Welcome, Introductions, Background and CSP Website

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

The Chemical Security Engagement Program (CSP)

US. Department of State
Washington, DC 20520

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

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What is CSP? - Program Goals

The Chemical Security Engagement Program (CSP) seeks to improve global chemical security and safety by raising awareness and improving security and safety best practices.

Program Goals:

- Raise awareness about chemical threats and dual-use nature of chemicals.
- Provide technical assistance to improve chemical security and safety best practices.
- Foster national and regional dialogue focused on improving chemical security and safety.
- Promote and strengthen international scientific cooperation among chemical professionals.
- Establish cadres of safety and security officers.

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What do we do? - CSP Strategy

- Work with host countries to assess priorities and gaps in chemical security and safety
- Bring together experts to identify chemical security assistance needs
- Partner with :
  - National chemical organizations (HKI, IKM, etc.)
  - Regional chemical organizations (FACS, FASC, etc.)
  - International chemical organizations (OPCW, IUPAC, UNFAO, etc)
  - Chemical Industry (ACC)
- Engage countries with:
  - Growing chemistry capabilities and industry
  - Regional security concerns
  - Active producers/exporters of industrial chemicals

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Initial Workshops Identified Risks and Gaps

In Industry:

- Theft of unsecured chemicals
- Improper chemical management
- Improper disposal of chemicals
- Lack of enforcement of safety rules/laws

At Universities:

- Lack of safe practices
- Presence of dual-use of chemicals
- Improper chemical management
- Improper storage of chemicals
- Lack of enforcement of safety rules/laws

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Involving Academia and Industry

To address chemical threat, both sectors must be involved.

- Academia/laboratories have a large variety of chemicals in small amounts
- Industry has a smaller variety of chemicals but in large amounts
- Quite different in needs, outlook, security issues

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Chemical Safety and Security Training

Course Goals:

- Increase awareness of the importance of chemical safety and security
- Increase awareness of methods for improving chemical safety and security
- Determine needs for future training/actions

Safety vs. Security:

- Chemical Safety: Protecting people from chemicals
- Chemical Security: Protecting chemicals from people (i.e., terrorists or thieves)

- Half-day seminars
- 1.5-2 day workshops
- 5 day trainings

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Training Events Timeline

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2008:			Philippines			Malaysia, Thailand		Pakistan, Indonesia		Philippines, Malaysia		
2009:	Egypt			Iraq, Jordan, UAE, Morocco	Malaysia, Bahrain			Indonesia		Philippines, Thailand		
2010:	Pakistan	Indonesia, Mid-East, Jordan	Pakistan	Philippines (academia & industry)	Turkey, Saudi Arabia, Malaysia	Philippines, Malaysia	Turkey, Philippines (academia & industry)	Indonesia (academia & industry)		Philippines, Thailand		Malaysia
2011:		Mekong Delta	Philippines, Malaysia (industry)		Qatar	Indonesia, Malaysia (academia & industry)	Indonesia	Advanced Waste Course, Morocco		UAE, Malaysia, Jordan, Egypt (academia & industry)	Yemen, Ukraine (academia & industry)	Algeria, Indonesia (academia & industry)

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Sandia National Laboratories

The International Chemical Threat
Reduction Team is located in Albuquerque, New Mexico

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CSP Website

- Offers Networking Opportunities
- Provide Resources
- Discussion boards
  - Share best practices
  - Ask questions/get answers
- Upload/view photos from workshop
- View/download training materials
- See upcoming and past events

https://chemsecurity.sandia.gov/

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CSP Website – Home Page

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CSP Website – Workshops

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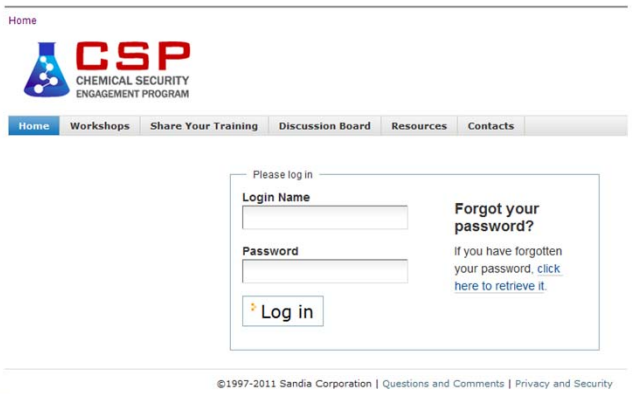
CSP Website – log in



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CSP Website – Workshops

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CSP Website – Photos

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CSP Website – Past event photos

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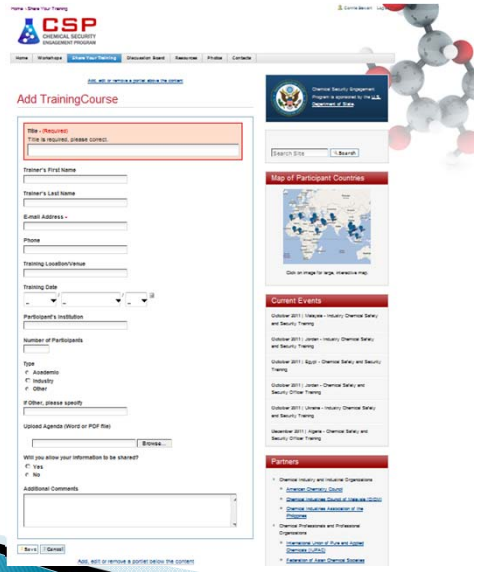
CSP Website - Share Your Training



CSP Website – Discussion Board

Summary

- Defined the Goals and Objectives of the Chemical Security Engagement Program
- Briefly stated the Strategy of the Program
  - Work with host countries, national and regional organizations,
  - Work with Industry and Universities
- Chemical Safety & Security Training
  - Increase awareness of chemical safety and security
  - Determine needs for future training/actions
- Highlight of the CSP Website
  - Networking Opportunities
  - Provide Resources
  - View/download training materials

Chemical Safety and Security Overview

SAND No. 2009-8395P
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.

Why practice chemical safety?

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

Industrial Safety Incidents

Catastrophic process incidents:

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

More recently:

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

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

U. S Chemical Safety Board Video

CSB Video – Reactive Hazards 20 minutes
Reactives_clipped.mpg

Center for Chemical Process Safety

- Anyone can subscribe
- Delivers monthly process safety messages to plant operators and other manufacturing personnel.
- Presents a real-life accidents, lessons learned, and practical means to prevent accidents at your plant.
- Published in 29 languages, including Malay
  - http://www.aiche.org/CCPS/Publications/Beacon/index.aspx

Adakah anda bersedia untuk bencana alam?

Regulations and Standards

- Individual country regulations
  - EU REACH
  - U.S. OSHA Process Safety 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

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What about chemical security?

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

Abandoned Bhopal Plant
Photo credit: AP/Saurabh Das

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What are the threats to chemical security?

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

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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 shuts down 13 Daimler Chrysler Plants

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International Resolutions & Organizations Related to Chemical Security

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

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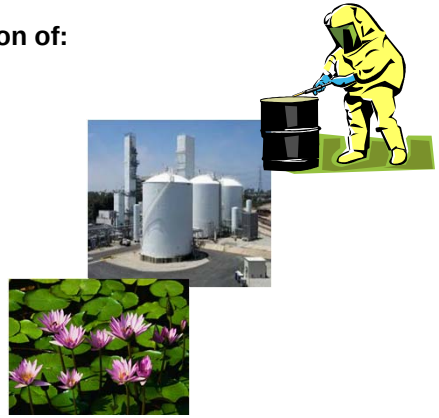
How are chemical safety and chemical security related?

Both Ensure Protection of:

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



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Reflect and Consider

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

…Are they effective?

…Could they be improved?

…How?

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Hazards Identification and Process Hazard Analysis

SAND 2012-3363C
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Acronyms

- **ETA** – Event Tree Analysis
- **FMEA** – Failure Modes and Effects Analysis
- **FTA** – Fault Tree Analysis
- **HAZOP** – Hazards and Operability Study
- **MSDS** – Material Safety Data Sheets
- **P&ID** – Piping & Instrument Drawings
- **PFD** – Process Flow Diagrams
- **PHA** – Process Hazards Analysis
- **RAGAGEP** - Recognized And Generally Accepted Good Engineering Practices
- **SAPHIRE** – Systems Analysis Programs for Hands-on Integrated Reliability Evaluations

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Primary Section Objectives

- Define Process Hazard Analysis
- Detail hazard identification methods
- Practice hazard identification methods

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Process Hazard Analysis

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

a) Identify previously unrecognized hazards

b) Identify opportunities to make the operation inherently safer

c) Identify loss event scenarios

d) Evaluate the scenario risks to identify where existing safeguards may be not adequate

e) Document team findings and recommendations

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Process Hazard Analysis

- 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)

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Process Hazard Analysis

- 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

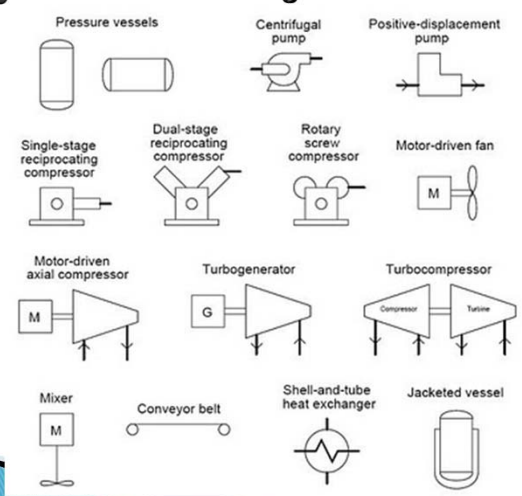
Hazard Identification Methodologies

- What-if
- Checklist (may be combined with other PHA)
- Hazard and operability study (HAZOP)
- Failure mode and effects analysis (FMEA)
- Fault Tree Analysis (FTA primarily covered in Risk Analysis course)
- Event Tree Analysis (ETA primarily covered in Risk Analysis course)
- Appropriate, equivalent methodology

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

Common P&ID Legend



Common P&ID Legend

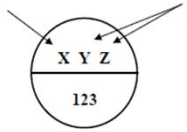
Valves

- Gate Valve, Hand-operated
- Globe Valve, Hand-operated
- Plug or Cock Valve, Hand-operated
- Check Valve
- Butterfly Valve
- Angle Valve, Hand-operated
- Control Valve
- Solenoid Valve
- Motor-operated
- Piston-operated
- Safety Valve or Relief Valve

Common P&ID Legend

*The first letter is used to designate the **measured variable***

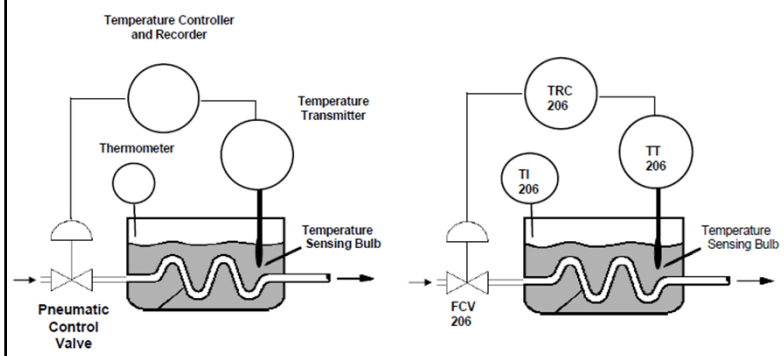
*The succeeding letter(s) are used to designate the **function** of the component, or to **modify** the meaning of the first letter.*



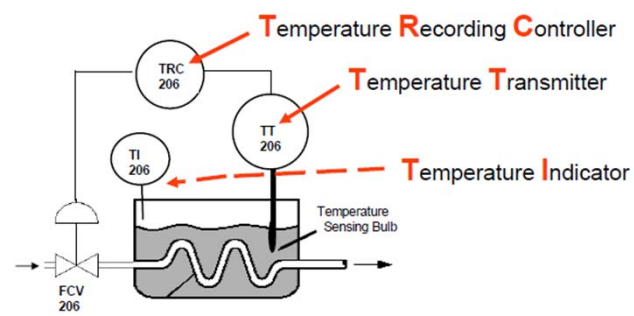
Pressure
Level
Flow
Temperature

Indicator
Recorder
Controller
Transmitter

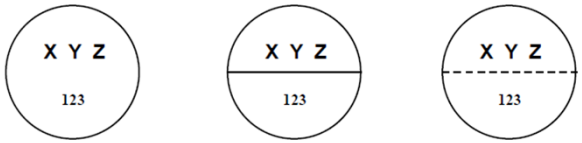
Common P&ID Legend



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)

Dashed Line

The instrument is mounted out of sight (not accessible to the operator)

Hazard Identification Methodologies

What-if analysis

Hazard Identification Methodologies

What-if analysis

- Group of **experienced** people familiar with subject processes ask questions and voice concerns
- Identify hazards, hazardous situations, event sequences which may lead to undesirable consequences
- Investigate topics which includes:
  - Electrical safety
  - Fire protection
  - Personnel safety
  - Chemical handling

Hazard Identification Methodologies

What-if analysis

- Start-up, normal operation, maintenance, shift changes
- Can be performed at any stage of plant life
- Produces list of questions and answers on processes which may be displayed in a table form

PROCESS SEGMENT:	SCOPE:	What-If Analysis
REVIEW DATE:	INTENT:	

What If …	Consequences	Safeguards	Finding/Recommendation Comments

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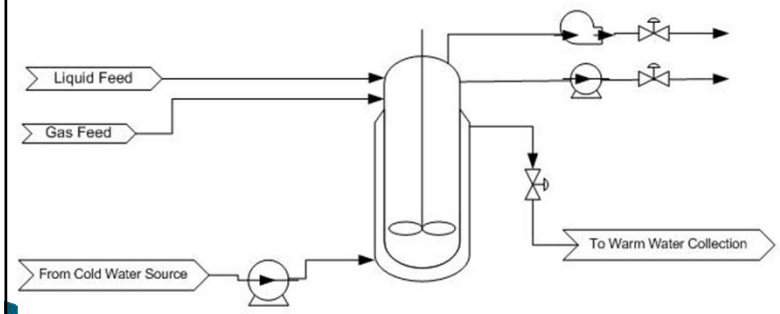
Hazard Identification Methodologies

Look at the simply process, identify some what-if questions



https://controls.engin.umich.edu/wiki/images/0/06/PID.Safety.JPG

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Hazard Identification Methodologies

Checklists

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Hazard Identification Methodologies

- 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

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Hazard Identification Methodologies

Checklist Activity – Form small groups and provide very generic questions for a checklist. After, please present your results.

- Materials:
  - 1)
  - 2)
  - 3)
- Equipment:
  - 1)
  - 2)
  - 3)
- Procedures:
  - 1)
  - 2)
  - 3)

Hazard Identification Methodologies

- Materials:
  - Do raw materials meet documented specifications?
  - Are chemicals tested after being produced?
  - Do staff have material safety data sheets (MSDS)?
- Equipment
  - Has equipment been inspected and replaced as scheduled?
  - Have pressure relief valves and other safety valves been tested?
  - Have fire protection systems been inspected and tested as scheduled?
- Procedures
  - Are there operating procedures for start-up, normal operation, maintenance, and shutdown?
  - Are operators following the written procedures?
  - Are hot work permitting processes and lockout/tagout procedures being implemented?

