **Evaluate PPS** → **Accept Risk** / **Evaluate Upgrades**

Define PPS Requirements
- Process of PPS Design and Evaluation
- Facility Characterization
- Target Identification – Vital Areas
- Threat Definition DBT

Characterize PPS
- Physical Protection Systems
  - **Detection**: Intrusion Detection Systems; Alarm Assessment; Alarm Communication & Display; Entry Control; Contraband and Explosives Detection
  - **Delay**: Access Delay; Vehicle Barriers; Stand-Off Protection; Fences; Target Task Time
  - **Response**: Response; Weaponry; Communications Tactics; Backup Forces Training; Night Fighting Capability
- Gathering Performance Data

Evaluate PPS
- Evaluation of PPS
- Scenario and Path Analysis – LSPTs
- ASSESS VA Model
- JCATS Simulations
- Blast Simulations
- Overpressure Analysis
- Insider Analysis – Personnel Reliability
- Risk Evaluation
- Cost Benefit Analysis

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

988

Detect Adversary

- Technology
  - Intrusion Detection
  - Entry Control
  - Contraband Detection
  - Unauthorized Action Detection
- Supporting elements
  - Alarm Assessment
  - Alarm Communication
  - Alarm Annunciation




Delay Adversary

Delay Definition :

- The element of a physical protection system designed to slow an adversary after they have been detected by use of
  - Walls, fences
  - Activated delays-foams, smoke, entanglement
  - Responders
- Delay is effective only after there is first sensing that initiates a response

Respond to Adversary

Guard and Response Forces

Guards: A person who is entrusted with responsibility for patrolling, monitoring, assessing, escorting individuals or *transport*, controlling access. Can be armed or unarmed.

Response forces: Persons, on-site or off-site who are armed and appropriately equipped and trained to counter an attempted theft or an act of sabotage.

Guards can sometimes perform as initial responders as well (both guards and response force)

Summary

- Security systems should attempt to prevent, but be prepared to defeat an intentional malevolent act that could result in unacceptable consequences at a chemical facility
- Security awareness is an essential element
- An effective system depends on an appropriate integration of:
  - Detect
  - Delay
  - Respond

Break

Investigating Safety & Security Incidents

SAND No. 2011-1036C
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

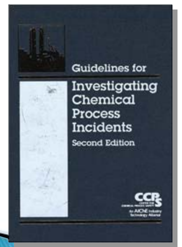
Key acronyms

RCA = *root cause analysis*

SVA = *security vulnerability analysis*

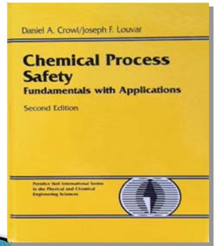
Resources

CCPS 2003. Center for Chemical Process Safety, *Guidelines for Investigating Chemical Process Incidents, 2nd Edition*, NY: AIChE.



Resources

D.A. Crowl and J.F. Louvar 2001. ***Chemical Process Safety: Fundamentals with Applications, 2nd Ed.,*** Upper Saddle River, NJ: Prentice Hall.

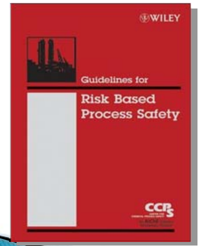


CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

997

Resources

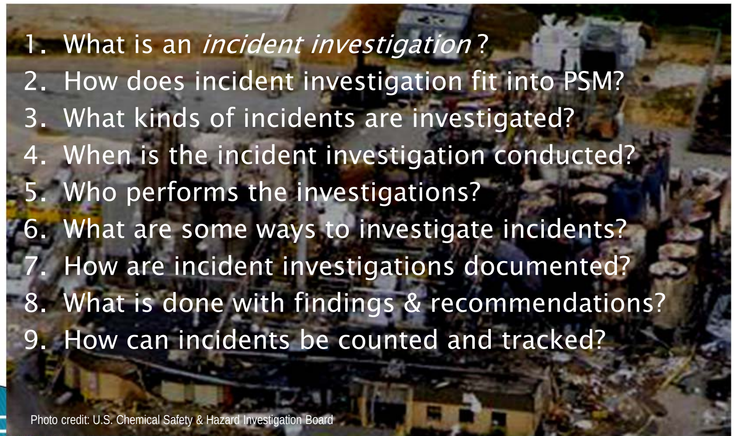
CCPS 2007a. Center for Chemical Process Safety, *Guidelines for Risk Based Process Safety*, NY: AIChE.



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

998

Investigating Safety/Security Incidents



1. What is an *incident investigation*?
2. How does incident investigation fit into PSM?
3. What kinds of incidents are investigated?
4. When is the incident investigation conducted?
5. Who performs the investigations?
6. What are some ways to investigate incidents?
7. How are incident investigations documented?
8. What is done with findings & recommendations?
9. How can incidents be counted and tracked?

Photo credit: U.S. Chemical Safety & Hazard Investigation Board

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

999

Investigating Safety/Security Incidents

1. What is an *incident investigation*?

Results of explosion and fire at a waste flammable solvent processing facility
(U.S. CSB Case Study 2009-10-I-OH)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1000

What is an *incident investigation*?

An *incident investigation* is the management process

by which underlying causes of undesirable events are uncovered

and steps are taken to prevent similar occurrences.

– CCPS 2003

Learning from incidents

Investigations that will enhance learning

- are fact-finding, not fault-finding
- must get to the *root causes*
- must be reported, shared and retained.

Definition – Root cause

Root Cause: A fundamental, underlying, system-related reason why an incident occurred that identifies a correctable failure or failures in management systems.

There is typically more than one root cause for every process safety incident.

– CCPS 2003

Investigating Safety/Security Incidents

What kinds of incidents are investigated?

- The first step in an incident investigation is *recognizing that an "incident" has occurred!*

What kinds of incidents are investigated?

- The first step in an incident investigation is *recognizing that an "incident" has occurred!*

Yes

What kinds of incidents are investigated?

- The first step in an incident investigation is *recognizing that an "incident" has occurred!*

?

Definitions

Incident: An unplanned event or sequence of events that either resulted in or had the potential to result in adverse impacts.

Incident sequence: A series of events composed of an initiating cause and intermediate events leading to an undesirable outcome.

Source: CCPS 2008a

Incident types

Three categories of incidents, based on outcomes:

- **Loss event**
- **Near miss**
- **Operational interruption**

1009

Incident types

Three categories of incidents, based on outcomes:

Loss event

– Actual loss or harm occurs (also termed *accident* when not related to security)

Near miss

Operational interruption

– Actual impact on production or product quality occurs

1010

Incident types

Three categories of incidents, based on outcomes:

- **Loss event**
- **Near miss**
- **Operational interruption**

Near miss: An occurrence in which an accident (i.e., property damage, environmental impact, or human loss) or an operational interruption could have plausibly resulted if circumstances had been slightly different. - CCPS 2003

1011

DISCUSSION

Give three or four examples of simple near-miss scenarios.

Include at least one related to facility security.

1.

2.

3.

4.

1012

Investigating Safety/Security Incidents

When is the incident investigation conducted?

- Basic answer: *As soon as possible.*
- Reasons:
  - Evidence gets lost or modified
    - Computer control historical data overwritten
    - Outside scene exposed to rain, wind, sunlight
    - Chemical residues oxidize, etc.
  - Witness memories fade or change
  - Other incidents may be avoided
  - Restart may depend on completing actions to prevent recurrence
  - Regulators or others may require it

    (E.g., U.S. OSHA PSM: Start within 48 h)

When is the incident investigation conducted?

Challenges to starting as soon as possible:

- Team must be selected and assembled
- Team may need to be trained
- Team may need to be equipped
- Team members may need to travel to site
- Authorities or others may block access
- Site may be unsafe to approach / enter

DISCUSSION

What might be done to overcome some of the challenges to starting an investigation?

-
-
-
-

Investigating Safety/Security Incidents

1. What is an *incident investigation*?
2. How does incident investigation fit into PSM?
3. What kinds of incidents are investigated?
4. When is the incident investigation conducted?
5. Who performs the investigations?

1017

Who performs the investigations?

Options:

- Single investigator
- Team approach

1018

Who performs the investigations?

Options:

- Single investigator
- Team approach

Advantages of team approach: (CCPS 2003)
- Multiple technical perspectives help analyze findings
- Diverse personal viewpoints enhance objectivity
- Internal peer reviews can enhance quality
- More resources are available to do required tasks
- Regulatory authority may require it

1019

Who performs the investigations?

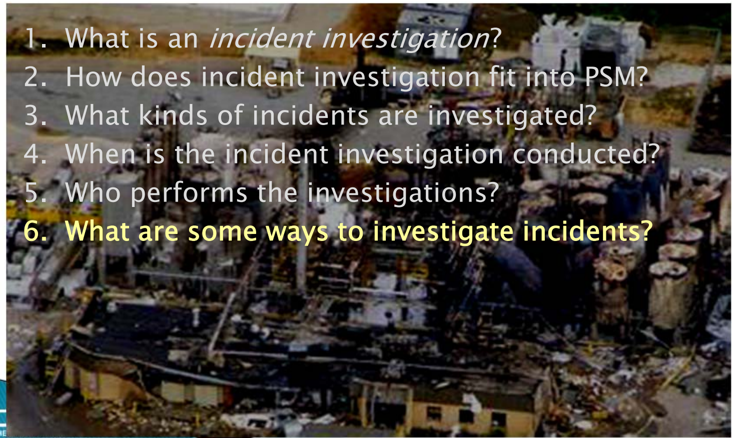
The "best team" will vary depending on the nature, severity and complexity of the incident.

Some possible team members:

- Team leader / investigation method facilitator
- Area operator
- Process engineer
- Safety/security specialist
- I&E / process control or computer systems support
- Union safety representative
- Contractor representative
- Other specialists (e.g., metallurgist, chemist)

1020

Investigating Safety/Security Incidents



1. What is an *incident investigation*?
2. How does incident investigation fit into PSM?
3. What kinds of incidents are investigated?
4. When is the incident investigation conducted?
5. Who performs the investigations?
6. What are some ways to investigate incidents?

1021

Older investigations

- Only identified obvious causes; e.g.,
  - "The line plugged up"
  - "The operator messed up"
  - "The whole thing just blew up"
- Recommendations were superficial
  - "Clean out the plugged line"
  - "Re-train the operator"
  - "Build a new one"

1022

Layered investigations

- Deeper analysis
- Additional layers of recommendations:
  1. Immediate technical recommendations
     - *e.g., replace the carbon steel with stainless steel*
  2. Recommendations to avoid the hazards
     - *e.g., use a noncorrosive process material*
  3. Recommendations to improve the management system
     - *e.g., keep a materials expert on staff*

1023

Case Study

- Pool is very crowded
- Older children are engaged in "horseplay"
- 5 year old child pushed into deep end of pool
- Lifeguard does not notice child in deep end

1024

Technical Recommendations

- Paint pool to indicated deep end
- Add more lifeguards
- Reduce number of swimmers

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

10 25

Avoiding the Hazard

- Zone the pool–young children at one end of the pool
- Swimming lessons
- All new swimmers get pool orientation
- Add another roving lifeguard

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

10 26

Improve the Management System

- Train lifeguards to alert supervision of potential problems
- Assign a supervisor to make formal inspections on a regular basis

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

10 27

Investigation process

1 Choose investigation team
2 Make brief overview survey
3 Set objectives, delegate responsibilities
4 Gather, organize pre-incident facts
5 Investigate, record incident facts
6 Research, analyze unknowns
7 Discuss, conclude, recommend
8 Write clear, concise, accurate report

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1028

Discovery phase

- Develop a plan
- Gather evidence
  - Take safety precautions; use PPE
  - Preserve the physical scene and process data
  - Gather physical evidence, samples
  - Take photographs, videos
  - Interview witnesses
  - Obtain control or computer system charts and data

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1029

Analysis of facts

- Develop a timeline
- Analyze physical and/or electronic evidence
  - Chemical analysis
  - Mechanical testing
  - Computer modeling
  - Data logs
  - etc.
- Conduct multiple-root-cause analysis

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1030

Some analysis methods

- Five Why's
- Causal Tree
- RCA (Root Cause Analysis)
- FTA (Fault Tree Analysis)
- MORT (Management Oversight and Risk Tree)
- MCSOII (Multiple Cause, Systems Oriented Incident Investigation)
- TapRooT®

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1031

Some analysis methods

General analysis approach:

- Develop, by brainstorming or a more structured approach, possible incident sequences
- Eliminate as many incident sequences as possible based on the available evidence
- Take a closer look at those that remain until the actual incident sequence is discovered (if possible)
- Determine the underlying root causes of the actual incident sequence

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1032

Incident sequence questions

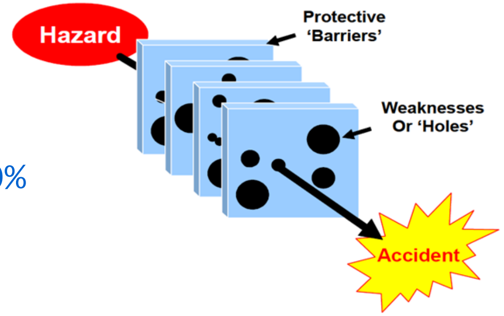
Determine, for the incident being investigated:

- What was the *cause* or *attack* that changed the situation from "normal" to "abnormal"?
- What was the actual (or potential, if a near miss) *loss event*?
- What safeguards failed? What did not fail?

1033

"Swiss cheese model" review

REMEMBER:
No protective barrier is 100% reliable.



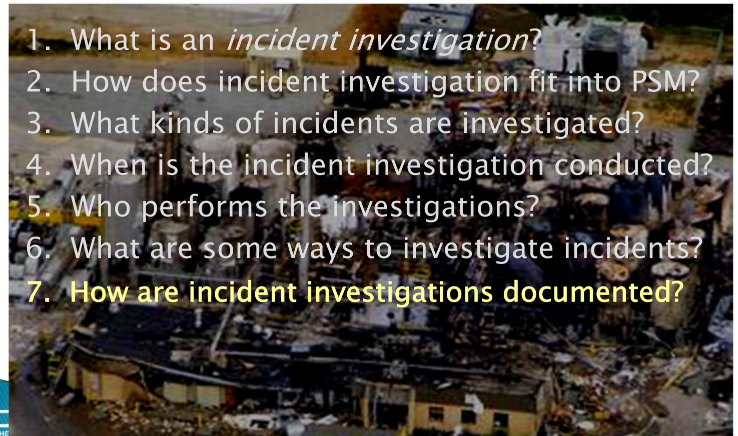
1034

Discuss, conclude, recommend

- Find the most likely scenario that fits the facts
- Determine the underlying management system failures
- Develop layered recommendations

1035

Investigating Safety/Security Incidents



1. What is an *incident investigation*?
2. How does incident investigation fit into PSM?
3. What kinds of incidents are investigated?
4. When is the incident investigation conducted?
5. Who performs the investigations?
6. What are some ways to investigate incidents?
7. How are incident investigations documented?

1036

How are incident investigations documented?

A written report documents, as a minimum:

- Date of the incident
- When the investigation began
- Who conducted the investigation
- A description of the incident
- The factors that contributed to the incident
- Any recommendations resulting from the investigation

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM 1037

Typical report format

1. Introduction
2. System description
3. Incident description
4. Investigation results
5. Discussion
6. Conclusions
7. Layered recommendations

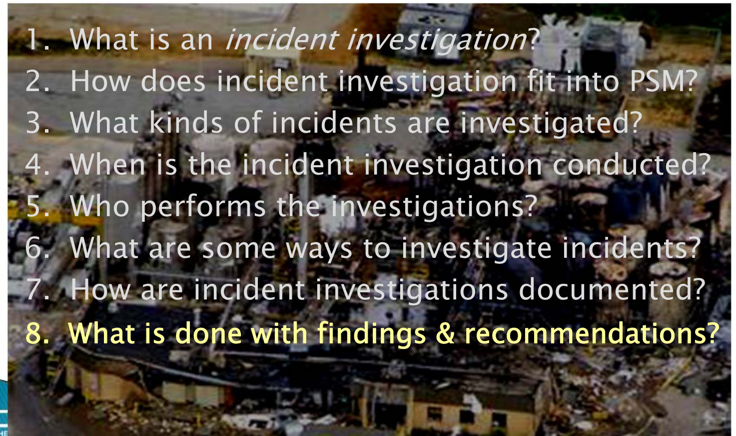
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM 1038

Investigation Summary

- The investigation report is generally too detailed to share the learnings to most interested persons
- An Investigation Summary can be used for broader dissemination, such as to:
  - Communicate to management
  - Use in safety or security meetings
  - Train new personnel
  - Share lessons learned with sister plants

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM 1039

Investigating Safety/Security Incidents



1. What is an *incident investigation*?
2. How does incident investigation fit into PSM?
3. What kinds of incidents are investigated?
4. When is the incident investigation conducted?
5. Who performs the investigations?
6. What are some ways to investigate incidents?
7. How are incident investigations documented?
8. **What is done with findings & recommendations?**

1040

Findings and recommendations

What is the most important product of an incident investigation?

1. The incident report
2. Knowing who to blame for the incident
3. Findings and recommendations from the study

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1041

Findings and recommendations

What is the most important product of an incident investigation?

1. The incident report
2. Knowing who to blame for the incident
3. Findings and recommendations from the study
4. The actions taken in response to the study findings and recommendations

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1042

Findings and recommendations

Example form to document recommendations:

ORIGINAL STUDY FINDING / RECOMMENDATION			
Source: ☐ PHA ☐ Incident Investigation ☐ Compliance Audit ☐ Self-Assessment ☐ Other			
Source Name			
Finding No.		**Risk-Based Priority** *(A, B, C or N/A)*	
Finding / Recommendation			
Date of Study or Date Finding / Recommendation Made			

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1043

Aids for recommendations

Overriding principles (Crowl and Louvar 2001, p. 528):

- Make safety [and security] investments on cost and performance basis
- Improve management systems
- Improve management and staff support
- Develop layered recommendations, especially to eliminate underlying causes

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1044

Aids for recommendations

Overriding principles:

- Make safety [and security] investments on cost and performance basis
- Improve management systems
- Improve management and staff support
- Develop layered recommendations, especially to eliminate underlying causes and hazards

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1045

Implementation

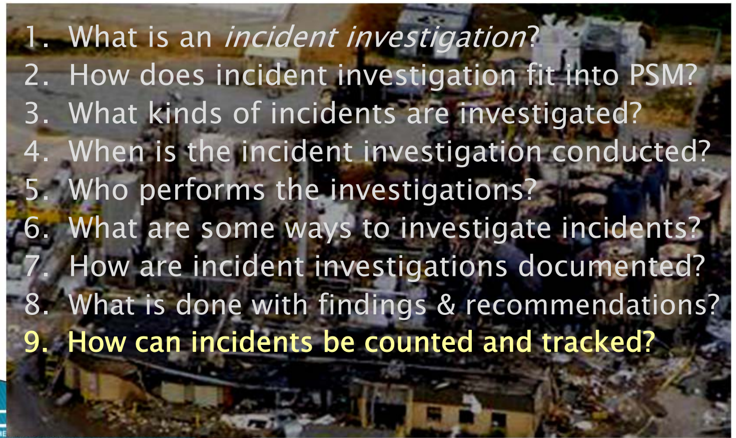
A system must be in place to ensure all incident investigation action items are completed on time and as intended.

- Same system can be used for both hazard analysis and incident investigation action items
- Include regular status reports to management
- Communicate actions to affected employees

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1046

Investigating Safety/Security Incidents



1. What is an *incident investigation*?
2. How does incident investigation fit into PSM?
3. What kinds of incidents are investigated?
4. When is the incident investigation conducted?
5. Who performs the investigations?
6. What are some ways to investigate incidents?
7. How are incident investigations documented?
8. What is done with findings & recommendations?
9. How can incidents be counted and tracked?

1047

How can incidents be counted and tracked?

"Lagging indicators" — ***actual loss events***

- Major incident counts and monetary losses
- Injury/illness rates
- Process safety incident rates

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1048

How can incidents be counted and tracked?