Hazard Identification Methodologies

Hazard and Operability Study

Hazard Identification Methodologies

Hazards and Operability Study (HAZOP)

- Team based systematic review of processes and operations
  - Identify and evaluate safety hazards
  - Identify operability problems which could compromise a plant's ability to achieve optimal productivity
- Mostly used when detailed Process Flow Diagrams (PFD) and Piping & Instrument Diagrams (P&ID) drawings are available

Hazard Identification Methodologies

Hazards and Operability Study (HAZOP)

- Product results in a table which includes:
  - Items (by equipment such as a storage tank)
  - Deviations from normal operation for the equipment (e.g., high level of liquid chemical)
  - Causes (e.g., failure of components such as a valve)
  - Consequences (e.g., potential release of chemical)
  - Safeguard (e.g., level indicator on storage tank)
  - Action (e.g., none, maintenance schedule)

HAZOP Guide Words

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

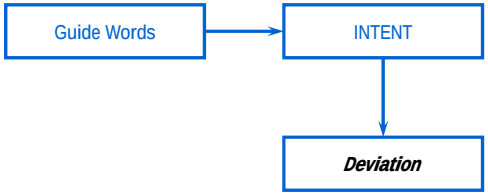
NONE
MORE OF
LESS OF
PART OF
AS WELL AS
REVERSE
OTHER THAN

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

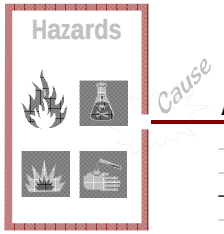
Deviations from Intent

- 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.



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.

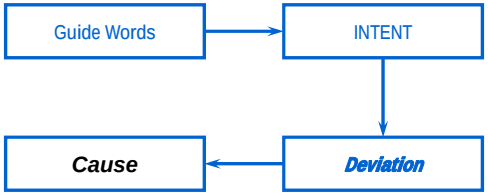
HAZOP Deviations Guide

Design Intent *Apply each guide word to intent.* A complete design intent for each line/vessel/node includes: • All functions and locations • Controlled variables' SOCs • Expected compositions • Equipment used E.g., the intent of a reaction step might be to "Contain and control the complete reaction of 1000 kg of 30% A and 750 kg of 98% B in EP-7 by providing mixing and external cooling to maintain 470-500 ºC for 2 hours, while venting off-gases to maintain < 1 bar g"	NO/NONE	MORE OF	LESS OF
	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

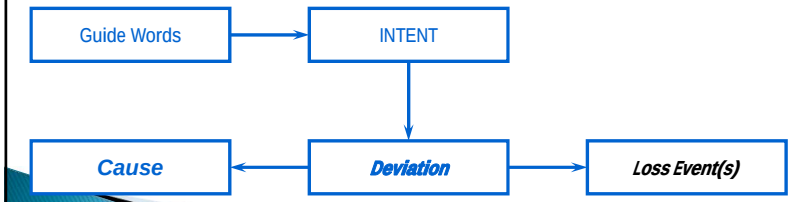
Identify deviation cause(s).

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



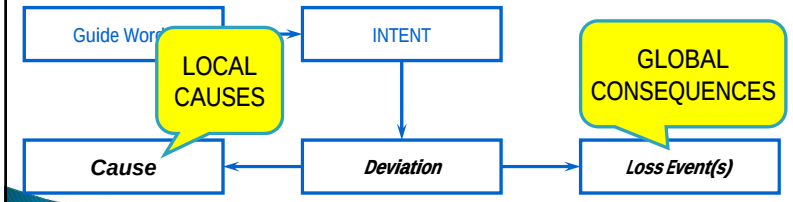
Loss events

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



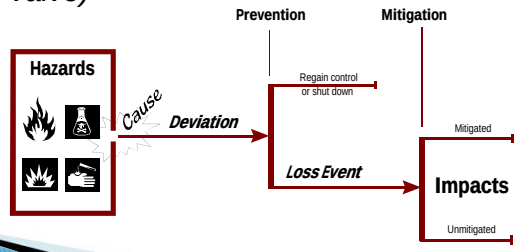
Loss events

- 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** intervening between the specific Cause-Consequence pair
- Note that different Consequences are possible, depending on safeguard success or failure *(e.g., relief valve)*



Node 1	Fuel Transfer Line			HAZOP Study
Review Date:	SCOPE: From fuel supply to EP16 inlet, including fuel pump and fuel flow control loop INTENT: Feed fuel (50/50 KA mix) at 50-55 gpm, 20-25 C and 100-120 psig from fuel supply system to reactor EP-16			
Guide Word, Deviation	**Cause**	**Consequences**	**Safeguards**	**Finding/Rec. #** Comments
NONE No feed of KA to EP16	Pump stops	High oxidant-to-fuel ratio in reactor; temperature increase in reactor; reaction rate increase; pressure increase in reactor; runaway reaction; vessel rupture explosion, with resulting blast effects causing severe injuries or fatalities to persons nearby and NOx plume drifting off-site	[] Cascade control system stops oxidant flow automatically [] Operator response to high temperature reading (close manual oxidant valve); adequate time to respond, but valve is in same general area as EP16 [] SIL1 high-high temperature trip system shuts off oxidant feed; off same temperature sensor as temperature recorder	1, 2 PRV not designed to relieve runaway reaction
NONE No feed of KA to EP16	Fuel flow control valve fails closed or commanded to close	High oxidant-to-fuel ratio in reactor; temperature increase in reactor; reaction rate increase; pressure increase in reactor; runaway reaction; vessel rupture explosion, with resulting blast effects causing severe injuries or fatalities to persons nearby and NOx plume drifting off-site	[] Operator response to high temperature reading (close manual oxidant valve); adequate time to respond, but valve is in same general area as EP16 [] SIL1 high-high temperature trip system shuts off oxidant feed; off same temperature sensor as temperature recorder	1, 2 PRV not designed to relieve runaway reaction
NONE No feed of KA to EP16	Line blocked upstream of pump	High oxidant-to-fuel ratio in reactor; temperature increase in reactor; reaction rate increase; pressure increase in reactor; runaway reaction; vessel rupture explosion, with resulting blast effects causing severe injuries or fatalities to persons nearby and NOx plume drifting off-site	[] Cascade control system stops oxidant flow automatically [] Operator response to high temperature reading (close manual oxidant valve); adequate time to respond, but valve is in same general area as EP16 [] SIL1 high-high temperature trip system shuts off oxidant feed; off same temperature sensor as temperature recorder	1, 2 PRV not designed to relieve runaway reaction

	NODE:				HAZOP Study
REVIEW DATE	SCOPE: INTENT:				
Guide Word	**Deviation**	**Cause**	**Consequences**	**Safeguards**	**Finding/Recommendation** Comments

Hazard Identification Methodologies

Failure Mode and Effects Analysis

Hazard Identification Methodologies

Failure Modes and Effects Analysis (FMEA)

- Purpose is to identify single equipment and system failure mode
  - Valve
  - Chiller System
- Couple failure mode with potential effect(s) on system or plant
  - Leaking, sticking, rupturing, on, off, open, closed
  - Over-heating, vapor generation
- General outcome is recommendations to increase equipment reliability, (e.g., maintenance schedule)

Hazard Identification Methodologies

Failure Modes and Effects Analysis (FMEA)

- Necessary resources include to conduct FMEA
  - System or plant equipment list
  - P&ID or PFD
  - Knowledge of equipment or system or plant function and failures
  - Responses of failures
- FMEA may be done singularly, but should be checked for completeness

Hazard Identification Methodologies

Failure Modes and Effects Analysis (FMEA)

- Each individual failure is considered as independent occurrence with no relation to failures in the system
- Rarely incorporates damage or frequency of failure
- FMEA not as efficient as other hazard identification methodologies

Hazard Identification Methodologies

Failure Modes and Effects Analysis (FMEA)

- Human operator error not usually examined directly
- Human error is examined as it manifests into failure
  - Inadequate design
  - Improper installation/operation
  - Lack of maintenance

Hazard Identification Methodologies

Failure Modes and Effects Analysis (FMEA)

- Three steps to FMEA
  - Defining the study problem
  - Performing the review
  - Documenting the results

Hazard Identification Methodologies

Defining the study problem for FMEA

- Appropriate level of resolution
  - Plant or system level
- Defining boundary conditions
  - Physical system boundaries
  - Analytical boundaries
  - Collecting current references that identify equipment and relationship to plant

Hazard Identification Methodologies

- Performing the review for FMEA
  - Equipment identification
    - Provide a unique identifier for equipment
    - Typically P&ID have unique identification for components
  - Equipment description
    - Type, configuration, service characteristics
  - Failure modes
  - Effects
  - Safeguard
  - Actions
- Document results of FMEA (tabular)

Hazard Identification Methodologies

- Brief FMEA activity! With a partner:

1. Define a piece of equipment
2. Provide a type and service characteristics
3. Detail failure modes of equipment
4. Describe the effects of the failure
5. List the safeguards
6. Provide necessary actions

Hazard Identification Methodologies

1. Define a piece of equipment
   - Motor-Operated Valve
2. Provide a type and service characteristics
   - Normally operating at high pressure CO_2
3. Detail a failure mode of equipment
   - Valve body ruptures
4. Describe the effects of failure
   - Release of high pressure CO_2
5. List a safeguard
   - Maintenance schedule on semi-annual cycle
6. Actions
   - Automatically replace valve at five years

Hazard Identification Methodologies

Fault Tree Analysis

Hazard Identification Methodologies

- Fault Tree Analysis (FTA)
  - Deductive technique that focuses on one particular incident or main system failure
  - Provides a method for determining cause of failure
  - Identifies combinations of equipment failures and human errors that can result in an incident
  - Graphical method that is well suited for highly redundant systems
  - Systems vulnerable to single-failures leading to incidents, use FMEA or HAZOP Study
- FTA is more of a photograph in time

Hazard Identification Methodologies

- Developed due to FMEA's inadequacy to analyze complex systems
- Able to handle concurrent events
- Integrates mechanical, human, process, external events
- Usually not a team-based approach

Hazard Identification Methodologies

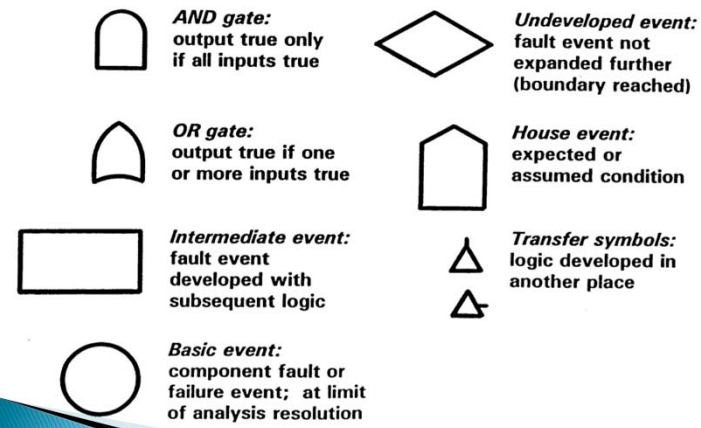
- Risk analysis "power tool"
  - Resource-intensive
  - Logic models can get very large
  - Quantitative studies can take 3-6 months
  - Used in nuclear power risk assessments
  - Used for analyzing complex control systems
- Deductive, graphical logic modeling method

Hazard Identification Methodologies

"TOP" Event

- Establishes scope of analysis
- Should be a physical, irreversible loss event
  - Example: vessel rupture explosion
- FTA is NOT a system-wide review
  - Only analyzes events contributing to TOP event

Fault tree symbols



Fault tree construction

Trace event sequence backwards in time.

- No gate-to-gate connections.
- Include all necessary and sufficient conditions.
- Trace all branches back to basic events or boundaries.

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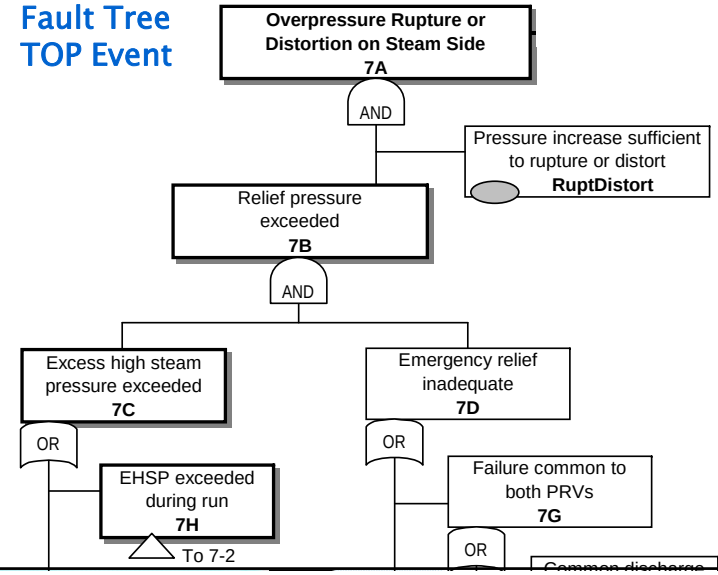
Fault Tree TOP Event



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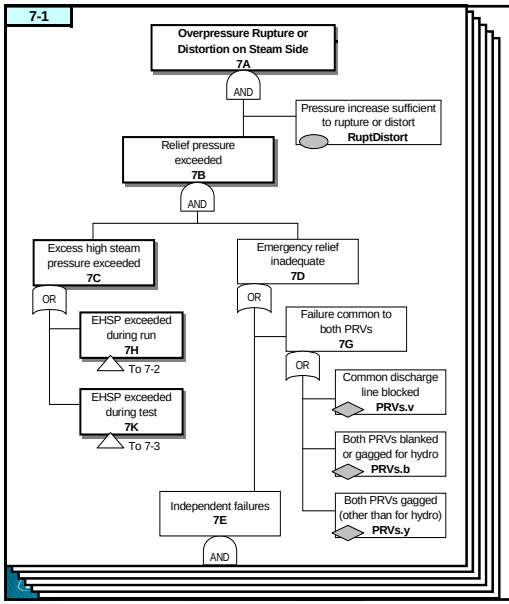

Reference: Kauffman et al., "Combustion Safeguards Test Intervals - Risk Study and Industry Survey," presented at AIChE Loss Prevention Symposium, Houston, April 2001.