"Lagging indicators" — ***actual loss events***

- Major incident counts and monetary losses
- Injury/illness rates
- Process safety incident rates

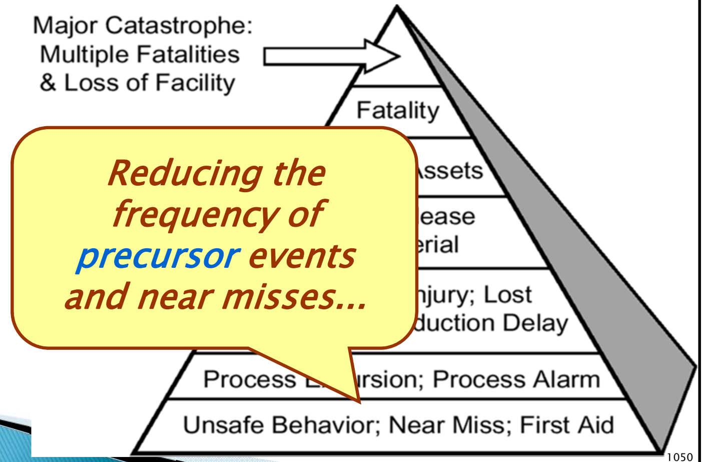
"Leading indicators" — ***precursor events***

- Near misses
- Abnormal situations
  - E.g., Overpressure relief events
  - Safety alarm or shutdown system actuations
  - Flammable gas detector trips
- Unsafe acts and conditions
- Other PSM element metrics

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1049

Pyramid Principle



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1050

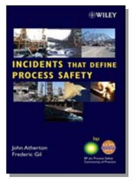
Pyramid Principle

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1051

Additional resources

- AIChE ***Loss Prevention Symposium***, Case Histories session (every year)
- www.csb.gov reports and videos
- CCPS 2008b, Center for Chemical Process Safety, ***Incidents that Define Process Safety***, NY: AIChE
- CCPS, **"Process safety leading and lagging metrics – You don't improve what you don't measure,"** www.aiche.org/uploadedFiles/CCPS/Publications/CCPS_ProcessSafety2011_2-24.pdf



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1052

Lunch

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Security Vulnerability Assessment

Table Top Exercise

SAND No. 2012-2012-4001 C , 2012-4378 P
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Terminology

- Turnstile = باب دوار
- Barrier = حاجز
- Video = فيديو
- Locks = أقفال
- Sensors = الاستشعار
- Alarm control display =التنبيه مراقبة العرض
- Fence improvement =سياج تحسن
- Badge Reader PIN = شارة قارئPIN

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Day 5

DEPARTMENT OF STATE · UNITED STATES OF AMERICA

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sandia National Laboratories

Management of Change

SAND No. 2011-0550 C
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-AC04-94AL85000

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

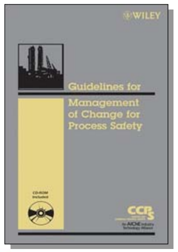
Key Acronyms

MOC = *management of change*
RIK = *replacement in kind*
PSSR = *pre-startup safety review*

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC/PSSR Resources

Center for Chemical Process Safety, *Guidelines for Management of Change for Process Safety*, NY: American Institute of Chemical Engineers.



1 Introduction
2 Relationship to Risk-Based Safety
3 Designing an MOC System
4 Developing an MOC System
5 Implementing and Operating an MOC System
6 Monitoring and Improving an MOC System
7 The Future of Change Management
CD-ROM (tools; example procedure, forms)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

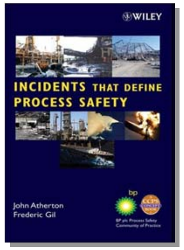
MOC/PSSR Resources

U. S. Chemical Safety Board, Safety Bulletin No. 2001-04-SB, "Management of Change." Washington, DC: U.S. Chemical Safety and Hazard Investigation Board.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC/PSSR Resources

CCPS 2008b. Center for Chemical Process Safety, *Incidents that Define Process Safety*, NY: American Institute of Chemical Engineers.

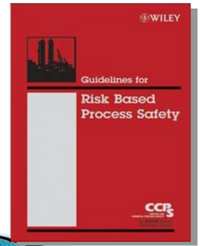


Chapter 8 Management of Change

- Chernobyl, USSR: How a safety enhancement experiment turned into a world-scale disaster, April 26, 1986
- Dutch State Mines Nypro Plant, Flixborough, UK, June 1, 1974

MOC/PSSR Resources

CCPS 2007a. Center for Chemical Process Safety, *Guidelines for Risk Based Process Safety*, NY: American Institute of Chemical Engineers.

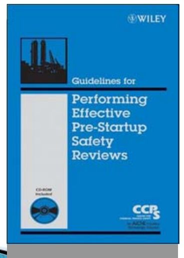


Chapter 15 Management of Change
Chapter 16 Operational Readiness

§ .1 Element Overview
§ .2 Key Principles and Essential Features
§ .3 Possible Work Activities
§ .4 Examples of Ways to Improve Effectiveness
§ .5 Element Metrics
§ .6 Management Review

MOC/PSSR Resources

CCPS 2007b. Center for Chemical Process Safety, *Guidelines for Performing Effective Pre-Startup Safety Reviews*, NY: Amer Inst of Chem Engineers.



1 Introduction
2 What Is a Pre-Startup Safety Review?
3 Regulatory Issues
4 A Risk-Based Approach to PSSR
5 The Pre-Startup Safety Review Work Process
6 Methodologies for Compiling and Using a PSSR Checklist
7 Continuous Improvement
CD-ROM

Management of Change

1. Why manage change?
2. What is a "change"?
2. What is “replacement in kind”?
3. What types of changes need to be managed?
4. What is needed to manage changes?
5. What about temporary and emergency changes?
6. What information needs to be updated?
7. What else needs to be done pre-startup?
8. How are changes communicated?

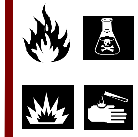
Management of Change

1. Why manage change?

> If you want to make enemies, try to change something.
>
> *- Woodrow Wilson*

Review

Hazards



During “normal operation,” all hazards are contained and controlled, so the plant is operating safely.

Key concept

Changes

Either:

(1) shift the bounds of “Normal Operation”

or

(2) put the facility into an “Abnormal Situation”

Flixborough, England 1974

CCPS — Center for Chemical Process Safety

Process Safety Beacon
Special Issue
http://www.aiche.org/ccps/safetybeacon.htm
Messages for Manufacturing Personnel

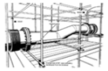
Sponsored by the 5th Global Congress on Process Safety

Flixborough — In June 2009 it will be 35 Years since the tragedy…

Originally published in June 2004, Re-issued April 7, 2009

What Happened?

One of the six reactors in series needed repairs. To minimize downtime, it was decided to bypass that one reactor and repair it off line. A temporary bypass line was installed using a pipe with an expansion bellows on each end and supported by scaffolding. Because of the rush to resume production, the new bypass was not tested prior to start up nor were engineering standards or manufacturer's recommendations considered.



Approximately three months later, the expansion bellows in the bypass line failed and released an estimated 30 tons of flammable cyclohexane. The resultant vapor cloud ignited killing 28 people and injuring 89 more. The entire plant was destroyed and hundreds of homes and stores were damaged.

See the Chemical Safety Board web site: http://www.csb.gov/safety_publications/docs/moc082801.pdf for MOC related accidents.

PSID Sponsors see: Free Search—Management of Change

Why this Happened

The temporary modification was not adequately reviewed for potential adverse consequences!

- The temporary bypass was made with two bends in it because the nozzles on the two tanks were at different levels. The impact of internal forces and flow stresses were not considered on the expansion bellows.
- Expansion bellows were left in place on each end of the bypass line. The suitability of this design and manufacturer's recommendations were not considered.
- The weight of the temporary bypass was not securely supported—it was simply placed on scaffolding. The amount of movement and the effect of that movement on the bellows were not considered.

What You Can Do

- Always follow your company's Management of Change (MOC) procedure. *Remember, temporary changes demand the same rigorous review as do permanent changes.* If you do not utilize a MOC procedure, discuss the value it could provide to your facility.
- Make changes only after thorough hazard reviews have been conducted and approved by qualified experts.
- Use good engineering practices and manufacturer's recommendations.

Evaluate Every change, even Temporary ones—for Expected and Unexpected Consequences

Discussion

Changes

Either:

(1) shift the bounds of "Normal Operation"

or

(2) put the facility into an "Abnormal Situation"

Which of these occurred at Flixborough?

Management of Change

1. Why manage change?
2. What is a "change"?

What is a "change"?

Definition:

Change - Any addition, process modification, or substitute item (e.g., person or thing) that is not a replacement-in-kind.

- CCPS 2008c Glossary

What is a "replacement-in-kind"?

Definition:

Replacement-in-kind (RIK) - An item (equipment, chemicals, procedures, organizational structures, people, etc.) that meets the design specification, if one exists, of the item it is replacing.

- CCPS 2008c Glossary; see Appx. A for change vs RIK examples

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What is a "replacement-in-kind"?

Additional information in RIK definition:

This can be an identical replacement or any other alternative specifically provided for in the design specification, as long as the alternative does not in any way adversely affect the function or safety of the item or associated items.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What is a "replacement-in-kind"?

Additional information in RIK definition:

- For nonphysical changes (relating to procedures, personnel, organizational structures, etc.), no specification *per se* may exist.
- In these cases, the reviewer should consider the design and functional requirements of the existing item (even if nothing is written down) when deciding whether the proposed modification is an RIK or a change.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Discussion

Is the following a *change* or a *replacement in kind*?

1. Adding a block valve beneath a pressure relief valve so the relief valve can be removed and tested while the system is still in operation.
2. Making minor editorial changes or typographical corrections to an operating procedure.
3. Adding a break room inside the control building.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Discussion

Is the following a *change* or a *replacement in kind*?

4. Ordering the same chemical ingredient from a different supplier.
5. Bringing on board a new production supervisor.
6. Installing a gear pump with the same motor, flow capacity and materials of construction as the piston pump it is replacing.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Discussion

Is the following a *change* or a *replacement in kind*?

7. Sampling a waste stream on Tuesday and Friday of each week instead of Monday and Thursday.
8. Replacing a section of piping with a higher grade of steel.
9. Going from 8 hour shifts to 12 hour shifts.
10. Changing a process set-point within previously established safe operating limits.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Management of Change

1. Why manage change?
2. What is a "change"?
3. What types of changes need to be managed?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What is a "change"?

There are many types of changes, such as:

- Equipment changes
- Procedural changes
- Chemical changes
- Process changes
- Control / limit changes
- ITM changes
- Personnel changes
- Infrastructure changes

***All* must be managed !**

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Discussion:
Give 1 example of each type of change

- Equipment change –
- Procedural change –
- Chemical change –
- Process change –

Discussion:
Give 1 example of each type of change

- Control / limit change –
- ITM change –
- Personnel change –
- Infrastructure change –

Reminder

* Changes that are proposed as improvements can have unintended consequences, so they must be managed like all other changes! *

Example: Chernobyl disaster (see CCPS 2008b).

"Any change, even a change for the better, is always accompanied by drawbacks and discomforts."

- Arnold Bennett

Discussion:

Give some reasons why a permanent change might need to be made to a process plant.

It is not necessary to change.
Survival is not mandatory.

- W. E. Deming

Management of Change

1. Why manage change?
2. What is a "change"?
3. What types of changes need to be managed?
4. What is needed to manage changes?

MOC ingredients of success[1]

To manage change successfully and safely, you must have:

- A robust management-of-change program in place
- Clear ownership of the program and its constituent parts

[1]CCPS 2008b p. 193

MOC program essential elements[2]

Essential elements of a robust MOC program:

1 Agree on the technical justification for the change
- at the appropriate management level

2 Risk-assess the proposed change
- Using a multi-disciplined team of competent people
- Including specialists and vendors when needed

[2]CCPS 2008b pp. 193-194

MOC program essential elements

Essential elements of a robust MOC program (cont'd):

3 Put in place a rigorous design approval system
- To ensure that the proper engineering standards are applied to the design
- To ensure any deviations from design are approved by an engineering authority of sufficient knowledge and experience

4 Write formal operating procedures for the change
- Train all staff who are directly affected
- Obtain confirmation that training has been effective

MOC program essential elements[2]

Essential elements of a robust MOC program (cont'd):

5 Carry out a pre-startup safety review to:

- Ensure all recommendations from the risk assessment process have been incorporated into the design
- Ensure any deviations from established standards or practices have been approved at the appropriate level
- Confirm that all integrity testing has been successfully completed
- Confirm that operating procedures and training are complete

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC program essential elements

Essential elements of a robust MOC program (cont'd):

6 Monitor the period of change closely

- With people of sufficient knowledge and experience
- Feeding back any lessons learned for the benefit of future projects

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Management of Change

1. Why manage change?
2. What is a "change"?
3. What types of changes need to be managed?
4. What is needed to manage changes?
5. What considerations need to be addressed?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC considerations

All staff must follow a written MOC procedure to assure that all of the following considerations are addressed prior to making any change:

- Technical basis for the proposed change
- Impact of change on safety and health
- Modifications to operating procedures
- Necessary time period for the change
- Authorization requirements

- U.S. OSHA Process Safety Management Standard, 29 CFR 1910.119(l)(2)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC considerations

Aids in developing / implementing an MOC procedure:

- Workflow diagrams
  - See Simplified MOC Flowchart on last 2 slides
- Forms
  - Example forms given in CCPS 2008c appendices
- Electronic MOC tracking systems
  - From simple to sophisticated
  - Can tie into plant's work order system
  - Can inform personnel by email
  - Can route MOCs for approvals

CCPS 20 YEARS CENTER FOR CHEMICAL PROCESS SAFETY An AIChE Industry Technology Alliance

Process Safety Beacon

http://www.aiche.org/ccps/safetybeacon.htm

Messages for Manufacturing Personnel

Sponsored by CCPS Supporters

June 2005

Too Many Start-Stop Switches

PSID Members see: Free Search--Agitator

Here's What Happened

The evening shift was assigned to clean an agitated mixing vessel. The supervisor asked the lead operator to complete the "Lock out." The lead operator tagged and locked out the motor starter in the Motor Control Center, verified the motor would not start by pressing the Start button and put a lock and "Danger—Do Not Operate" tag on the Start-Stop station near the vessel. The supervisor then issued the Confined Space Entry permit and two workers entered the vessel and cleaned it for the rest of the shift.

The oncoming day shift needed to reissue the Confined Space Entry permit. When they tried the Start button on the Start-Stop station, the agitator started! The agitator motor was **NOT** locked out!

http://www.psidnet.com

How Did This Happen ?

Easier than you might imagine. Did the Lock-out undo itself? No, but the wrong motor was locked out. How can that happen when the starter was labeled the same as the agitator? And, why didn't the agitator start when the Start button was tested the first time?

Here's how. Several months before, the agitator motor was changed out to a larger size. The size increase required a larger motor starter and wiring. Because the plant might need the "old" system again some day, it was not removed. Instead, a new Start-Stop station was installed near the vessel, in fact, right next to the old Start-Stop station. The "old" Start-Stop station was on the flange part of a column next to the vessel and the "new" Start-Stop station was in the web of that same column. When the technician locked out and tested the system, he was testing the "old" system which was disconnected. The "new" system was still active!

What You Can Do

- Follow all safety procedures as written. Do not take short cuts or assign your duties to someone else.
- Keep abreast of changes in your unit. Know what has been changed and how that change might affect your job.
- Use your Management of Change procedures to ensure that all out-of-service equipment is labeled so that it cannot be confused with equipment being used.
- Consider disconnecting electrical leads whenever uncertainty exists.
- Check and re-check, especially where safety is concerned. Look around the area. Is anything unusual?
- Remember that your safety depends on others and your own personal actions. Don't bet your life on someone else's word. Verify safety checks yourself.

When you do a safety check, make sure it is on the right equipment !

Discussion:

Discuss the lockout near-miss situation.

- What could have happened?
- How could this been avoided?
- Where does this fit into Management of Change?

Management of Change

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

What is a "temporary change"?

Definition:

Temporary change - A change that is implemented for a short, predetermined, finite period.

- CCPS 2008c Glossary

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Discussion:

Give some reasons why a *temporary* change might need to be made to a process plant.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Temporary changes

"Temporary" changes have led to many severe process safety incidents.

Flixborough (1974) is an example of a temporary equipment modification

* See CSB 2001 (on CD-ROM) for two incidents involving ***deviations from normal operating procedures due to abnormal situations***


Safety Bulletin
Management of Change

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Temporary changes

A temporary change must go through the same documentation, review and authorization procedure as a permanent change.

IN ADDITION:

- Change is only authorized for a specific time period
- Plant must then be put back to its original state

What is an "emergency change"?

Definition:

Emergency change - A change needed in a situation where the time required for following the normal MOC procedure could result in an unacceptable safety hazard, a significant environmental or security incident, or an extreme economic loss.

- CCPS 2008c Glossary

Discussion:

Give some reasons why an *emergency* change might need to be made to a process plant.

Emergency changes

Typical considerations for emergency changes:

- Have a procedure in place ahead of time to deal with emergency changes, including authorization requirements
- Obtain and document at least verbal approval from line management (often the plant manager or designee)
- Communicate the change to all affected persons
- Follow up through the normal MOC process as soon as possible

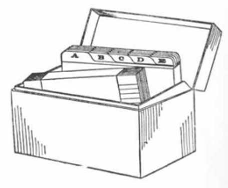
Management of Change

1. Why manage change?
2. What is a "change"?
3. What types of changes need to be managed?
4. What is needed to manage changes?
5. What considerations need to be addressed?
6. What about temporary and emergency changes?
7. What information needs to be updated?

Information updates

The MOC procedure needs to assure that <u>all information defining "normal operation</u>" is updated when changes are made. e.g.:

- Process safety information, including
  - Drawings
  - Chemical data
  - Equipment files
  - Process chemistry
  - Facilities design data
  - Material / energy balances
  - Safe upper and lower limits
- Impact of change on safety and health
- Modifications to operating procedures
- Necessary time period for the change
- Authorization requirements



Information updates

The MOC procedure needs to assure that <u>all information defining "normal operation"</u> is updated when changes are made; e.g.:

- Process safety information
- Written procedures
  - Operating
  - Maintenance
  - Emergency
  - Safe work practice

Information updates

The MOC procedure needs to assure that <u>all information defining "normal operation"</u> is updated when changes are made; e.g.:

- Process safety information
- Written procedures
- Inspection / testing / maintenance schedules

Information updates

The MOC procedure needs to assure that all information defining "normal operation" is updated when changes are made; e.g.:

- Process safety information
- Written procedures
- Inspection / testing / maintenance schedules
- Control system documentation

Discussion:

- What are some challenges to getting the process safety documentation updated?
- How can they be overcome?

Management of Change

1. Why manage change?
2. What is a "change"?
3. What types of changes need to be managed?
4. What is needed to manage changes?
5. What considerations need to be addressed?
6. What about temporary and emergency changes?
7. What information needs to be updated?
8. What else needs to be done pre-startup?

Pre-startup safety reviews

PSSR = ***pre-startup safety review***

Pre-startup safety reviews

A PSSR confirms that, before re-starting a process:

- ☐ Construction and equipment is in accordance with design specifications
- ☐ Safety, operating, maintenance, and emergency procedures are in place and are adequate
- ☐ Training of each employee involved in operating a process has been completed
- ☐ Modified facilities have completed the MOC process
- ☐ For new facilities, a process hazard analysis has been completed and recommendations are resolved

- U.S. OSHA Process Safety Management Standard, 29 CFR 1910.119(i)(2)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Pre-startup safety reviews

Key elements of successful PSSRs:

- Performed by team of knowledgeable persons
- Includes a field inspection of modified facilities
- Uses a checklist to ensure completeness (see CCPS 2007b)
- Generates list of pre-startup follow-up items
- Is integrated with the MOC procedure

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Pre-startup safety reviews

Note:

- Larger projects may require multiple PSSRs
- Non-physical changes, such as modifications to operating procedures, may not require PSSRs
- PSSRs are part of the more general idea of "operational readiness" (see CCPS 2007a)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Management of Change

1. Why manage change?
2. What is a "change"?
3. What types of changes need to be managed?
4. What is needed to manage changes?
5. What considerations need to be addressed?
6. What about temporary and emergency changes?
7. What information needs to be updated?
8. What else needs to be done pre-startup?
9. How are changes communicated?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Communication of changes

Inform of and train in the change:

WHO?

- Employees involved in operating a process
- Maintenance and contract employees whose job tasks will be affected by a change in the process

WHEN?

- before starting up the process or affected part of the process.

- U.S. OSHA Process Safety Management Standard, 29 CFR 1910.119(l)(3)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Communication of changes

Inform of and train in the change:

HOW?

- Train through plant training program when needed
  - Use appropriate techniques
  - Verify understanding
- Otherwise inform, such as by
  - Safety meetings
  - Beginning-of-shift communications
  - E-mail
- Document training / informing

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Communication of changes

Inform of and train in the change:

WHAT?