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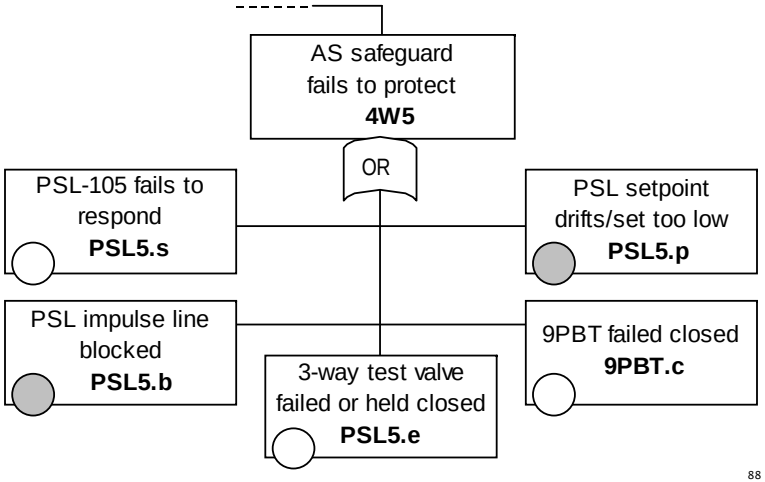
Combustion air low pressure switch



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Fault tree solution

The Fault Tree is a Boolean algebra expression of the system.

- Solving the expression yields *minimal cut sets*.
  - Minimal cut sets are all non-redundant **scenarios** that lead to the TOP event
  - Common mode failures must have same ID
  - Solution usually done by computer
- Quantifying basic event frequencies and probabilities yields a TOP event frequency.

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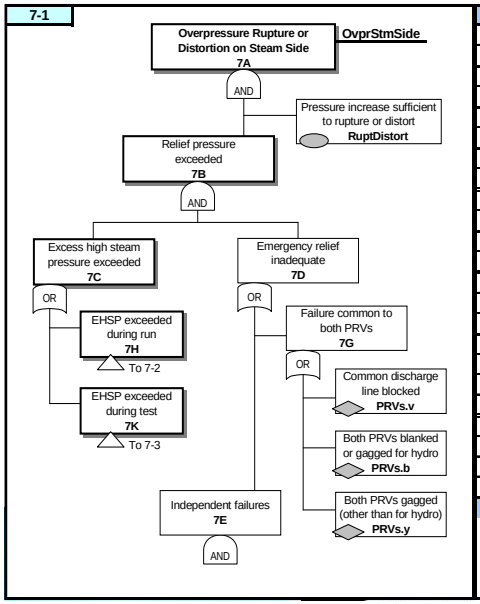

Type	Name	Freq (/yr)	Dur (h)	Prob
Conseq	OvprStmSide	1.3E-06		
AND	7A	1.3E-06		
	RuptDistort			1
AND	7B	1.3E-06		
OR	7C	0.0071		
OR	7D			0.00018
	7H	0.0006		
	7K	0.0065		
OR	7E			8.E-05
OR	7G			1E-04
OR	7F1			0.0091
OR	7F2			0.0090
	PRVs.v			0
	PRVs.b			0.0001
	PRVs.y			0
	PRV1.v	0.004	4400	0.00201
	PRV1.s	0.009	4400	0.005
	PRV1.b	0.004	4400	0.00201
	PRV1.y			0.0001
	PRV2.v	0.004	4400	0.00201
	PRV2.s	0.009	4400	0.005
	PRV2.b	0.004	4400	0.00201
	PRV2.y			0

Notes:

1. hydro = hydrotest
2. PRV settings: PRV1, 180 psig; PRV2, 185 psig
3. PRVs tested once/year, by either bench testing or testing in place

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Hazard Identification Methodologies

Event Tree Analysis

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Hazard Identification Methodologies

- Event Tree Analysis (ETA)
  - Event sequences (failures or errors) that lead to incident
  - All possible outcomes following the success or failure of protective systems given initiating cause
  - Identifies various incidents in complex processes that have several layers of safety systems
  - Graphical event trees represent logical <u>and</u> combinations of events
  - Results input into FTA for qualitative analysis
- Time propagation or evolution of accident scenario

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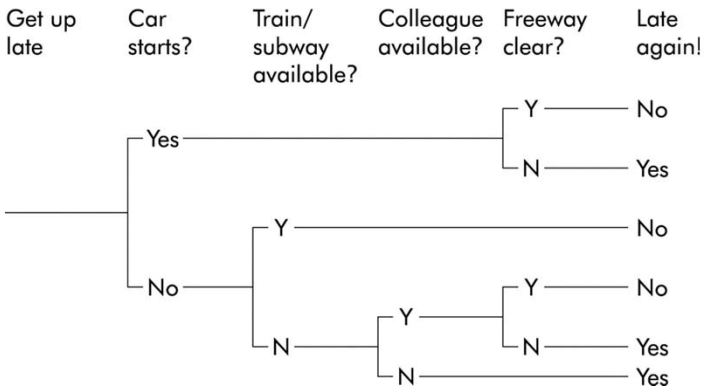
Hazard Identification Methodologies

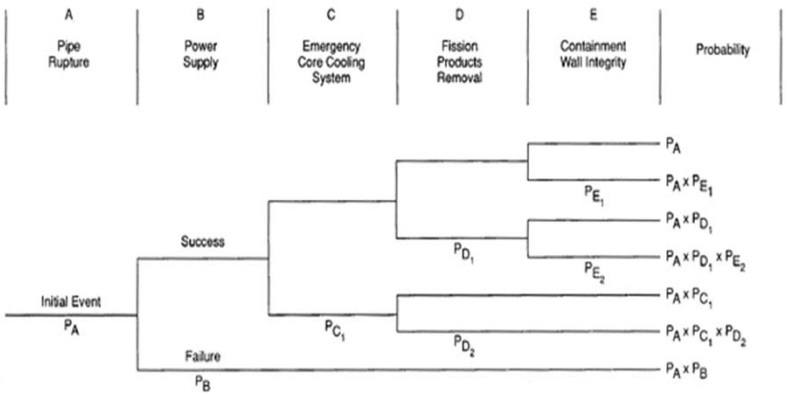


Hazard Identification Methodologies

Event Tree Analysis (ETA) initial steps

1. Identify an initiating event of interest
2. Identify safety features designed to deal with initiating event
3. Construct the event tree
4. Describe the resulting accident event sequence

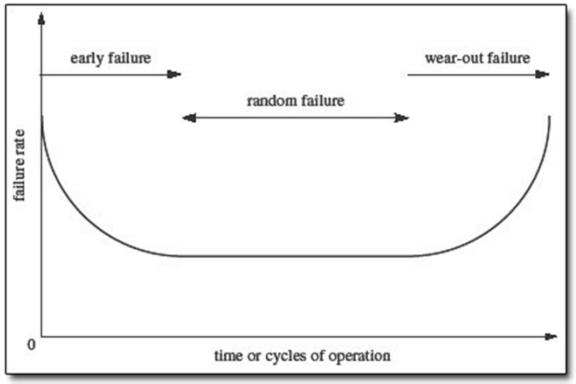
Hazard Identification Methodologies



Hazard Identification Methodologies

- Data input may come from a variety of sources
  - Historical data (e.g., international incidents, individual plant data, country specific)
  - Fault tree analysis
  - Expert opinion
  - Equipment geometry or specification
- Sequence of events leads to outcome
- Frequency of outcome depends on data input
- Computational codes (e.g., SAPHIRE) are very useful

Hazard Identification Methodologies



Hazard Identification Methodologies

- What are some causes of high early failure rates?
  -
  -
  -

Hazard Identification Methodologies

What are some causes of high early failure rates?

- Installation error
- Inappropriate use of equipment
- Manufacturer's defect

Hazard Identification Methodologies

What are some causes of high wear out failure rates?

-
-
-

Hazard Identification Methodologies

What are some causes of high wear out failure rates?

- Environmental consideration (e.g., corrosive, weather exposure)
- Temperature, pressure, flow rate of process
- Frequency of start-ups
- Duration of operations

Section Recap

- Need for Process Hazard Analysis
  a) Identify previously unrecognized hazards
  b) Identify opportunities to make the operation inherently safer
  c) Identify loss event scenarios
  d) Evaluate the scenario risks to identify where existing safeguards may be not adequate
  e) Document team findings and recommendations
- Detail hazard identification methodologies
  - What-if, checklist, HAZOP, FMEA, FTA, ETA
- Practice the various techniques

Questions

LUNCH

An Introduction to Process Safety Management

SAND No. 2012-3414C
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

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Sandia National Laboratories

Key Terms

- **Process** – a series of operations or treatments to manufacture, transform, transport, or store a product or bulk material (i.e., pressurized gases and potentially hazardous liquids)
- **Chemical Process Industry** – an industry whose products result from either chemical changes, physical operations such as separation or purification, or the preparation of specifically formulated mixtures of materials

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Key Terms

- **Hazard** – a chemical or physical condition that has the potential for causing damage to people, property, or the environment
- **Incident** – the loss of containment of material or energy
- **Consequence** – a measure of the expected effects of an incident
- **Likelihood** – a measure of the expected probability or frequency of occurrence of an event (e.g., events/year, probability of occurrence, conditional probability)

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Key Terms

- **Risk** – a measure of human injury, environmental damage, or economic loss in terms of both the incident likelihood and magnitude of the loss or injury
- **Risk analysis** – the development of a quantitative estimate of risk based engineering evaluation and mathematical techniques for combining estimates of incident consequences and frequencies
- **Risk assessment** – the process by which the results of a risk analysis are used to make decisions, either through a relative ranking of risk reduction strategies or through comparison with risk targets

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Acronyms Used Throughout Course

- **BLEVE –** Boiling Liquid Expanding Vapor Explosion
- **CAAA** – Clean Air Act Amendments
- **FMEA** - Failure Mode and Effects Analysis
- **HAZOP** – Hazard and Operability Study
- **OSHA** – Occupational Safety and Health Administration
- **NFPA** – National Fire Protection Association
- **PEPCON** - Pacific Engineering Production Company of Nevada
- **PHA** – Process Hazard Analysis
- **PSM** – Process Safety Management
- **RAGAGEP** - Recognized And Generally Accepted Good Engineering Practices
- **SDS** –Safety Data Sheet
- **TCDD** – 2,3,7,8-tetrachlorodibenzoparadioxin

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Process safety

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

(Event-focused definition)

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Process safety

= 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)

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Process safety

Loss event:

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

– CCPS 2008a Glossary

Examples:

- Hazardous material <u>release</u>
- Flammable vapor or dust cloud <u>ignition</u>
- Tank or vessel overpressurization <u>rupture</u>

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Key questions

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

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

Material hazards

Inherently hazardous characteristics:

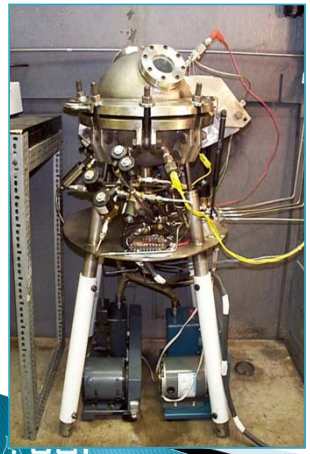
Flammability

Instability

Toxicity

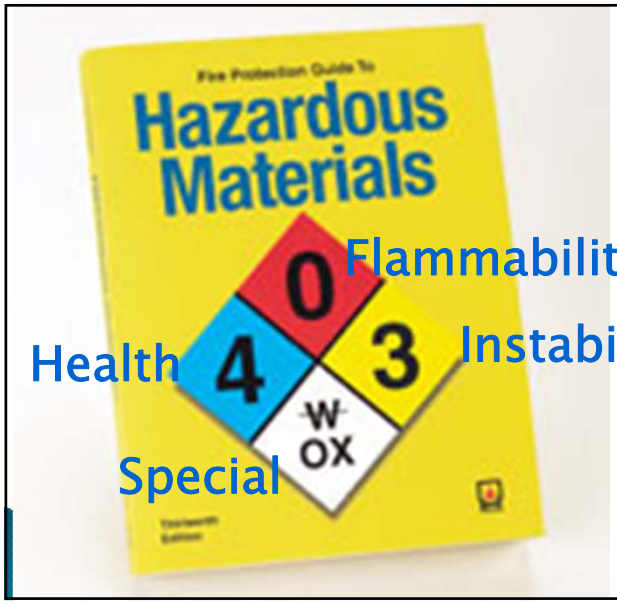
Corrosivity

Example: 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

SDS

- 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 SDS 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

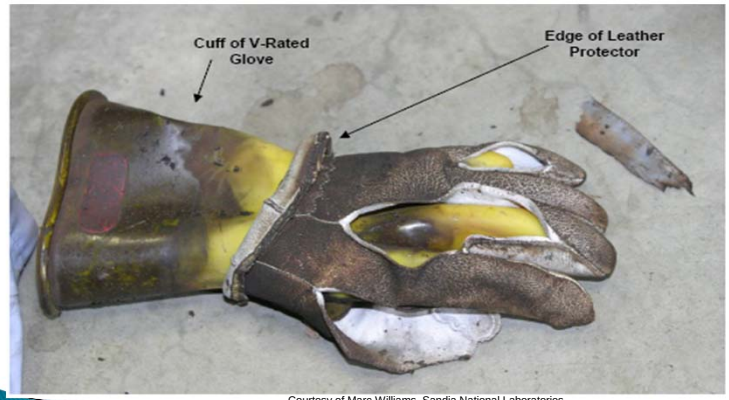
- Material hazard
- Energy hazard: Some form of physical energy contained within or connected to the process with the potential for loss or harm
- Chemical interaction hazard

Example: Electrical Hazards

- Fifth highest cause of industrial fatalities
- Electrical energy which may cause shock breaker explosion, or arc flashing to personnel
- May be alternating current (ac) or direct current (dc) sources
  - Exposures may occur from plugs, cabling, wirin circuit breakers
  - Stored electrical sources such as capacitors and batteries must also be considered

http://static.emedco.com/media/catalog/product/cache/1/image/9df78eab33525d08d6e5fb8d27136e95/ANSI-Warning-Labels-QS3622-ba.jpg

Example: Electrical Hazards



Courtesy of Marc Williams, Sandia National Laboratories

Example: Mechanical Hazards

- Thermal: extreme colds (cryogenics), extreme heat (steam)
- Kinetic: moving or rotational forces
- Hydraulic: liquid under pressure
- Pneumatic: gas/vapor under pressure
- Physical: pinch points, sharp or pointed objects or edges
- Gravitational: elevated component or equipment
- Tension/Compressive: springs

http://www.mysafetysign.com/img/lg/S/Caution-Mechanical-Crushing-Hazard-Sign-S-8291.gif

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

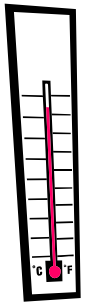
Example Compatibility Chart for an Acetic Anhydride Handling Facility

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

Degree of hazard

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



Key questions

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

HOW do loss events happen?

- Anatomy of an incident
- Unsafe act & condition precursors

Incident sequence: Hazard

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

Normal operation

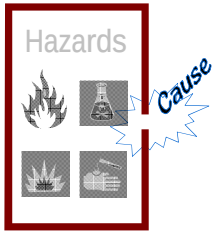
During normal operation, all hazards are contained and controlled, *but they are still present.*

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".*

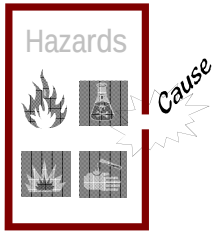


Example initiating causes:

- 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.