- Physical changes
- Personnel or responsibility/accountability updates
- Operating / maintenance procedures
- Emergency procedures; Emergency Response Plan
- Safe work practice procedures
- Control limits or practices

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Discussion:

A process manufactures a key chemical intermediate by an exothermic chemical reaction.

The plant chemist has an idea that if a particular new catalyst is used, the yield will be increased by 5%.

- *This change might lead to what kinds of process safety issues?*
- *What kind of training or informing might be needed?*

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC "To Do" List

- ☐ Regularly train all staff to recognize change.
  - MOC awareness training
  - Changes vs RIKs
  - Refresher training

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC "To Do" List

- ☐ Regularly train all staff to recognize change.
- ☐ Follow a written procedure to manage changes.
  - Assign roles, responsibilities and accountabilities
  - Include temporary and emergency changes
  - Describe the entire process for managing changes

NOTE: Different procedures can be followed for different types of changes (equipment, personnel, control system, operating procedure changes, etc.)

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC "To Do" List

- ☐ Regularly train all staff to recognize change.
- ☐ Follow a written procedure to manage changes.
- ☐ Review all proposed changes for safety impact.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC "To Do" List

- ☐ Regularly train all staff to recognize change.
- ☐ Follow a written procedure to manage changes.
- ☐ Review all proposed changes for safety impact.
- ☐ Have all changes approved before making them.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC "To Do" List

- ☐ Regularly train all staff to recognize change.
- ☐ Follow a written procedure to manage changes.
- ☐ Review all proposed changes for safety impact.
- ☐ Have all changes approved before making them.
- ☐ Properly reverse all temporary changes.
  - Go back to exactly how it was before, or do a MOC
  - Don't exceed the authorized time limit
  - Go through the MOC process again to make permanent
  - Inform all affected persons of the reversal
  - Document the reversal

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC "To Do" List

- ☐ Regularly train all staff to recognize change.
- ☐ Follow a written procedure to manage changes.
- ☐ Review all proposed changes for safety impact.
- ☐ Have all changes approved before making them.
- ☐ Properly reverse all temporary changes.
- ☐ Update all affected process safety information.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC "To Do" List

- ☐ Regularly train all staff to recognize change.
- ☐ Follow a written procedure to manage changes.
- ☐ Review all proposed changes for safety impact.
- ☐ Have all changes approved before making them.
- ☐ Properly reverse all temporary changes.
- ☐ Update all affected process safety information.
- ☐ Communicate changes to all affected persons.
  - Including reversal of temporary changes
  - Re-training may be required for some changes

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC "To Do" List

- ☐ Regularly train all staff to recognize change.
- ☐ Follow a written procedure to manage changes.
- ☐ Review all proposed changes for safety impact.
- ☐ Have all changes approved before making them.
- ☐ Properly reverse all temporary changes.
- ☐ Update all affected process safety information.
- ☐ Communicate changes to all affected persons.
- ☐ Field-inspect changes before re-starting.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

MOC “To Do” List

- ☐ Regularly train all staff to recognize change.
- ☐ Follow a written procedure to manage changes.
- ☐ Review all proposed changes for safety impact.
- ☐ Have all changes approved before making them.
- ☐ Properly reverse all temporary changes.
- ☐ Update all affected process safety information.
- ☐ Communicate changes to all affected persons.
- ☐ Field-inspect changes before re-starting.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Final Suggestions

- Assign an MOC Coordinator who is
  - Knowledgeable
  - Consciencious
  - Persistent
  - Detail-oriented
  - Well-organized

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Final Suggestions

- Assign an MOC Coordinator
- Keep an MOC Log
  - E.g., spreadsheet by MOC number
  - Keeps track of status of all MOCs
  - Helps ensure temporary MOCs do not exceed authorized closure date
  - Helps report key MOC metrics to management

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Final Suggestions

- Assign an MOC Coordinator
- Keep an MOC Log
- Complete PSSR follow-up items before restarting
  - Signage
  - Painting
  - Insulation
  - Clean-up
  - Procedure revisions and approvals
  - Training and Communications
  - Paperwork
  - etc.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Final Suggestions

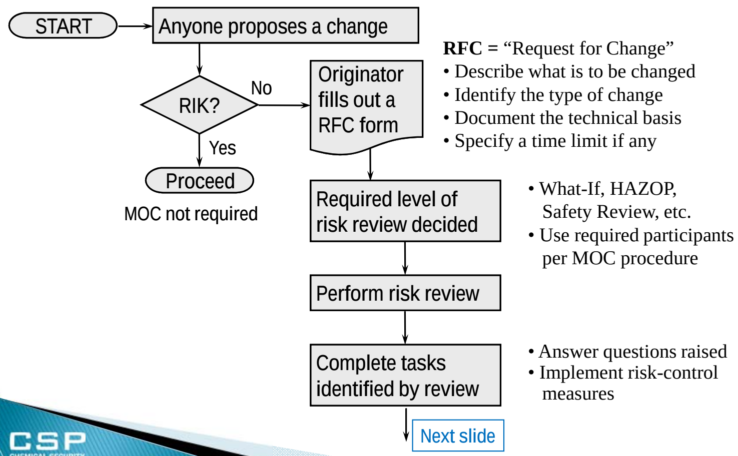
- Assign an MOC Coordinator
- Keep an MOC Log
- Complete PSSR follow-up items before restarting
  - Signage
  - Painting
  - Insulation
  - Clean-up
  - Procedure revisions and approvals
  - Training and Communications
  - Paperwork
  - etc.

Possible exception:
Red-lined P&IDs not re-drafted

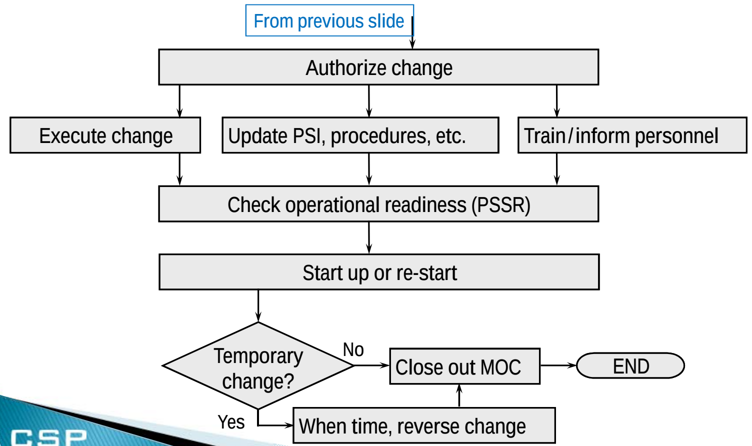
Final Suggestions

- Assign an MOC Coordinator
- Keep an MOC Log
- Complete PSSR follow-up items before restarting
- Don't short-cut the safety & health review!
  - (Same as the risk assessment)

Simplified MOC Flowchart



Simplified MOC Flowchart (continued)



Summary of Presentation

- Listed MOC resources
- Defined “Change”
- Defined “Replacement in Kind”
- Described the types of changes that need to be managed
- Described the essential elements of a robust MOC program
- Described temporary and emergency changes
- Defined and described a Pre-startup Safety Review
- Emphasized the importance of communication and training
- Made final suggestions for a robust MOC program

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1137

Emergency Management

SAND No. 2011-0722C
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-AC04-94AL85000.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Overview of Presentation

- *Emergency* Defined
- Types of Emergencies
- Emergency Management
  - Emergency Planning
  - Incident Command System
  - Emergency Response
- Emergency Management Exercise

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1139

Emergency defined

“An unforeseen combination of circumstances or the resulting state that calls for immediate action”

“An urgent need for assistance or relief”

“May occur without advance warning”

Merriam Webster definition
Photo Credit:http://www.fema.gov/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1140

Emergencies

- Hazardous materials releases
  - Accidental
  - Intentional
- Fires
- Explosions
- Medical

- Natural Occurrences
  - Earthquakes, typhoons, fires, floods, etc.
- Other incidents
  - Bomb threat
  - Terrorism

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1141

Emergency management

- Planning
  - A continuous process
  - Purpose:
    - Avoid the emergency
    - Reduce the impact
- Response/Mitigation
  - Requires highly-trained personn
- Recovery/Stabilization
  - Community or government support

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1142

Emergency planning

<u>General Plant Emergency Plan</u>

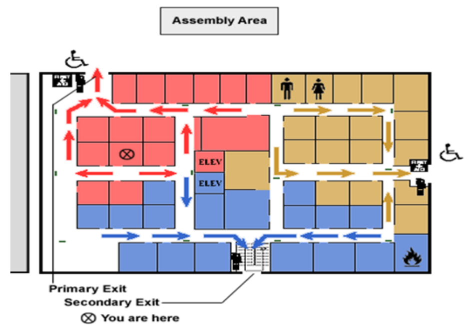
- Involve engineering, safety, & security
- Distribute to and train all employees
- Include in the plan:
  - Roles and responsibilities
  - Procedures for reporting emergencies
  - Emergency phone numbers
  - Procedures for specific emergencies
  - Maps
    - Evacuation routes
    - Assembly areas

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

11
43

Emergency planning

Have an evacuation map for all buildings and areas and POST IT

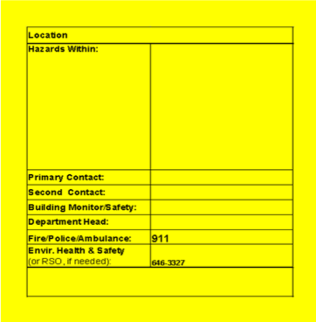


CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1144

Emergency planning

Post each area with:
- Emergency phone numbers
- After hours phone numbers
- Person(s) to be contacted
- Alternate person(s)
- Unique hazards & procedures



Location	
Hazards Within:	
Primary Contact:	
Second Contact:	
Building Monitor/Safety:	
Department Head:	
Fire/Police/Ambulance:	911
Envir. Health & Safety (or RSO, if needed):	646-3327

Emergency planning

Plant Emergency Response Procedures
- Evacuate or shelter in place?
- Respond?
- Who will respond?
  - On-site HAZMAT team?
    - Require training
  - Community fire department?
    - Establish memorandum of understanding
- Medical support
  - In-house?
  - When to call for outside assistance
- Emergency shutdown procedures
- Decontamination procedure

Emergency planning

General Fire Protection
- Identify your fire and life safety codes
- Inventory your flammable materials
  - Quantity
  - Location
- Secure appropriate flammable liquid storage
- Identify & control ignition sources
- Housekeeping
  - Control combustible materials

Emergency planning

Post exit signs
Keep exits unlocked or equipped with panic bars.