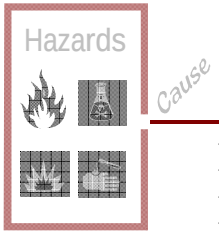


Incident sequence: Deviation

- *(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.

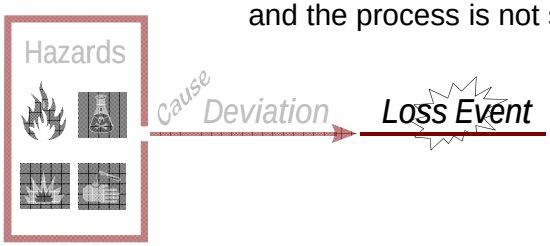
- No Flow
- Low Temperature
- **High Pressure** *(exceed upper limit of normal range)*
- Less Material Added
- Excess Impurities
- Transfer to Wrong Tank
- Loss of Containment
- etc.

Incident sequence: Loss event

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

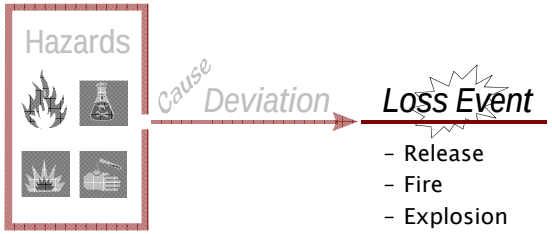
Loss event

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

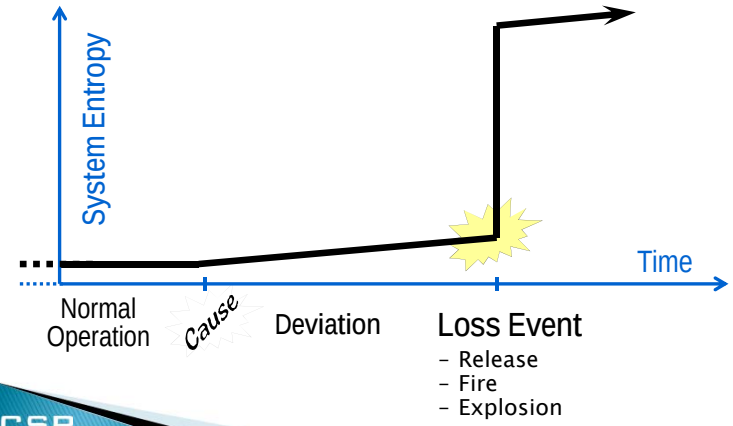


Loss event

Loss events are generally <u>irreversible process material/energy releases</u>.

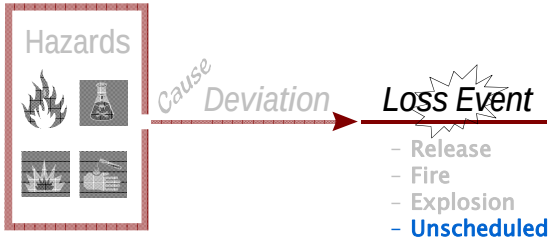


Loss event: Step change in system entropy



Loss event

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

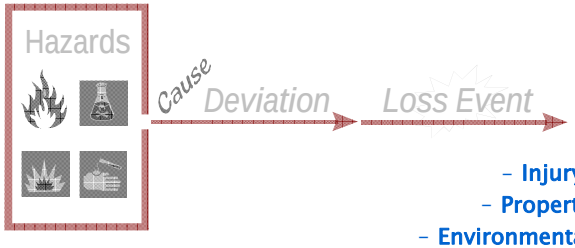


Incident sequence: Impacts

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

Impacts

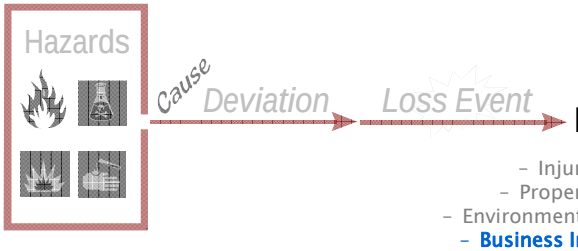
Impacts are the losses and injuries that can result from a loss event.



- Injury / Fatality
- Property Damage
- Environmental Damage

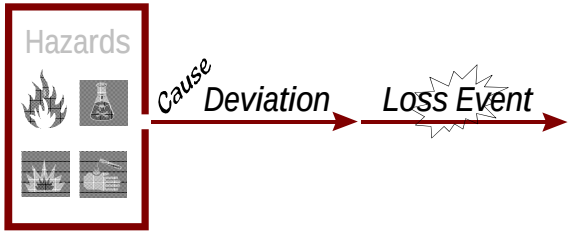
Impacts

There are often other, less tangible impacts as well.



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

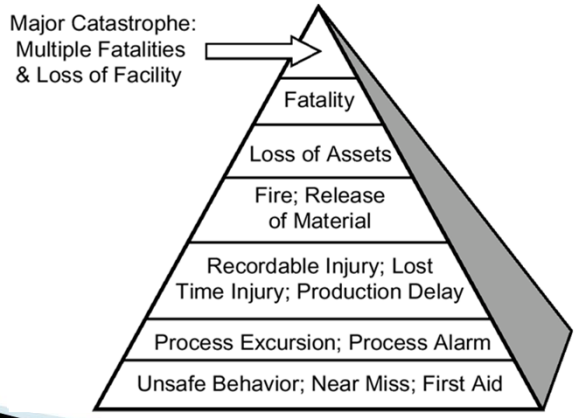
Incident sequence without safeguards



HOW do loss events occur?

- Anatomy of an Incident
- Unsafe act & condition precursors

Unsafe act & condition precursors



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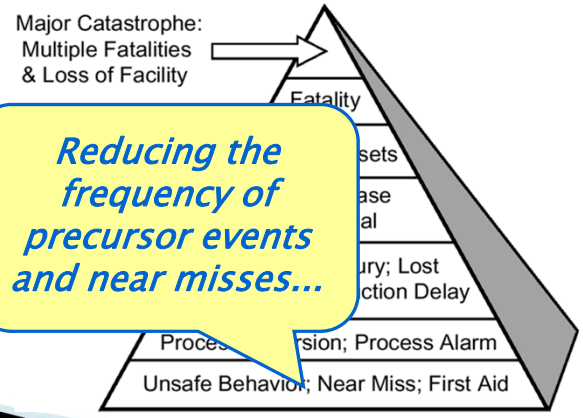
Pyramid principle of safety



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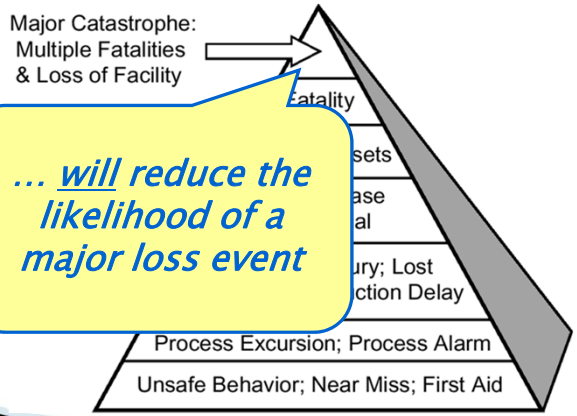
Pyramid principle of safety



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Key questions

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

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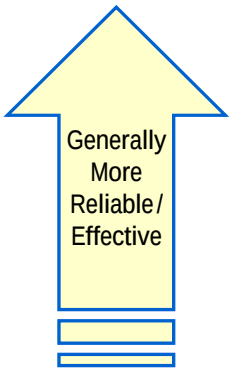
Process Safety Overview

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

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



Using past experience

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

- Learnings 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.
```

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

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*

Contain & control

Contain & Control

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

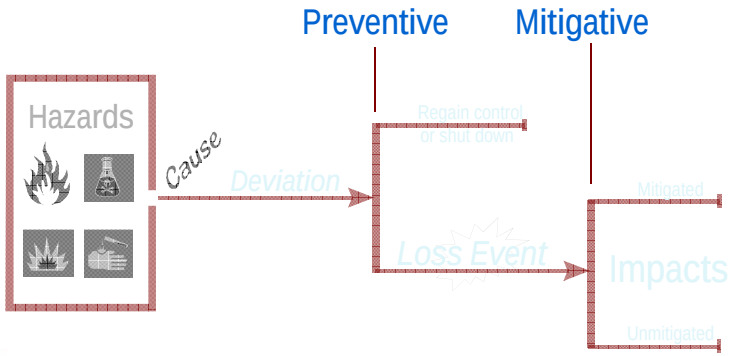
Key definition

Safeguard:

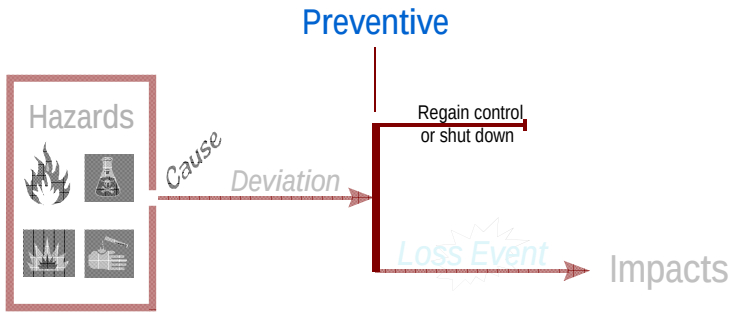
Any device, system, or action that would likely interrupt the chain of events following an initiating cause or that would mitigate loss event impacts.

– CCPS 2008a Glossary

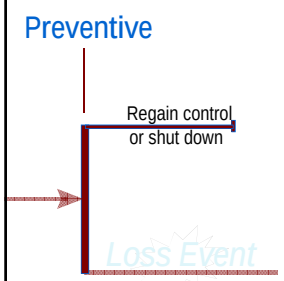
Two types of safeguards



Preventive safeguards



Preventive safeguards



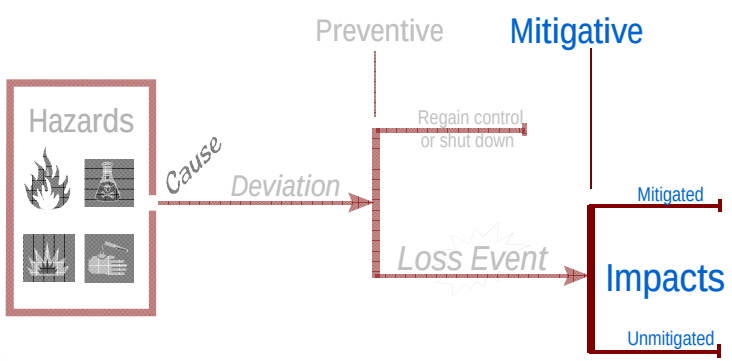
Operational Mode: Abnormal operation

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

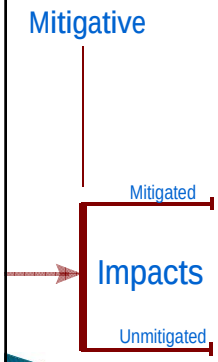
Examples of Preventive Safeguards:

- 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

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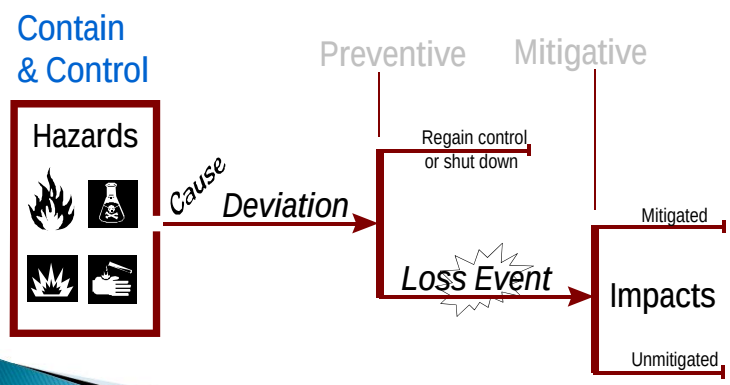
Contain & control: Before initiating cause



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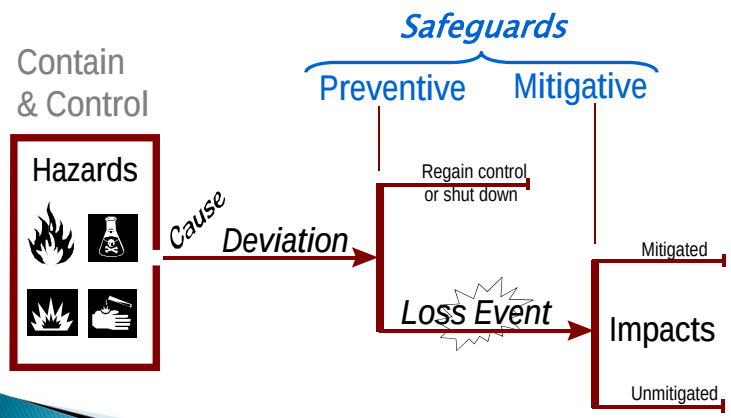
Safeguards: After cause



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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

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What's the driving force behind PSM?

- Provide historical perspective
- Discuss the elements of process safety management
- Detail incidents which shaped the way PSM is performed

Historical Perspective of PSM

Unexpected releases of toxic, reactive, flammable gases and liquids were reported throughout the world

- Environmental impacts
  - 1976: Seveso Disaster
- Fatalities and injury
  - 1984: Bhopal disaster
- Large property loss
  - 1988: PEPCON disaster

http://www.srai.org

http://safetymatters.aonfpe.com

http://www.h2it.org

Historical Perspective of PSM

- OSHA proposed "Process Safety Management of Highly Hazardous Chemicals" in 1990
  - Emphasized the management of hazards associated with highly hazardous chemicals
  - Established a management program that integrated technologies, procedures, and management practices
- Clean Air Act Amendments were enacted into law which defined 14 minimum elements of the OSHA standard

Historical Perspective of PSM

Summary of CAAA main points (1 – 5)

1. Develop and maintain written safety information
2. Perform workplace hazard assessment
3. Consult with employees on the development and conduct of hazard assessments and accident prevention plans
4. Establish a system to respond to hazard assessment findings
5. Review periodically the hazard assessment and response system

Historical Perspective of PSM

Summary of CAAA main points (6 – 10)

6. Develop and maintain written operating procedures for chemical processes
7. Provide written safety and operating information for employees
8. Ensure contractors are provided with appropriate information and training
9. Train and educate employees in emergency response procedures
10. Establish a quality assurance program to ensure process-related equipment, maintenance materials, spare parts are consistent with design specifications

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Historical Perspective of PSM

Summary of CAAA main points (11 – 14)

11. Establish maintenance systems for critical process-related equipment
12. Conduct pre-startup safety reviews of all newly installed or modified equipment
13. Establish and implement written procedures managing change to process chemicals, technology, and equipment facilities
14. Investigate every incident that results in or could have resulted in a major workplace accident

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Elements of PSM

Information on hazardous chemicals

- Toxicity
- Permissible exposure limits
- Physical data
- Reactivity data
- Corrosivity data
- Thermal and chemical stability data

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Elements of PSM

Information on processes

- Block flow diagram or simplified process flow diagram
- Process chemistry
- Maximum intended inventory
- Safe upper and lower limits (temperature, pressure, flows)
- Evaluation of consequences of deviations

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Elements of PSM

Information on equipment in the process

- Materials of construction
- Piping and instrument diagrams
- Electrical classification
- Relief system design and design basis
- Ventilation system design
- Design codes and standards (if any)
- Safety systems (e.g., interlocks, detection, suppression systems)

Elements of PSM

- Hazard of the process
- Identification of any previous incident that had the potential for catastrophic consequences
- Engineering and administrative controls
- Consequences of failure of engineering and administrative controls
- Facility siting
- Human factors
- Qualitative evaluation of a range of possible safety and health effects is there is a failure of controls

Perspectives of PSM

Seveso, Italy (1976)

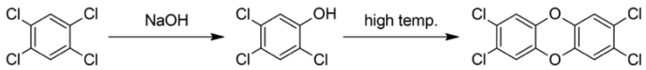
- Population of 17,000
- 15 km north of Milan
- Manufactured bactericide (hexachlorophene) with trichlorophenol as intermediate
- Tetrachlorodibenzoparadioxin (TCDD) was normally produced
- TCDD is perhaps the most potent toxin known to humans
  - Carcinogenic
  - Endocrine disruptor
  - Birth defects

http://www.yourchildlearns.com

Perspectives of PSM

Seveso, Italy (1976)

- Trichlorophenol reactor went out of control producing higher than normal temperatures and an increase of TCDD
- 2 kg of dioxin release from relief system
- Heavy rain then washed the dioxin cloud into soil
  - TCDD is water insoluble
- Over 17 km^2 affected



1 2 3

Perspectives of PSM

Seveso, Italy (1976)

- 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
- 30 years later, children found to be nearly 7 times more likely to have reduced thyroid function
- Areas **still** quarantined from public

http://ehp03.niehs.nih.gov/

http://www.fmglobalreason.com

Perspectives of PSM

Bhopal, India (1984)

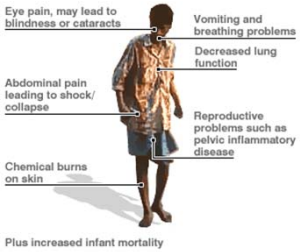
- Dense population area
- Pesticide manufacturing facility
- Union Carbide Company
- Storage of 42 tons of methyl isocyanate (MIC)
- Poor maintenance of system
  - Clogs in pipes
  - Faulty gauges
  - Leaking valves
- Cost cutting activities
  - Lack of skilled operators
  - Reduction of safety management
  - Insufficient maintenance
  - Inadequate emergency action plans

http://www.yourchildlearns.com

Perspectives of PSM

Bhopal, India (1984)

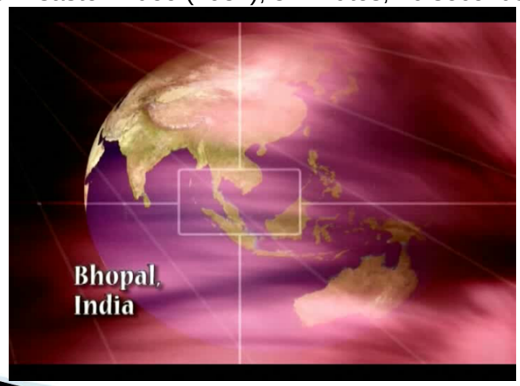
- Water introduced into MIC storage causing exothermic reaction
- ~30 metric tons of MIC released over 45 – 60 minute period
- 3000 early fatalities; ~560,000 injuries reported
- Two theories
  - Malicious (insider threat)
  - Maintenance related
- Plant shut down; Union Carbide eventually sold



http://www.epa.gov

Perspectives of PSM

Bhopal Disaster Video (1984), 3 minutes, 10 seconds



Perspectives of PSM

Henderson, Nevada, USA (1988)

- Located just outside Las Vegas
- Pacific Engineering Production Company of Nevada (PEPCON)
- One of two companies in the US to produce ammonium perchlorate, an oxidizer used in solid rocket fuel
- 4000 tons of finished product stored on-site in 55-gallon, high-density polyethylene drums

http://www.destination360.com

Perspectives of PSM

Henderson, Nevada, USA (1988)

- Windstorm damaged fiberglass structure
- Repair consisted of hotwork and welding activities
- Hotwork ignited fiberglass structure and ammonium perchlorate residue
- 2 fatalities, $100M US in damages

http://safetymatters.aonfpe.com

Perspectives of PSM

PEPCON Disaster Video (1988), 3 minutes, 30 seconds

[redacted]

Primary Section Goals

- Recognize key terms and acronyms
- Define process safety
  - the absence of loss and harm resulting from fires, explosions and hazardous material releases at process facilities.
  - 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.
- Identify elements of the process safety management process
- Learn from catastrophic events impacting people, facilities, and the environment prompted more formalized assessment methodologies

Questions

Tea Break

SAND No. 2012-1608C
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.

Chemical Reactivity Hazards

SAND No. 2012-1608C
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.

Introduction

Chemical reactivity hazard:

A situation with the potential for an <u>uncontrolled chemical reaction</u> that can result directly or indirectly in serious harm to people, property and/or the environment.

Introduction

The worst process industry disasters worldwide have involved <u>uncontrolled chemical reactions</u>.

Examples?

-
-
-

Introduction

- ***Problem:*** Chemical reactivity hazards are more difficult to <u>anticipate</u> and <u>recognize</u> than other types of process hazards.
- **Inadequate recognition and evaluation of reactive chemical hazards was a causal factor in 60% of investigated reactive chemical incidents with known causes.** (U..S. Chemical Safety Board Hazard Investigation)

Very-short-course Syllabus

- **Course texts**
- **Pretest**
- **Key concepts**
- **Extra-credit activities**

Course Texts

Texts

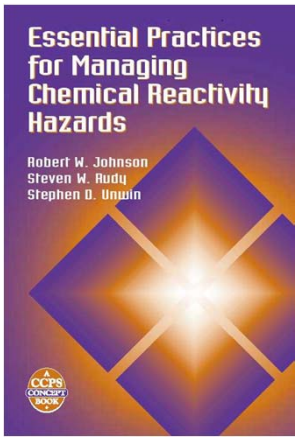
CCPS Safety Alert 2001.
Reactive Material Hazards: What You Need to Know.
New York: AIChE. 10 pages.

On course CD-ROM:
ccps-alert-reactive-materials.pdf

Texts

Johnson et al. 2003.
Essential Practices for Managing Chemical Reactivity Hazards.
New York: AIChE. 193 p.

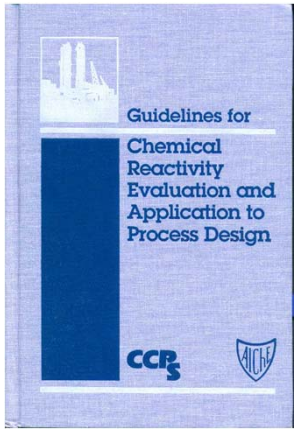
Register for free access at
www.knovel.com/ccps



Texts

CCPS 1995.
Guidelines for Chemical Reactivity Evaluation and Application to Process Design.
New York: AIChE. 210 p.

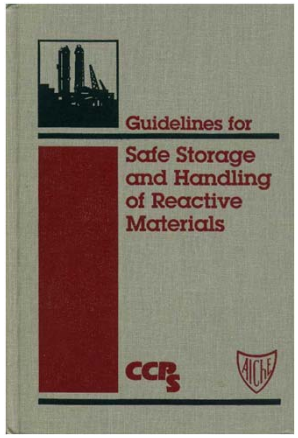
AIChE members can access
for free at www.knovel.com



Texts

CCPS 1995.
Guidelines for Safe Storage and Handling of Reactive Materials.
New York: AIChE. 364 p.

AIChE members can access
for free at www.knovel.com



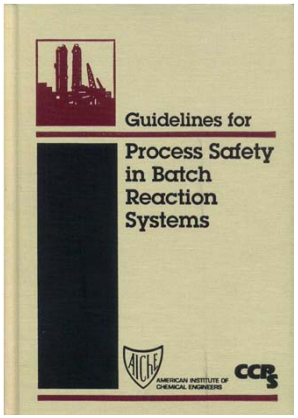
Texts

CCPS 1999.

Guidelines for Process Safety in Batch Reaction Systems.

New York: AIChE. 171 p.

Available from www.wiley.com



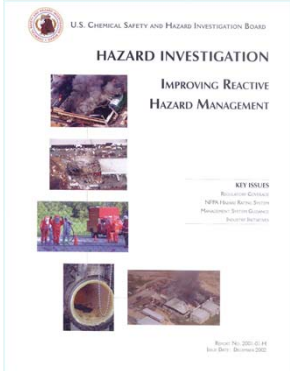
Texts

CSB 2002.

Improving Reactive Hazard Management.

Washington, D.C.: U.S. Chemical Safety and Hazard Investigation Board. 150 p.

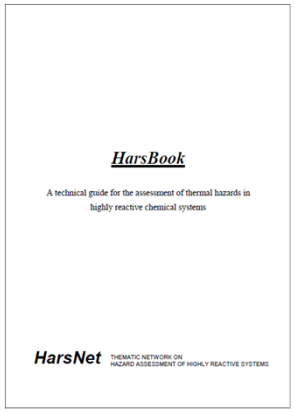
Download for free at www.csb.gov



Texts

HarsBook: A technical guide for the assessment of thermal hazards in highly reactive chemical systems.

HarsNet Thematic Network on Hazard Assessment of Highly Reactive Systems. 143 p.



Download for free at www.harsnet.net/harsbook/harsbook_02.htm

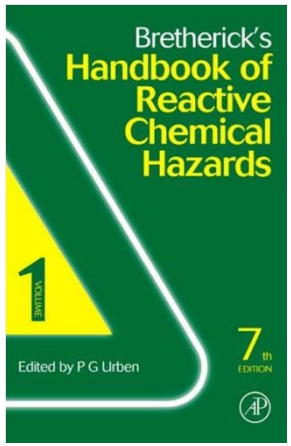
Texts

P.G. Urben (ed.) 2006.

Bretherick's Handbook of Reactive Chemical Hazards (2 vols).

Academic Press. 2680 p.

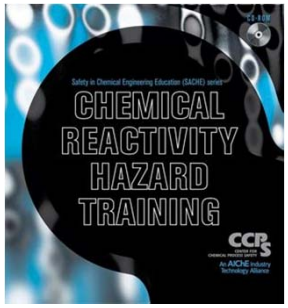
~US$500 from Amazon.com; also available electronically



Software

CCPS 2006.
Chemical Reactivity Training CD-ROM.
New York: AIChE.

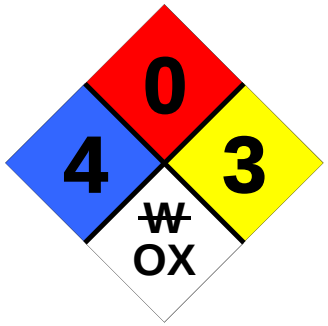
US$316 from wiley.com; free to all SAChE members (www.sache.org)



Pretest

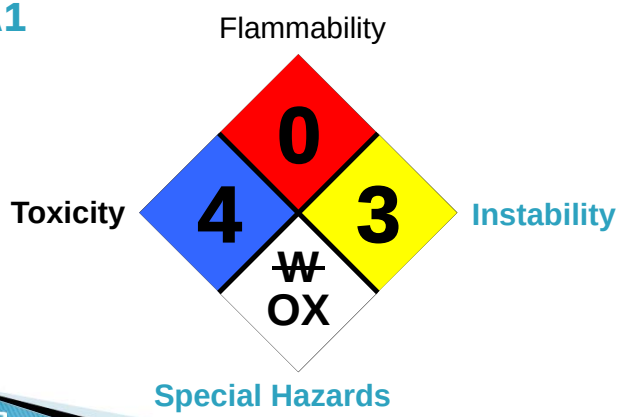
Pretest

Q1 *On the NFPA 704 'diamond', which color(s) or position(s) are associated with* ***chemical reactivity hazards****?*



Pretest

A1



Pretest

Q2 *Your new research calls for the piloting of a process involving* ***acetone cyanohydrin****.*

What should you do first?

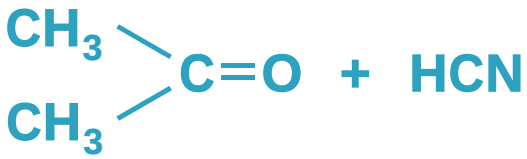
Pretest

A2 *First, find out the inherent hazards of acetone cyanohydrin.*

C_4H_7NO

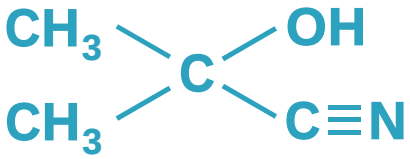
Pretest

A2 *First, find out the inherent hazards of acetone cyanohydrin.*



Pretest

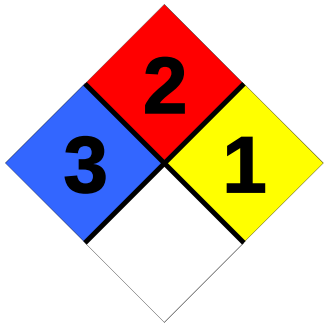
A2 *First, find out the inherent hazards of acetone cyanohydrin.*



Acetone cyanohydrin

NFPA 49

Severe health hazard; combustible; readily decomposes, producing HCN; not water-reactive or oxidizer; reacts with acids, alkalis, oxidizing materials, reducing agents



Acetone cyanohydrin

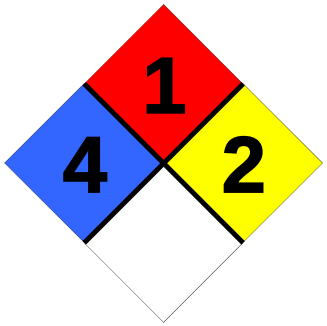
International Chemical Safety Card

Extremely toxic,

Class IIIB combustible,

unstable at elevated temperatures,

decomposes in water

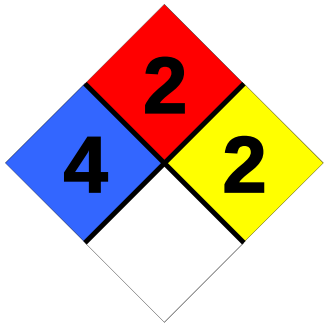


Acetone cyanohydrin

WISER (wiser.nlm.nih.gov)

HIGHLY FLAMMABLE: Easily ignited by heat, sparks or flames

DO NOT GET WATER on spilled substance or inside containers



Acetone cyanohydrin

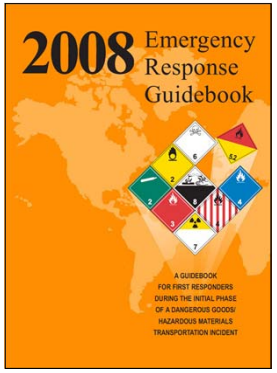
U.S. DOT

Class 6.1 Poisonous material

Acetone cyanohydrin

U.S. DOT Emergency Response Guidebook

"A water-reactive material that produces large amounts of HCN when spilled in water"



Acetone cyanohydrin

NOAA Chemical Reactivity Worksheet

Chemical Profile

Readily decomposes to acetone and poisonous hydrogen cyanide gas on contact with water, acids (sulfuric acid) or when exposed to heat. Should be kept cool and slightly acidic (pH 4-5) [Sax, 2nd ed., 1965, p. 388].