Emergency planning

Detection & Mitigation Equipment

Alarms, smoke & heat detectors, sprinklers, emergency lighting and fire extinguishers need to be properly located, maintained, and serviced regularly.

Emergency planning

Response Equipment

- Initial hazard assessment
- Place in accessible locations
  - Fire extinguishers
  - Spill control kits
  - PPE
  - Respirators
  - DECON showers
- Schedule routine maintenance and inspection of all response equipment

Emergency planning

American Industrial Hygiene Association Emergency Response Planning Guidelines

- *ERPG-1*

  The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor.
- *ERPG-2*

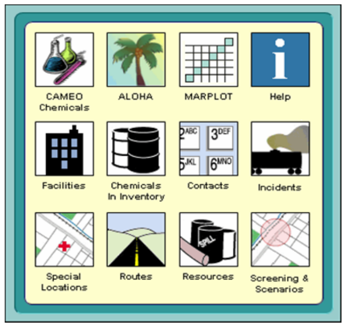
  The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.
- *ERPG-3*

  The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

Emergency planning

Software Applications

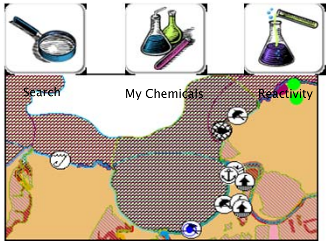
- Assist first responders with accessible and accurate response information
  - Interactive *Cameo* software modules
  - *Cameo Data Management*
    - Location of chemicals
    - Chemical quantities
    - Storage conditions



http://www.epa.gov/emergencies/content/cameo/request.htm

Emergency planning

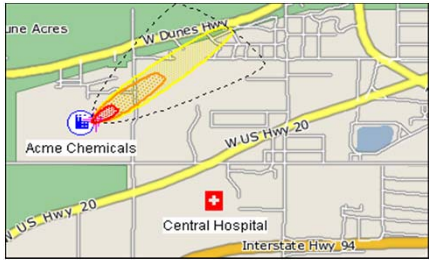
- Cameo Chemicals
  - Supplies information on the substance released and safe response actions
  - Outputs *chemical response datasheets*
  - http://cameochemicals.noaa.gov
- Mapping applications
  - *MARPLOT*
  - Can overlay a contaminated area over a map
  - Displays threat zones



http://www.epa.gov/emergencies/content/cameo/request.htm

Emergency planning

- Atmospheric dispersion models
- *Aloha* software
- Estimates threat zones associated with chemical releases, including toxic gas clouds, fires, and explosions



http://www.epa.gov/emergencies/content/cameo/request.htm

Emergency planning

Aloha Software:

- Example of Inputs
  - Enter date, time, location
  - Choose a chemical (Aloha library)
  - Enter atmospheric information
  - Choose a source:
    - direct, puddle, pipeline, or tank
  - Enter source information
    - Release amount, chemical fire
  - Specify the Levels of Concern (LOCs)
  - Choose the type of hazard
    - Toxic vapor cloud or a vapor cloud explosion

Emergency planning

Unity of Effort:

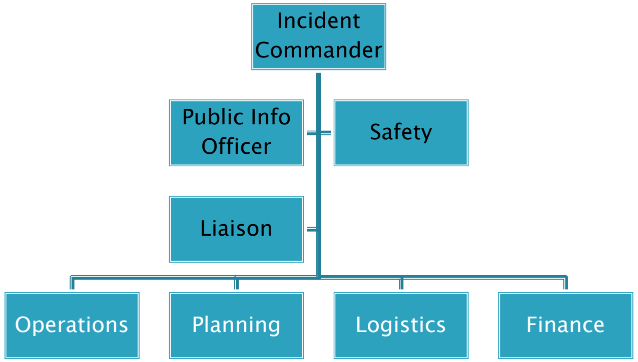
- Success in managing an emergency depends on clear roles and responsibilities and a clear chain of command.
- Use of an Incident Command System (ICS) allows coordination among different jurisdictions and functional responsibilities to interact effectively on the scene.

Emergency planning

Incident Command System:

- Developed to resolve:
  - Ineffective communication
  - Lack of common command structure
  - Lack of accountability
  - Inability to coordinate resources
- Based on basic business management
  - Plan
  - Direct
  - Organize
  - Communicate
  - Delegate
  - Evaluate

Incident Management System



Emergency planning

Community Involvement

- Prepare for emergencies involving local communities
  - Communicate!
  - Develop an emergency planning committee
  - Select notification method to community
  - Inform community of hazardous materials at your plant
    - Safety data sheets
    - TOXNET

http://toxnet.nlm.nih.gov/index.html

EMERGENCY RESPONSE

SAND No. 2011-0722C
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-AC04-94AL85000.

Response to Hazardous Materials Incidents

What makes hazardous materials incidents so dangerous?

- Material characteristics may be unknown
- Chemical, physical hazards, biological (?) hazards
  - Toxic
  - Corrosive
  - Flammable
  - Reactive

- Conditions may be confusing
- Limited time to respond to the incident

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

11 61

Who Will Respond?

- Employees?
- Local police and fire department?
- Local ambulance, hospital?
- Military?
- Local HAZMAT team?
- Plant HAZMAT team?

OR, ALL OF THE ABOVE

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

11 62

Emergency Response Decision Making

DECIDE Process

- Detect hazmat presence
- Estimate likely harm
  - Material properties
  - Containment
  - Weather
  - Modeling data
- Decide on objectives
- Identify action options
- Do best option
- Evaluate progress

Benner, L. (1978) DECIDE for Hazardous Materials Emergencies, Presented Papers.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

11 63

Emergency Response Decision Making

Detect Hazardous Material Presence

- Worker reports incident/spill/injury
- Odors, smoke, flames, reactions
- Response team detection
  - Instrumentation must be calibrated!
  - Direct reading instruments
    - LEL, oxygen monitors
    - Photoionization detectors
    - Gas detectors-methane, NH_3,, CO, Cl_2, H_2S
  - Personal sampling and analysis

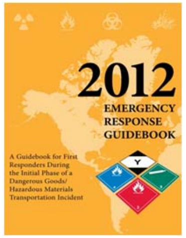
Industrial Scientific. http://www.indsci.com/products/#multi
RAE Instruments. http://www.raesystems.com/products
Sensidyne Air pumps. http://www.sensidyne.com

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

11 64

Emergency Response
Estimate likely harm

- Determine material properties
  - Safety data sheets
  - Emergency Response Guidebook
  - ERPGs
- Access site conditions
  - Size of spill / release
  - Weather
  - Models
    - Cameo software



Emergency Response
Estimate likely harm

<u>Evaluate chemical(s) released:</u>

- By quantity
  - Greater than 500 grams ? (40 CFR 302 & 355)
- Toxicity
  - $LC_{50} \leq$ 200 ppm or 20mg/liter
- Dispensability
  - Boiling point $\leq$ 100º C, $\leq$ 10 microns particle size
- Flammability/Reactivity
  - Flashpoint < 60º C
- Dispersion Modeling
  - Example: AIHA ERPG 1 at 30 meters

(ERPG-1: 2 ppm; ERPG-2: 50 ppm; ERPG-3: 170 ppm)

Emergency Response
Decide on objectives

<u>Priorities</u>

1. Persons
   - Responders
   - Workers
   - Community
2. Property
   - At the site
   - Protecting community
3. Environment
   - Air, ground and surface water, soil, wildlife

Emergency Response

<u>Initiate the Incident Command System:</u>

- Incident Commander
  - Establishes the strategy and tactics
  - Has ultimate responsibility for incident outcome
  - The position is established for <u>every</u> incident
  - May establish a command post
- Command Staff positions
  - Safety officer
  - Liaison officer
  - Information officer

Identify Action Options– Spill size may determine response

Emergency Response Identify Action Options

Large Catastrophic Incidents

- Perform a risk analysis of response options
  - Risk analysis should be a continuous process during an event
- Response options are dependent on plant capabilities and approach
  - Mode of response–defensive or offensive?
  - Training levels of responders (HAZMAT trained?)
  - Technical resources
  - External support available?
    - Local fire department or HAZMAT
    - Military

Defensive or Offensive Approach?

Identify Action Options Defensive Options Large Event

- Persons
  - Evacuate if possible
  - Shut off air intakes
  - Shelter-in-place/safe rooms
- Property/Equipment
  - Emergency shut offs
  - Emergency ventilation
  - Purging hazardous gas systems
- Environment
  - Diking water sources

http://earthbagbuilding.wordpress.com/
http://www.sb.fsu.edu/~xray/emergency.html
http://www.lpgventures.com/compliance/page2.html

Identify Action Options
Defensive Options Large Event

- Written Standard Operating Procedures
  - For each hazardous material or process on-site
- Select action from alternative strategies
- Select PPE/equipment for responders
  - http://osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9767
  - Ensure compatibility of PPE with hazards
- Safe approach is to select the highest PPE level
- Then, reduce the level when sufficient information on the hazard

Identify Action Options
Laboratory incidents

- Perform an emergency response risk assessment
  - Identify potential hazards associated with laboratory tasks
  - Identify equipment and personal protective equipment required in the event of an incident
  - Document response and evacuation procedures (SOPs)
  - Train laboratory personnel to procedures
  - Report incidents and revise procedures as needed

Identify Action Options
Laboratory incidents

- What is the worst thing that could happen?
  - inconvenience
  - skin burns
  - fire
  - explosion
  - chemical exposure (fatality; injury, disability)
- How you would respond to an emergency situation?
- Evacuate?
- What are the appropriate clean-up and decontamination procedures?

Identify Action Options
Laboratory incident spills

- Ensure you have considered
  - Internal and external communication
    - Telephone (Label all phones with emergency numbers)
    - Alarms
- Emergency equipment
  - Eyewash
  - Safety Shower Always know their location!
  - Spill Kits
  - Fire Extinguisher/fire blankets
  - First Aid Kits

Are there are maintenance or inspection requirements?