Slowly dissociates to acetone, a flammable liquid, and hydrogen cyanide, a flammable poisonous gas, under normal storage and transportation conditions. Rate of dissociation increased by contact with alkalis and/or heat.

Special Hazards

- *Water-reactive*
- *No rapid reaction with air*

Air and Water Reactions

Soluble in water. Readily decomposes on contact with water to form acetone and poisonous hydrogen cyanide.

General Description

A colorless liquid. Flash point 165°F. Lethal by inhalation and highly toxic or lethal by skin absorption. Density 7.8 lb / gal (less dense than water). Vapors heavier than air. Produces toxic oxides of nitrogen during combustion (© AAR, 1999).

Acetone cyanohydrin

NIOSH Pocket Guide to Chemical Hazards

www.cdc.gov/niosh/npg/search.html

Incompatibilities and reactivities: *Sulfuric acid, caustics*

Note: *Slowly decomposes to acetone and HCN at room temperatures; rate is accelerated by an increase in pH, water content, or temperature.*

Acetone cyanohydrin

CHRIS U.S. COAST GUARD

Chemical Hazards Response Information System (CHRIS)

Click on the desired CHRIS Code to view the chemical sheet:

CHRIS Code	Chemical Name	Description
ACY	ACETONE CYANOHYDRIN	Color: Colorless Odor: Mild, almond odor. Physical State Shipped: Watery liquid Characteristics In Water: Floats and mixes with water. Poisonous vapor is produced. IMO-UN Number: 6.1/1541 DOT ID Number: 1541 NFPA Hazard Classification: Health Hazard (Blue) - Flammability (Red) - Reactivity (Yellow) - Special (White) - View Synonyms

cameochemicals.noaa.gov

Ace

CHRIS

4. FIRE HAZARDS

4.1 **Flash Point:** 165°F C.C.
4.2 **Flammable Limits in Air:** 2.2%-12%
4.3 **Fire Extinguishing Agents:** Water spray, dry chemical, alcohol foam, carbon dioxide
4.4 **Fire Extinguishing Agents Not to Be Used:** Not pertinent
4.5 **Special Hazards of Combustion Products:** Toxic hydrogen cyanide is generated when heated
4.6 **Behavior in Fire:** Not pertinent
4.7 **Auto Ignition Temperature:** 1270°F
4.8 **Electrical Hazards:** I, D
4.9 **Burning Rate:** Currently not available
4.10 **Adiabatic Flame Temperature:** Currently not available
4.11 **Stoichometric Air to Fuel Ratio:** Currently not available
4.12 **Flame Temperature:** Currently not available
4.13 **Combustion Molar Ratio (Reactant to Product):** Currently not available
4.14 **Minimum Oxygen Concentration for Combustion (MOCC):** Not listed

5. CHEMICAL REACTIVITY

5.1 **Reactivity with Water:** No reaction
5.2 **Reactivity with Common Materials:** No reaction
5.3 **Stability During Transport:** Stable
5.4 **Neutralizing Agents for Acids and Caustics:** Not pertinent
5.5 **Polymerization:** Not pertinent
5.6 **Inhibitor of Polymerization:** Not pertinent

7. SHIPPING INFORMATION

7.1 **Grades of Purity:** 98-99%
7.2 **Storage Temperature:** Ambient
7.3 **Inert Atmosphere:** No requirement
7.4 **Venting:** Pressure-vacuum
7.5 **IMO Pollution Category:** A
7.6 **Ship Type:** 2
7.7 **Barge Hull Type:** 1

8. HAZARD CLASSIFICATIONS

8.1 **49 CFR Category:** Poison
8.2 **49 CFR Class:** 6.1
8.3 **49 CFR Package Group:** I
8.4 **Marine Pollutant:** No
8.5 **NFPA Hazard Classification:**

Category	Classification
Health Hazard (Blue).....	4
Flammability (Red).....	2
Instability (Yellow).....	2

8.6 **EPA Reportable Quantity:** 10
8.7 **EPA Pollution Category:** A
8.8 **RCRA Waste Number:** P069
8.9 **EPA FWPCA List:** Yes

9. PHYSICAL & CHEMICAL PROPERTIES

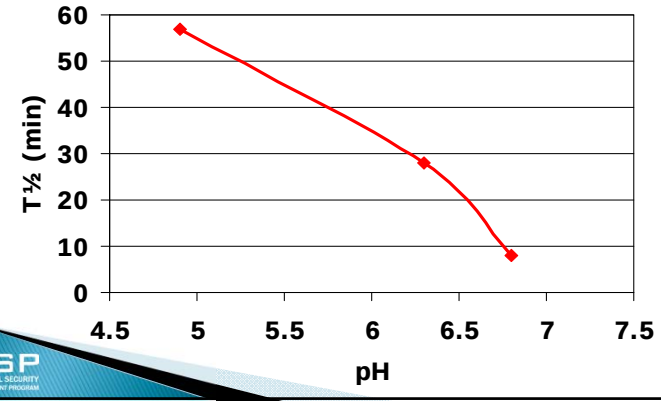
9.1 **Physical State at 15° C and 1 atm:** Liquid
9.2 **Molecular Weight:** 85.11
9.3 **Boiling Point at 1 atm:** Decomposes (~74.4C)
9.4 **Freezing Point:** −5.8°F = −21°C = 252°K

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Acetone cyanohydrin

SIDS: Stability in Water

(OECD Screening Information Dataset)



CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Acetone cyanohydrin

Conclusions:

- Extremely toxic; must keep contained and avoid all contact
- Combustible; must avoid flame, ignition
- Dissociates to produce highly toxic and flammable gases; dissociation increases with heat, moisture, alkalinity
- Must prevent spills into drains, etc.
- Must avoid incompatible materials

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Key Concepts

Key Concepts

- **Types of reactivity hazards**
- **Potential consequences**
- **Runaway reactions**
- **Contain and control measures**
- **Inherently safer systems**

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Key Concepts

- **Types of reactivity hazards**
- Potential consequences
- Runaway reactions
- Contain and control measures
- Inherently safer systems

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

- Intentional chemical reactions
- Unintentional reactions
  - **Materials reactive with common substances**
    - Spontaneously combustible
    - Peroxide-forming
    - Water-reactive
    - Oxidizing
  - **Self-reactive materials**
    - Polymerizing
    - Decomposing
    - Rearranging
  - **Reactive interactions**
    - Incompatibilities
    - Abnormal conditions

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

Main Category	Subcategory	Adjective	Noun	
READILY SELF-REACTS with energy input such as by shock, pressure, or temperature (UNSTABLE MATERIALS)	POLYMERIZES		MONOMERS	
	DECOMPOSES	SHOCK-SENSITIVE	EXPLOSIVES	Toxic / flammable decomposition products
		THERMALLY SENSITIVE (Decomposes upon heating; may require pressure/confinement)	EXPLOSIVES	
			Other unstable or thermally sensitive materials	
		SENSITIVE TO OTHER STIMULUS (e.g. friction, spark, light, pressure)		
	REARRANGES	ISOMERIZING / TAUTOMERIZING / DISPROPORTIONATING		
	CONDENSES			
READILY REACTS WITH COMMON ENVIRONMENTAL SUBSTANCES	REACTS WITH ATMOSPHERIC NITROGEN			
	REACTS WITH ATMOSPHERIC OXYGEN	SPONTANEOUSLY COMBUSTIBLE (including hypergolic, pyrophoric)		
		FLAMMABLE / COMBUSTIBLE (includes explosible dusts; usually treated separately from reactives)		
		PEROXIDE FORMING		
	REACTS WITH WATER	WATER REACTIVE (DANGEROUS WHEN WET)	Rate of reaction can vary from slow to explosively violent	
	REACTS WITH ORDINARY COMBUSTIBLES	OXIDIZING	ORGANIC PEROXIDES	
			Other OXIDIZERS	
	REACTS WITH METALS			
READILY REACTS WITH OTHER CHEMICALS (INCOMPATIBLE MATERIALS)	REACTS WITH ACIDS			
	REACTS WITH BASES			
	REACTS WITH HYDROGEN (etc.)			

Chemical reactivity hazards

Some chemicals have more than one reactive property.

R – O – O – R

For example, **organic peroxides** can be any or all of:

- **Oxidizing**
- **Decomposing** (shock-sensitive / thermally unstable)
- **Flammable** or **combustible**
- **Interacting** (incompatible with many other chemicals)

Chemical reactivity hazards

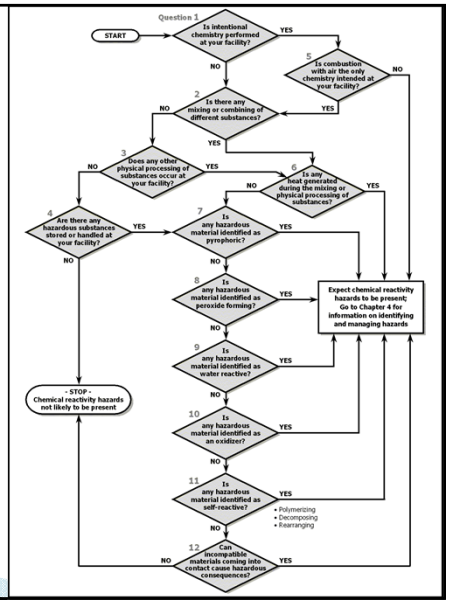
Some types of molecular structures tend to increase chemical reactivity, such as:

- Carbon-carbon double bonds not in benzene rings (ethylene, styrene...)
- Carbon-carbon triple bonds (e.g., acetylene)
- Nitrogen-containing compounds (NO_2 groups, adjacent N atoms...)
- Oxygen-oxygen bonds (peroxides, hydroperoxides, ozonides)
- Ring compounds with only 3 or 4 atoms (e.g., ethylene oxide)
- Metal- and halogen-containing complexes (metal fulminates; halites, halates; etc.)

Preliminary Screen for Chemical Reactivity Hazards

Summary Flowchart

Source: Johnson et al. 2003



Key Concepts

- Types of reactivity hazards
- **Potential consequences**
- Runaway reactions
- Contain and control measures
- Inherently safer systems

Normal situation

- Reactive materials contained
- Reactive interactions (incompatibilities) avoided
- Intended reactions controlled

Abnormal situation

- **Loss of containment**
- **Reactive interaction** (incompatibility)
- **Loss of reaction control**

Chemical reactivity loss events

From Johnson and Unwin, "**Addressing Chemical Reactivity Hazards in Process Hazard Analysis**," 18th Annual International CCPS Conference, NY: AIChE, Sept. 2003.

Loss Event

- Fire
- Explosion
- Release

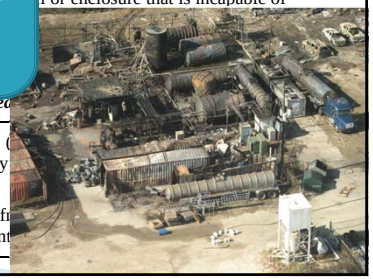
Loss events associated with reactivity hazards

Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Intentional Chemistry	***Containment rupture explosion*** (uncontrolled reaction resulting in liquid/vapor heating or gas generation inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Fire*** (e.g., excess heating or loss of cooling in unconfined configuration allows autoignition temperature to be attained) ***Toxic reaction products release*** (e.g., off-gas treatment system fails)
Spontaneously Combustible Materials	***Containment rupture explosion*** (self-ignition of vapor, dust or mist inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Fire*** (e.g., self-ignition of flash fire, jet fire, pool fire, pile fire, or building fire) ***Toxic combustion gases release***
Peroxide Formers	***Condensed-phase explosion*** (e.g., explosive decomposition of unstable peroxide initiated by heat, friction, spark, or mechanical shock) ***Fire*** (e.g., follow-on effects from condensed-phase explosion, such as flammable liquid containment rupture and ignition)

Loss events associated with reactivity hazards

Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Intentional Chemistry	***Containment rupture explosion*** (uncontrolled reaction resulting in liquid/vapor hea g or gas generation inside inadequately relieved vessel or enclosu t is incapable of withstanding peak pressure) ***F*** s of cooling in unconfined temperature to be attained) e.g., off-gas treatment system fails)
Spontaneously Combustible Materials	self-ignition of vapor, dust or mist l or enclosure that is incapable of ***Toxic combustion gases relea***
Peroxide Formers	***Condensed-phase explosion*** (unstable peroxide initiated by shock) ***Fire*** (e.g., follow-on effects f flammable liquid containment

T-2 Incident
Jacksonville, Florida
December 2007



Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Water-Reactive Materials	***Explosively violent reaction*** (e.g., reaction of sodium with water) ***Containment rupture explosion*** (reaction with water resulting in liquid/vapor heating or gas generation inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure, or flammable vapors generated by reaction with water ignited inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Flash fire*** (e.g., ignition of unconfined flammable vapors generated by reaction with water) ***Toxic vapor release*** (toxic vapors generated by reaction with water, or decomposition reaction initiated by heat of reaction with water)
Oxidizers	***Fire*** (initiated or accelerated by presence of oxidizer) ***Condensed-phase explosion*** (initiation of detonable mixture of oxidizer with reducing substance) ***Containment rupture explosion*** (ignition or spontaneous ignition of oxidation reaction inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Toxic combustion gases release*** • Note that many oxidizers are subject to decomposition, so also have ossible Self-Reactive Material consequences

Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Water-Reactive Materials	***Explosively violent reaction*** (e.g., reaction of sodium with water) ***Containment rupture explosion*** (reaction with water resulting in liquid/vapor heating or gas generation inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure, or flammable vapors generated by reaction with water ignited inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Flash fire*** (e.g., ignition of unconfined flammable vapors generated by reaction with water) ***Toxic vapor release*** (toxic vapors generated by reaction with water, or decomposition reaction initiated by heat of reaction with water)
Oxidizers	***Fire*** (initiated or ac ed by presence of oxidizer) ***Condensed-ph*** nable mixture of oxidizer wit ***Containmen*** ntaneous ignition of oxidation rea essel or enclosure that is incapable ***Toxic combu*** • Note that m position, so also have ossible Self

Bhopal
India
December 1984

Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Self-Reactive Materials (Polymerizing, Decomposing, Rearranging)	***Condensed-phase explosion*** (e.g., heat, friction, spark, or mechanical shock initiation of decomposition proceeding at detonation velocity) ***Containment rupture explosion*** (e.g., by self-reaction resulting in liquid/vapor heating, gas generation, or evolution and ignition of flammable vapors inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Toxic vapor release*** (e.g., from toxic decomposition products or heat from self-reaction resulting in vaporization of toxic component) ***Flash fire*** (e.g., by ignition of flammable off-gases) ***Pile fire*** (e.g., by self-heating to autoignition temperature)
Incompatible Materials	***Condensed-phase explosion*** (e.g., by initiation of detonable mixture) ***Containment rupture explosion*** (e.g., by liquid/vapor heating, gas generation, or evolution and ignition of flammable vapors inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Toxic vapor release*** (e.g., from toxic reaction products or from heating and vaporization of toxic component) ***Flash fire*** (e.g., by ignition of flammable off-gases) ***Hazardous material spill*** (e.g., loss of containment due to reaction rong material of construction)

Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Self-Reactive Materials (Polymerizing, Decomposing, Rearranging)	***Condensed-phase explosion*** (e.g., heat, friction, spark, or mechanical shock initiation of decomposition proceeding at detonation velocity) ***Containment rupture explosio*** e.g., by self-reaction resulting in liquid/vapor heating, gas gener or evolution and ignition of flammable vapors inside inade relieved vessel or enclosure that is incapable of withstanding pe re) ***Toxic vapor*** sition products or heat from self-re toxic component) ***Flash fire*** (ases) ***Pile fire*** (e. mperature)
Incompatible Materials	***Condensed*** of detonable mixture) ***Containme*** l/vapor heating, gas generation, able vapors inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Toxic vapor release*** (e.g., from toxic reaction products or from heating and vaporization of toxic component) ***Flash fire*** (e.g., by ignition of flammable off-gases) ***Hazardous material spill*** (e.g., loss of containment due to reaction with wrong material of construction)

Toulouse
France
September 2001

Incompatible materials

How would you define "chemical incompatibility"?

242

ASTM E 2012

"Standard Guide for the Preparation of a Binary Chemical Compatibility Chart"

- Define scenario
- Define incompatibility
- Compile chart

www.astm.org

ASTM E 2012

"Standard Guide for the Preparation of a Binary Chemical Compatibility Chart"

- Define scenario
  - Quantities
  - Temperatures
  - Confinement
  - Atmosphere (air, nitrogen, inerted)
  - Contact time

ASTM E 2012

"Standard Guide for the Preparation of a Binary Chemical Compatibility Chart"

- Define scenario
- Define incompatibility

"In a general sense, chemical incompatibility implies that there may be undesirable consequences of mixing these materials at a macroscopic scale. These consequences might be, in a worst case, a fast chemical reaction or an explosion, a release of toxic gas, or, in a less severe case, an undesirable temperature rise that might take the mixture above its flash point or cause an unacceptable pressure increase in the system…. Consequently, a working definition of incompatibility needs to be formulated before compatibility judgments can be effectively and accurately made."

ASTM E 2012

"Standard Guide for the Preparation of a Binary Chemical Compatibility Chart"

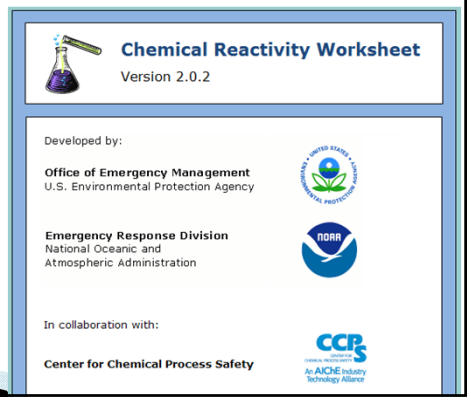
- Define scenario
- Define incompatibility
- Compile chart

NOAA Chemical Reactivity Worksheet

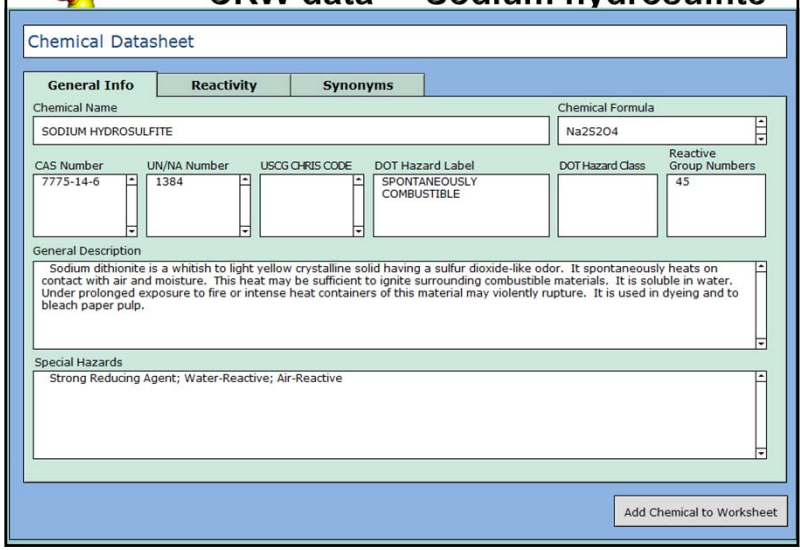
response.restoration.noaa.gov/crw

The NOAA Chemical Reactivity Worksheet predicts the results of mixing any binary combination of the 6,000+ chemicals in the CAMEO database, including many common mixtures and solutions.

For each substance, a general description and chemical profile are given, along with special hazards such as air and water reactivity.



CRW data - Sodium hydrosulfite



Sodium hydrosulfite + ethylene glycol

Reactivity Worksheet

Begin by searching for a chemical to add to the mixture. Return here to add water, reactive groups, and custom chemicals.

Reactivity Mixture

Chemical Name	2 chemical(s) and/or reactive group(s) in mixture	Reactive Hazard Numbers	Reactive Group Numbers
ETHYLENE GLYCOL			4
SODIUM HYDROSULFITE		105, 107, 108	45

Remove All | Remove Selected Chemical | Add Custom Chemicals | Add Reactive Group | Add Water

Predicted Hazards | **Mixture Documentation** (for the reactive groups of the items in the mixture)

1) SODIUM HYDROSULFITE mixed with
2) ETHYLENE GLYCOL
- Reaction proceeds with explosive violence and/or forms explosive products
- May become highly flammable or may initiate a fire, especially if other combustible materials are present
- Combination liberates gaseous products, at least one of which is flammable. May cause pressurization
- Exothermic reaction. May generate heat and/or cause pressurization

Possible Gases:
Hydrogen
Hydrocarbons

To print hazards or documentation: Copy all text in the field above and paste into a word processor program, format as desired, then print.

Save This Mixture | Predict Hazards | Show Compatibility Chart | Show Saved Mixtures | Preview Report

Sodium hydrosulfite + ethylene glycol

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Hydrocarbons

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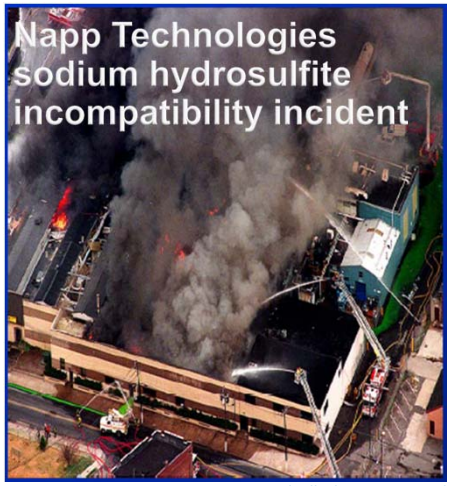
Save This Mixture | Predict Hazards | Show Compatibility Chart | Show Saved Mixtures | Preview Report

April 21, 1995

- 5 worker fatalities
- ~300 evacuated
- Facility destroyed
- Surrounding businesses damaged



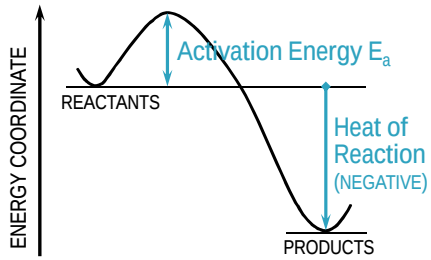
Ed Hill, The Bergen Record

Key Concepts

- Types of reactivity hazards
- Potential consequences
- **Runaway reactions**
- Contain and control measures
- Inherently safer systems

Chemical reactivity hazards

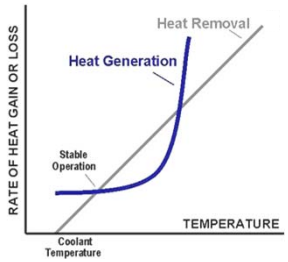
Energy diagram for exothermic reaction:



- Lower activation energy barrier ⮝ faster reaction
- Larger heat of reaction ⮝ more energy released

Key term to understand:

"Runaway reaction"



For an exothermic chemical reaction: FIRST-ORDER KINETICS

- Reaction rate is exponential *f* (temperature) $k = A\,e^{(-Ea/RT)}$
- If reaction temperature increases, rate increases and more heat is released by exothermic reaction
- If this heat is not removed, it further increases the reaction rate
- Then even more heat is released, etc.
- Temperature can rise hundreds of °C per minute!
- Pressure is generated by product gases and/or liquid boiling
- Reactor may rupture if pressure not safely vented

U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

INVESTIGATION REPORT

T2 LABORATORIES, INC.

RUNAWAY REACTION

(Four Killed, 32 Injured)

25
5

Key Concepts

- Types of reactivity hazards
- Potential consequences
- Runaway reactions
- **Contain and control measures**
- Inherently safer systems

Foresee, Avoid, Control

- Anticipate chemical reactivity hazards
- Identify all reactive materials and all possible reactive interactions
- Do whatever it takes to fully understand intended and unintended reactions
  - Boundaries of safe operation
  - Calculations, literature, testing, experts
- Design and operate to avoid unintended reactions and control intended reactions

Safe operation

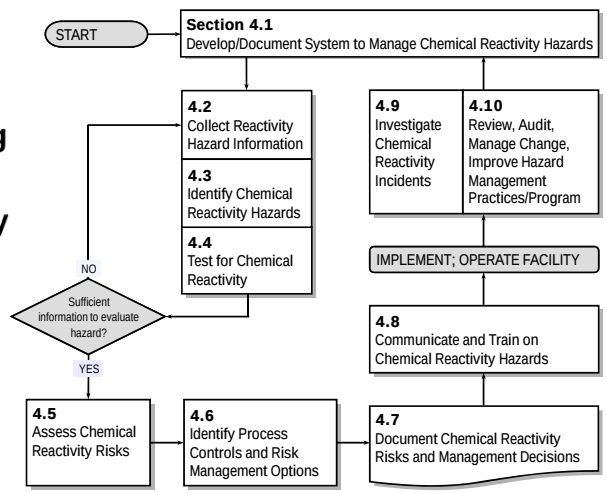
(with respect to chemical reactivity hazards)

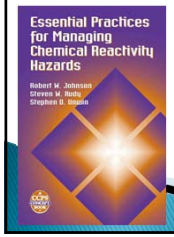
- Contain and control all chemical reactivity hazards throughout entire facility lifetime
- ***OR*** Reduce hazards or design safeguards such that even if hazard containment or control were lost, no injuries, property damage, environmental damage or business interruption would occur
- ***OR*** Eliminate chemical reactivity hazards

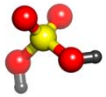
Managing chemical reactivity hazards

- More effort is required to identify and characterize the reactivity hazards
- This may require small-scale testing
- See flowchart on next page

Managing Chemical Reactivity Hazards

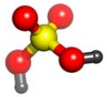






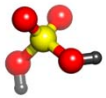
Key steps to avoid unintended chemical reactions

- Train all personnel to be aware of reactivity hazards and incompatibilities and to know maximum storage temperatures and quantities
- Design storage / handling equipment with all compatible materials of construction
- Avoid heating coils, space heaters, and all other heat sources for thermally sensitive materials
- Avoid confinement when possible; otherwise, provide adequate emergency relief protection
- Avoid the possibility of pumping a liquid reactive material against a closed or plugged line
- Locate storage areas away from operating areas in secured / monitored locations



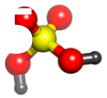
Key steps to avoid unintended chemical reactions (continued)

- Monitor material and building temperatures where feasible with high temperature alarms
- Clearly label and identify all reactive materials, and what must be avoided (e.g., heat, water)
- Positively segregate and separate incompatible materials using dedicated equipment if possible
- Use dedicated fittings and connections to avoid unloading a material into the wrong tank
- Rotate inventories for materials that can degrade or react over time
- Pay close attention to housekeeping and fire prevention around storage/handling areas



Key steps to control intended chemical reactions

- *Scale up very carefully!* – Heat generation increases with the system **volume** (by the cube of the linear dimension), whereas heat removal capability increases with the **surface area** of the system (by the square of the linear dimension).
- Ensure equipment can handle the maximum pressure and maxiumum adiabatic temperature rise of uncontrolled reactions
- Use gradual-addition processes where feasible
- Operate where the intended reaction will be fast
- Avoid using control of reaction mixture temperature as a means for limiting the reaction rate
- Use multiple temperature sensors in different locations
- Avoid feeding a material above the reactor contents' boiling point



Design safer facilities

The following slides are a summary of D.C. Hendershot, "A Checklist for Inherently Safer Chemical Reaction Process Design and Operation," *CCPS International Symposium on Risk, Reliability and Security,* New York: AIChE, October 2002

Reaction Hazard Identification

1 Know the heat of reaction for the intended and other potential chemical reactions.

You should identify all potential reactions that could occur in the reaction mixture and understand the heat of reaction of these reactions.

Reaction Hazard Identification

2 Calculate the maximum adiabatic temperature rise for the reaction mixture.

Use the measured or estimated heat of reaction, assume no heat removal, and that 100% of the reactants actually react.

Compare this temperature to the boiling point of the reaction mixture.

If the maximum adiabatic reaction temperature exceeds the reaction mixture boiling point, the reaction is capable of generating pressure in a closed vessel.

Reaction Hazard Identification

3 Determine the stability of all individual components of the reaction mixture at the maximum adiabatic reaction temperature.

This might be done through literature searching, supplier contacts, or experimentation.

It will only tell you if any of the individual components of the reaction mixture can decompose at temperatures which are theoretically attainable.

Reaction Hazard Identification

4 Understand the stability of the reaction mixture at the maximum adiabatic reaction temperature.

Are there any chemical reactions, other than the intended reaction, which can occur at the maximum adiabatic reaction temperature?

Consider possible decomposition reactions, particularly those that generate gaseous products.

Understanding the stability of a mixture of components may require laboratory testing.

Reaction Hazard Identification

5 Determine the heat addition and heat removal capabilities of the pilot plant or production reactor.

Don't forget to consider the reactor agitator as a source of energy – about 2550 Btu/hour/hp.

Understand the impact of variation in conditions on heat transfer capability.

Reaction Hazard Identification

6 Identify potential reaction contaminants. In particular, consider possible contaminants that are ubiquitous in a plant environment, such as air, water, rust, oil and grease.

Think about possible catalytic effects of trace metal ions such as sodium, calcium, and others commonly present in process water and cleaners.

Determine if these materials will catalyze any decomposition or other reactions, either at normal conditions or at the maximum adiabatic reaction temperature.

Reaction Hazard Identification

7 Consider the impact of possible deviations from intended reactant charges and operating conditions.

For example, is a double charge of one of the reactants a possible deviation, and, if so, what is the impact?

Reaction Hazard Identification

8 Identify all heat sources connected to the reaction vessel and determine their maximum temperature.

Assume all control systems on the reactor heating systems fail to the maximum temperature. If this temperature is higher than the maximum adiabatic reaction temperature, review the stability and reactivity information with respect to the maximum temperature to which the reactor contents could be heated by the vessel heat sources.

Reaction Hazard Identification

9 Determine the minimum temperature to which the reactor cooling sources could cool the reaction mixture.

Consider potential hazards resulting from too much cooling, such as freezing of reaction mixture components, fouling of heat transfer surfaces, increase in reaction mixture viscosity reducing mixing and heat transfer, precipitation of dissolved solids from the reaction mixture, and a reduced rate of reaction resulting in a hazardous accumulation of unreacted material.

Reaction Hazard Identification