Identify Action Options Laboratory incident: small spills

- Small spills are less than 4 liters of chemical substance
- Must have appropriate PPE, spill equipment and training
- Do not clean up small spills of :
  - Acutely toxic (Low LD_{50}) chemicals
  - Carcinogens
  - Flammable liquids
  - Flammable metals
  - Chemicals of unknown toxicity or hazard

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1177

Post-Incident Follow-up

- Have a debriefing meeting
- Perform post-incident investigation
  - Prepare a report of the incident
  - Revise response plans
  - Share lessons learned
  - Keep all records
  - Correct response deficiencies
  - Mitigate identified hazards

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1178

Summary of Presentation

- Defined “Emergency”
- Described the types of emergencies
- Discussed the elements of “Emergency Management”
  - Emergency Planning
  - Incident Command System
  - Emergency Response
  - Post incident follow-up

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1179

Video – A North Carolina town is evacuated due to fire at waste site

Apex Hazardous Waste Site Fire –
Video file = EmergencyinApe_pdl.wmv 17 min

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1180

Break

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1181

Sandia National Laboratories

Emergency Management Exercise Industrial Incident

SAND No. 2011-0722C

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-AC04-94AL85000.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Emergency Management Exercise

- This scenario was taken from an incident investigated by the U.S. Chemical Safety Board that took place on August 14, 2002.
- Approximately 20,000 kilograms of chlorine gas were released from a railroad tank car unloading operation.
- 66 persons in a nearby community sought medical evaluation following the release.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1183

Photo of Chlorine Release

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1184

Summary of Incident

Around 9:20 am on March 3, 2011, a 2.5 centimeter chlorine transfer hose used in a railroad tank car unloading operation at the XXX Company facility ruptured, releasing 20,000 kilograms of chlorine. Unloading activities involve transferring liquefied pressurized chlorine gas from the tank car to individual gas cylinders.

Prior to the event, the two employees who were transferring the chlorine put the system on standby, and took their morning break in the break room next to the unloading area.

NOTE THAT WHEN THE SYSTEM IS IN STANDBY MODE, THE HOSE REMAINS CONNNECTED TO THE TANK CAR.

Upon hearing a large pop, the employees ran outside and observed that chlorine gas was being released from the tank car. They manually activated the emergency shut-down (ESD) system. The ESD system was designed to close the valves on the tank car and prevent release of chlorine. Three of the five valves failed to close and chlorine continued to be released from the tank car.

**continued on next slide*

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Summary of Incident, cont.

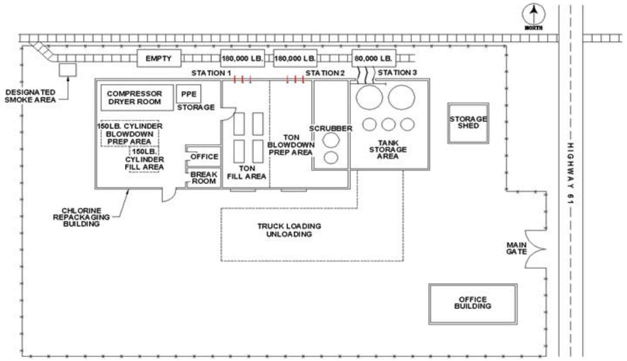
A chlorine detection sensor in the facility activated an evacuation alarm. The XXX Company employees, who were also the emergency response team, attempted to respond to the release, but were unable to access the emergency protective equipment (PPE). The equipment consisted of self-contained breathing apparatus (SCBA), a chemical *resistant* suit, gloves, and boots.

The employees evacuated to the designated assembly point. One of the employees called 911 from the assembly point at approximately 7 minutes after the release.

Upon receiving the 911 call, the Local HAZMAT team arrived at XXX Company, but did not have the appropriate PPE to respond to the release and could not shut down the chlorine leak. The HAZMAT team then evacuated the neighboring community. However, sixty-six people still required medical evaluation for respiratory distress. The release continued for 3 hours before the valve on the tank could be closed by the company's HAZMAT team who were finally able to access their emergency equipment (PPE). Two of the Company HAZMAT team received skin burns because they were not wearing fully-encapsulated PPE.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Facility Map



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Tanker Hose Rupture

Photo credit: US Chemical Safety Board

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Emergency Management Exercise

1. What emergency plans might XXX Company have had in place before the incident?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

11 89

Emergency Management Exercise

2. What procedures/practices might XXX Company have for potential equipment malfunctions?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

11 90

Emergency Management Exercise

3. How could the XXX Company emergency response team be better prepared?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

11 91

Emergency Management Exercise

4. How could the Local HAZMAT team be better prepared?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

11 92

Emergency Management Exercise

5. What improvements might be made in regards to communication between XXX Company and the community HAZMAT team?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1193

Emergency Management Exercise

6. What improvements might be made in regards to communication with the local community?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1194

Emergency Management Exercise

7. What did XXX Company and the community HAZMAT team do *right* in planning and responding to this emergency?

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1195

Lunch

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1196

Sandia National Laboratories

Industrial Waste Management

SAND No. 2011-0486P
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-AC04-94AL85000.

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Overview of Presentation

- Definitions of hazardous waste
- Why government regulation is necessary
- Key elements of chemical waste management
- Laboratory waste management
- Industrial waste management
- Disposal considerations
- References

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

11 98

Definition of Waste

- **Definition of Waste- Basel Convention 1992**

  "Substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law"

- **Definition of Hazardous Waste- EPA**

" Liquid, solid, contained gas, or sludge wastes that contain properties that are dangerous or potentially harmful to human health or the environment."

Characteristic – Ignitable-Corrosive-Reactive-Toxic

Listed – by industrial source

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

11 99

Why Government Intervention is Necessary

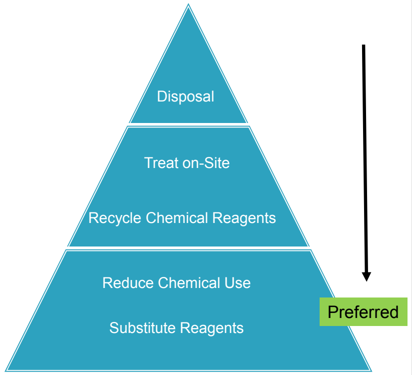
- Hazardous waste will be disposed of in the least expensive manner
- There is no profitable market for hazardous waste products
- Government regulations and fines provide an incentive for proper management
- Without regulation dumping will prevail

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1200

Chemical Waste Management

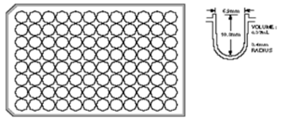
- Key Elements
  - Product substitution
  - Reduce use
  - Recycling
  - Treatment
  - Disposal
- *Chemical management is intrinsic to waste management*



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Laboratory Chemical Waste: Substitution and Reduction

- Substitution
  - Replace a hazardous solvent with a non-hazardous one
- When purchasing automated equipment think of chemical waste
- Reduction
  - Procure and use less
  - Control “orphan” chemicals
  - Use microscale instrumentation



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Industrial Chemical Waste Substitution and Reduction

- Substitute less hazardous raw materials for processes
- Improve process controls
  - –Separate waste streams
  - –Combine streams for waste neutralization (acid-base)
- Improve equipment design
- Perform regular preventive maintenance on process equipment
- Convert waste to energy when feasible

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Laboratory Chemical Waste: Recycling

- Appropriate for laboratory or small facilities
- Create an active chemical exchange program
- Reuse by others in the university
- Beware of accepting unusable chemicals
- Exchange for credit with suppliers by agreement

Donated chemicals are not always “free”

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Laboratory Chemical Waste: Recycling

May Recycle (examples)

- Excess unopened chemicals
- Excess laboratory glassware (unused or clean)
- Consumables with no expiration
- Some precious or toxic metals
  - Hg, Ag, Pt, Pd, Au, Os, Ir, Rh, Ru
- Solvents that can be purified
  - Lower purity suitable for secondary use

Do NOT Recycle (examples)

- Gas cylinders past their pressure testing date
- Used disposable pipettes and syringes
- Chemicals and assay kits past their expiration
- Obviously degraded chemicals
- Used tubing, gloves and wipes

Do NOT recycle if it presents a safety or security hazard

1205

Laboratory Chemical Waste: Recycling

Laboratory Solvents

- May be distilled
- Keep solvents segregated prior to separation
- Avoid contamination due to careless handling
  - Requires good labeling
    - A small amount of the wrong chemical can ruin a desired separation
- Azeotropes may prevent separation
- Boiling points must be widely different

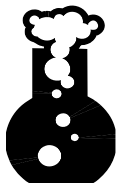
- Be aware of hazards
  - Do not evaporate or distill corrosive, radioactive, peroxides or peroxide formers
  - Beware of toxics and flammables
  - Use proper ventilation

1206

Solvents that should not be recycled by distillation

Accidents have been reported for these distillations

- Individual Substances
  - Di-isopropyl ether (isopropyl alcohol)
  - Nitromethane
  - Tetrahydrofuran
  - Vinylidene chloride (1,1 dichloroethylene)
- Mixtures
  - Chloroform + acetone
  - Any ether + any ketone
  - Isopropyl alcohol + any ketone
  - Any nitro compound + any amine



1207

Laboratory Chemical Waste: Dilution

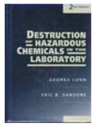
If legally allowed!

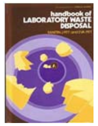
- Deactivate & neutralize some liquid wastes yourself
  - e.g., acids & bases
  - Don't corrode drain pipes
- Dilute with lots of water while pouring down the drain
  - Be sure that you do not form more hazardous substances
  - Check reference books, scientific literature, internet

1208

Laboratory Chemical Waste: Treatment References

- "Procedures for the Laboratory-Scale Treatment of Surplus and Waste Chemicals, Section 8.D in Prudent Practices in the Laboratory: Handling and Disposal of Chemicals," National Academy Press, 2011, available online: http://dels.nas.edu/Report/Prudent-Practices-Laboratory-Handling/12654
- "Destruction of Hazardous Chemicals in the Laboratory, 2nd Edition", George Lunn and Eric B. Sansone, Wiley Interscience, 1994, ISBN 978-0471573999
- "Hazardous Laboratory Chemicals Disposal Guide, Third Edition", Margaret-Ann Armour, CRC Press, 2003, ISBN 978-1566705677
- "Handbook of Laboratory Waste Disposal", Martin Pitt and Eva Pitt, 1986, ISBN 0-85312-634-8





CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1209

Industrial Hazardous Waste: Treatment Methods

- Thermal desorption
- Pyrolysis gasification
- Combustion
  - -Incineration
    - -Industrial furnaces
    - -Cement kilns
  - Molten glass solidification
  - Plasma
  - Stabilization
  - Waste to Energy

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1210

Thermal Desorption: Advantages-Disadvantages

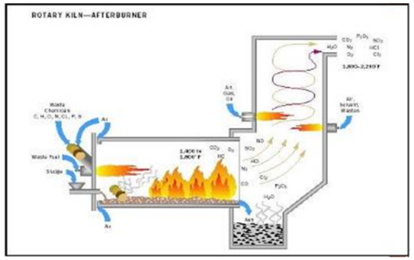
- Advantages
  - Low $$ compared to other thermal technologies
  - Low regulatory hurdles for permitting
  - Can be applied in the field
  - Allows for both destruction and recovery of organic contaminants
- Disadvantages
  - Material larger than 2 inches needs to be crushed or removed
  - Plastic soils tend to stick to equipment and agglomerate
  - Highly contaminated soils will require multiple cycles
  - Not amenable to semi-volatile or non-volatile, chlorinated hazardous constituents. (Example: PCBs, pesticides)
  - Fugitive emissions
    - Exposure risk to workers and environment

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1211

Incineration

- Incineration = "The controlled burning of waste"
- Requires 3 "T's":
  - Time: 2 seconds minimum
  - Temperatures: 1000°C–1200°C
  - Turbulence: Mixing during burn
- Rotary Kiln or Fixed Grate
- Secondary Combustion Chamber (afterburner)
- Rapid cooling of ash to prevent toxic air emissions (dioxins/furans)



Source :http://www.pollutionissues.com/

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1212

Incineration: Is NOT the same as Open Burning

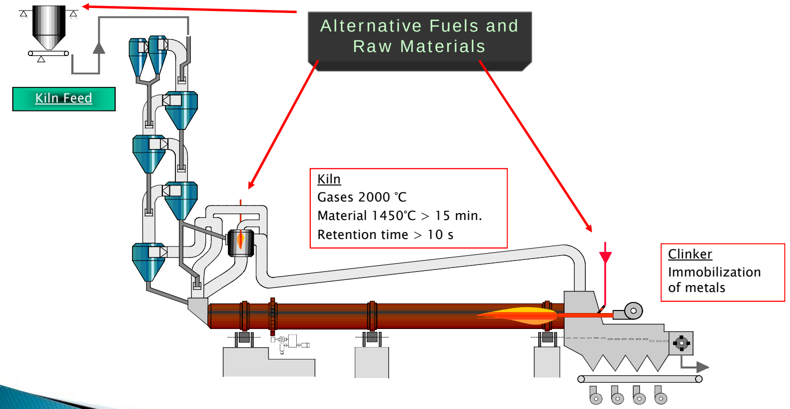
	Open Burn (µg/kg)	Municipal Waste Incinerator (µg/kg)
PCDDs	38	0.002
PCDFs	6	0.002
Chlorobenzenes	424150	1.2
PAHs	66035	17
VOCs	4277500	1.2

Source: EPA/600/SR-97/134 March 1998

Incineration: Advantages–Disadvantages

- Advantages:
  - Can be applied to a wide variety of hazardous wastes
  - Provides destruction and volume reduction of the waste
- Disadvantages
  - Not amenable to waste containing high concentration of heavy metals (> 1%)
  - Waste feed mechanisms often complex
  - High capital cost due to extensive Air Pollution Control (APC) system and sophisticated controls required to meet emission standards
  - Ash must be treated for leachable metals prior to land disposal

Typical Dry Process Cement Kiln



Industrial Furnaces: Kilns, Furnaces, and Boilers

- Advantages:
  - Owners of industrial furnaces make profit from treating waste
  - Air pollution control equipment is already in place
  - Cement kilns have a sufficient residence time and temperature for treating hazardous chemical waste
- Disadvantages
  - Some industrial waste may not be allowed
  - The waste feed mechanisms are complex
  - The admixture rate may be too low
  - Using industrial furnaces for waste treatment may interrupt industrial processes

Stabilization Processes

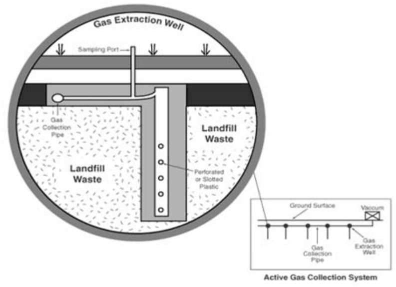
- Stabilization techniques chemically treat hazardous waste by converting them into a less soluble, or less toxic form.
- Principally used for metal-bearing wastes
- Stabilization has a limited applicability to organic wastes
- Advantage
  - Low cost, simple technology, suitable for many types of hazardous waste
- Disadvantages
  - Increases waste volume

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1217

Waste Disposal Methods

- Landfills
- Surface impoundment
- Waste pile
- Land treatment unit
- Injection well
- Salt dome formation
- Salt bed formation
- Underground mine
- Underground cave



http://www.epa.gov/lmop/basic-info/lfg.html#01

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1218

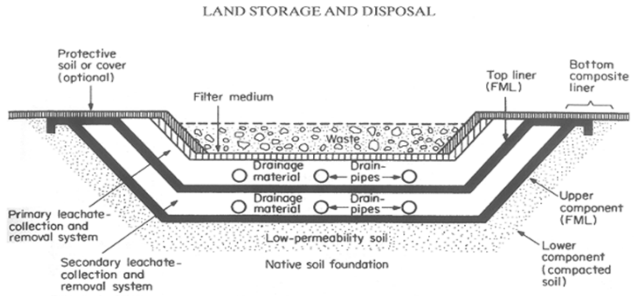
Waste Disposal: Landfills

- Design
- Must have liners compatible with waste
  - Clay, or
  - Flexible membrane
- Leachate
  - Primary and secondary collection systems
  - Removal system
  - Leak detection system
- Surface water collection
- Gas collection and removal
- Are capped and monitored

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1219

Example: Landfill Liner System



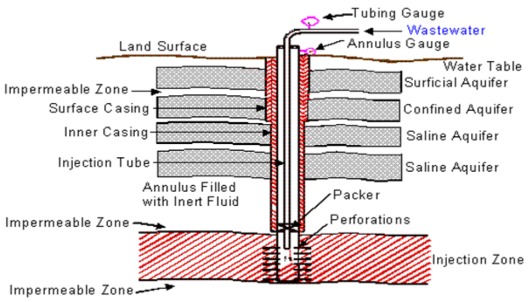
Groundwater and leachate monitoring are essential

http://www.epa.gov/wastes/hazard/tsd/td/disposal.htm

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

1220

Disposal: Deep Well Injection



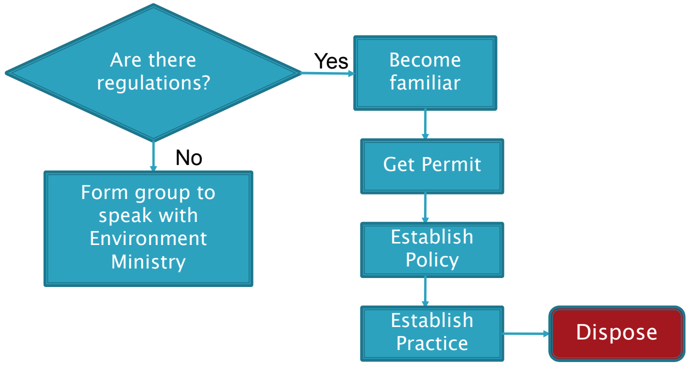
- *550 Class I wells in the United States*
- 43% of all hazardous waste in United States !!!

http://www.epa.gov/safewater/uic/index.html

Waste Disposal: Selection of Contractor

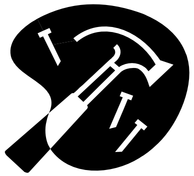
- Consider:
  - Disposal service licensed or compliant with your country's regulations
  - Employees are trained in handling and emergency response
  - Packaging requirements
    - Lab packs
  - How will waste be transported?
  - Where and how will waste be disposed?
  - Chain of custody
  - Always maintain records

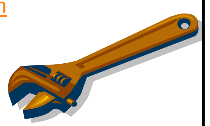
Waste Disposal Flow Chart



Waste Management: References

- "Training Resource Pack for hazardous waste management in developing economies", http://www.unep.fr/shared/publications/cdrom/3128/menu.htm
- "Microchemistry training curriculum", http://www.radmaste.org.za/amicroscience materialchemistry.htm
- "School cleanout campaign-US EPA",
  - http://www.epa.gov/epawaste/partnerships/sc3/index.htm
- "International Solid Waste Association"
  - http://www.iswa.org/





Waste management: References

- "Less is Better," American Chemical Society, Washington DC, 2003, available online:
  - http://portal.acs.org/portal/acs/corg/content?_nfpb=true&_pageLabel=PP_SUPERARTICLE&node_id=2230&use_sec=false&sec_url_var=region1&__uuid=ef91c89e-8b83-43e6-bcd0-ff5b9ca0ca33
- "School Chemistry Laboratory Safety Guide," US NIOSH Publication 2007-107, Cincinnati, OH, 2006, available on-line:
  - http://www.cpsc.gov/CPSCPUB/PUBS/NIOSH2007107.pdf
- "Prudent Practices in the Laboratory: Handling and Disposal of Chemicals," National Academy Press, 2011, available online:
  - http://dels.nas.edu/Report/Prudent-Practices-Laboratory-Handling/12654

US Environmental Protection Agency Resources

Summary of Discussion

- Gave definition of hazardous waste
- Provided reason for government regulation
- Discussed methods for reducing, treating, and disposing of laboratory waste
- Discussed methods for reducing, treating, and disposing of industrial waste
- Discussed the merits of using waste to energy technology Provided examples of hazardous waste methodologies

CSP Grant Programs: CRDF-Global

Break

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Breakout Session: Chemical Risk Management in Yemen

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sandia National Laboratories

Workshop Conclusions

Objectives

- Promote the safe and peaceful use of chemistry
- Encourage the creation of networks of people interested in CSS
  - Culture of Chemical Safety and Security

Goals:

- Train The Trainer: Propagate the Knowledge and Practices Forward

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

12 31

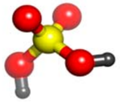
Evaluations

- Please find and fill out the evaluations for this workshop

Thank you for your participation and contributions!

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

12 32



Thank You!!

Drs. Joe and Linda

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

Sandia National Laboratories