10 Consider the impact of higher temperature gradients in plant scale equipment compared to a laboratory or pilot plant reactor.

Agitation is almost certain to be less effective in a plant reactor, and the temperature of the reaction mixture near heat transfer surfaces may be higher (for systems being heated) or lower (for systems being cooled) than the bulk mixture temperature.

For exothermic reactions, the temperature may also be higher near the point of introduction of reactants.

Reaction Hazard Identification

11 Understand the rate of all chemical reactions.

It is not necessary to develop complete kinetic models with rate constants and other details, but you should understand how fast reactants are consumed and generally how the rate of reaction increases with temperature.

Thermal hazard calorimetry testing can provide useful kinetic data.

Reaction Hazard Identification

12 Consider possible vapor-phase reactions.

These might include:

- combustion reactions
- other vapor-phase reactions such as the reaction of organic vapors with a chlorine atmosphere
- vapor phase decomposition of materials such as ethylene oxide or organic peroxide.

Reaction Hazard Identification

13 Understand the hazards of the products of both intended and unintended reactions.

If you find an unexpected material in reaction equipment, determine what it is and what impact it might have on system hazards.

For example, in an oxidation reactor, solids were known to be present, but nobody knew what they were. It turned out that the solids were pyrophoric, and they caused a fire in the reactor.

Reaction Hazard Identification

14 Consider doing a Chemical Interaction Matrix and/or a Chemistry Hazard Analysis.

These techniques can be applied at any stage in the process life cycle, from early research through an operating plant.

Reaction Process Design

1 Rapid reactions are desirable.

In general, you want chemical reactions to occur immediately when the reactants come into contact.

The reactants are immediately consumed and the reaction energy quickly released, allowing you to control the reaction by controlling the contact of the reactants.

However, you must be certain that the reactor is capable of removing all of the heat and any gaseous products generated by the reaction.

Reaction Process Design

2 Avoid batch processes in which all of the potential chemical energy is present in the system at the start of the reaction step.

If you operate this type of process, know the heat of reaction and be confident that the maximum adiabatic temperature and pressure are within the design capabilities of the reactor.

Reaction Process Design

3 Use gradual addition or "semi-batch" processes for exothermic reactions.

The inherently safer way to operate exothermic reaction process is to determine a temperature at which the reaction occurs very rapidly. Operate the reaction at this temperature, and feed at least one of the reactants gradually to limit the potential energy contained in the reactor.

A physical limit to the possible rate of addition of the limiting reactant is desirable – e.g. a metering pump, small feed line or restriction orifice.

Reaction Process Design

4 Avoid using control of reaction mixture temperature as a means for limiting the reaction rate.

If the reaction produces a large amount of heat, this control philosophy is unstable – an increase in temperature will result in faster reaction and even more heat being released, causing a further increase in temperature and more rapid heat release..... If there is a large amount of potential chemical energy from reactive materials, a runaway reaction results.

Reaction Process Design

5 Account for the impact of vessel size on heat generation and heat removal capabilities of a reactor.

Heat generation increases with the volume of the system – by the cube of the linear dimension.

Heat removal capability increases with the square of the linear dimension.

Reaction Process Design

6 Use multiple temperature sensors, in different locations in the reactor for rapid exothermic reactions.

This is particularly important if the reaction mixture contains solids, is very viscous, or if the reactor has coils or other internal elements which might inhibit good mixing.

Reaction Process Design

7 Avoid feeding a material to a reactor at a higher temperature than the boiling point of the reactor contents.

This can cause rapid boiling of the reactor contents and vapor generation.

Key Concepts

- Types of reactivity hazards
- Potential consequences
- Runaway reactions
- Contain and control measures
- **Inherently safer systems**

Where chemical reactivity hazard(s) are identified, one of the first questions to ask should be:

"Can the reactivity hazards be eliminated or reduced?"

WHY?

Those hazards that are <u>not</u> eliminated or reduced to insignificance must be managed throughout the lifetime of the facility,

to avoid uncontrolled chemical reactions that can result directly or indirectly in serious harm to people, property or the environment.

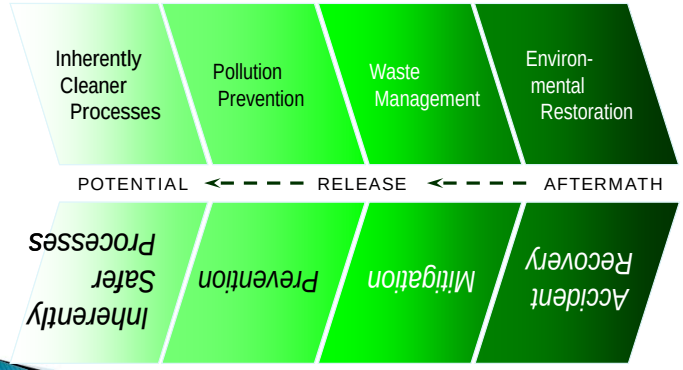
Eliminating or reducing the potential for uncontrolled chemical reactions makes a facility

"inherently safer"

If feasible, this has the possibility of affecting a facility in many different ways, such as:

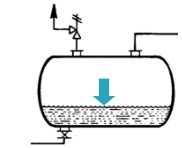
- Reduce the need for engineered controls and safety systems (including both initial and ongoing inspection, testing and maintenance costs)
- Reduce labor costs and potential liabilities associates with ongoing legal compliance
- Eliminate the need for personal protective equipment associated with particular hazards
- Reduce emergency preparedness and response requirements
- Improve worker safety and health
- Improve neighborhood / community relations

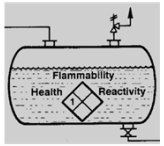
Inherently safer processes

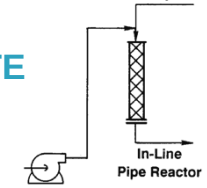


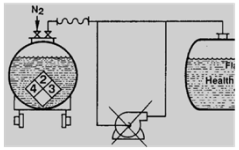
Inherently safer strategies

- MINIMIZE
- SUBSTITUTE
- MODERATE
- SIMPLIFY









Safe operation

(with respect to chemical reactivity hazards)

- Contain and control all chemical reactivity hazards throughout entire facility lifetime
- ***OR*** **Reduce hazards** or design safeguards such that even if hazard containment or control were lost, no injuries, property damage, environmental damage or business interruption would occur
- ***OR*** **Eliminate chemical reactivity hazards**

Inherently safer systems

Case history:
Methyl isocyanate

Bhopal

On December 4, 1984, approximately 40 metric tons of methyl isocyanate was released from the UCIL plant in Bhopal, India, resulting in an over 2,000 fatalities and many more injuries.

This was the worst disaster in chemical industry history.

The basic issue:

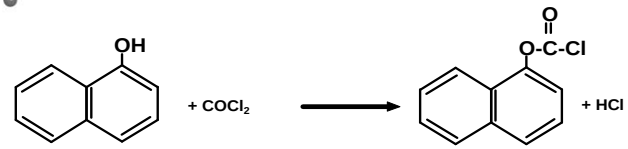
An uncontrolled chemical reaction occurred, resulting in devastating consequences.

Time 12/17/84 (Tucci/Liaison)

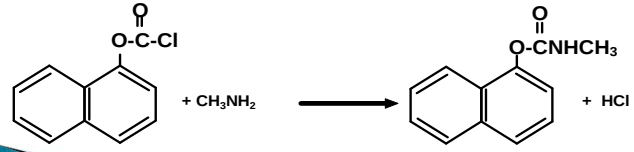
The two theories explaining the Bhopal tragedy both involve a significant amount of water getting into a 15,000 gal (56.5 m3) methyl isocyanate storage tank, resulting in an uncontrolled exothermic reaction that heated the MIC above its boiling point and led to the release of about 40 metric tons (~90,000 lb) of vaporized MIC from an elevated stack.

By comparison, the life-threatening concentration of MIC vapors in air is only 5 ppm (ERPG-3, 1 h exposure), which is only about 400 milligrams (~or about 0.001 lb by weight) of MIC in a room about the size of a medium to large bedroom or office (1200 ft3).

Non-MIC route



α- NAPHTHOL CHLOROFORMATE



MIC generated on demand

- One company previously received and stored methyl isocyanate (MIC) in bulk liquefied form, as an ingredient for agricultural chemical products
- A process modification was made so that the MIC was generated as needed in vapor form, and piped directly to the process that consumed it

MIC generated on demand

- Average MIC inventory was reduced from thousands of pounds to about 2 pounds (1 kg) of vapor in the transfer line between generation and consumption
- The possibility of interrupting production (if a problem occurred in the process that generated MIC) was considered to be more than offset by the reduced vapor release risks

Exercise

What opportunities are there in your field of research or interest to consider reducing chemical reactivity hazards?

Extra-Credit Activities

SAChE case histories

- Batch Polystyrene Reactor Runaway
- The Bhopal Disaster
- Methacrylic Acid Tankcar Explosion -video
- Explosion and Fire Caused By a Runaway Decomposition
- Rupture of a Nitroaniline Reactor
- Seveso Accidental Release
- T2 Runaway Reaction and Explosion

SAChE reactivity modules

Hazards awareness; hazard reduction

- An Introduction to Reactive and Explosive Materials (video)
- Acrylic Monomers Handling
- The Hazards of Hydroxylamine
- Chemical Reactivity Hazards (web-based)
- Introduction to Inherently Safer Design

SAChE reactivity modules

Emergency relief systems

- Design for Overpressure and Underpressure Protection
- Unit Operations Laboratory Experiment for Runaway Reactions and Vent Sizing
- Relief System Design for Single- and Two-Phase Flow
- Runaway Reactions -- Experimental Characterization and Vent Sizing
- Compressible and Two-Phase Flow with Applications Including Pressure Relief System Sizing

RMR

Reactivity Management Roundtable

Started in 2003

Most recent activity:

Reactivity Evaluation Software Tool

See description and download link at www.aiche.org/ccps/ActiveProjects/RMR/index.aspx

DIERS Users Group

AIChE Design Institute for Emergency Relief Systems

DIERS Users Group Meetings

See www.diers.net/diersweb/home.aspx for schedule and information

Loss Prevention Symposium

46th Annual Loss Prevention Symposium

Houston, Texas, USA
April 2-6, 2012

Sessions include presentations on:

- Material hazard characteristics
- Case histories and lessons learned

LPS'12 reactivity presentations

- A Mechanistic and Experimental Study of the Diethyl Ether Oxidation
- Phase Behavior of Poly-Substituted Mono-Nitrated Aromatic Compounds
- Global and Local QSPR Models to Predict the Impact Sensitivity of Nitro Compounds
- Thermal Safety of Ionic Liquids
- The CCPS Reactivity Evaluation Software Tool
- On the Catastrophic Explosion of the AZF Plant in Toulouse (September 21, 2001)

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Behavior Based Safety (BBS)

SAND No. 2011-0487C
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

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

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Behavior Based Safety is <u>NOT</u>:

- 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.

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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.

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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.

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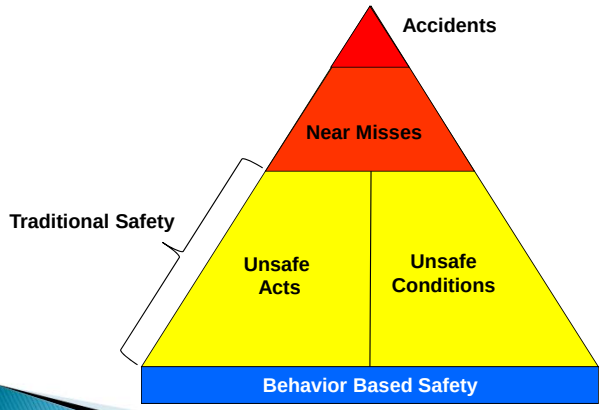
Behavior Based Safety underlies and benefits Traditional Safety



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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?

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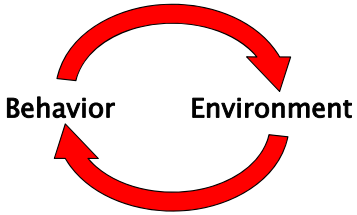
Remember: Behavior is "the manner of conducting oneself"

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.

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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

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How do Consequences Affect At-Risk Behavior?

Behavior → Accident Probability → No Accident

↓

Accident

↓

Severity Probability

Risk = exposure x probability

Consequence

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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?

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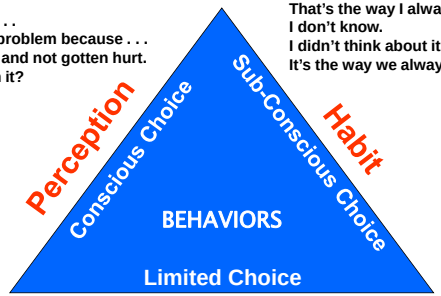
Worker's reasons for taking a risk:

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).

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Implementing Behavior Based Safety

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

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.

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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

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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.

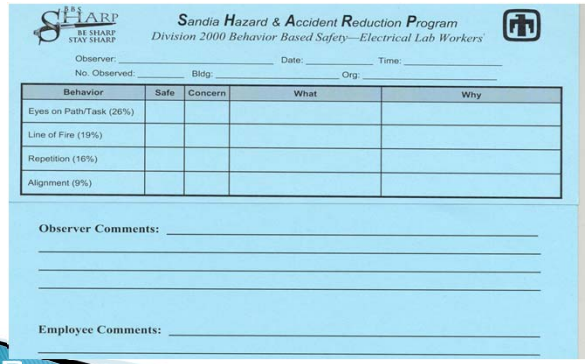
Step 2: Develop Observation Checklists

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).



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: _____

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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

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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

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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

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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

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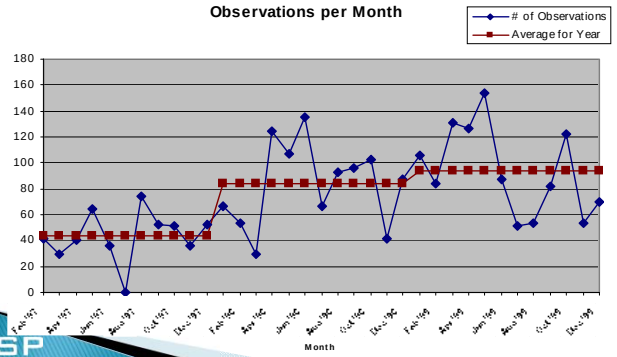
What happens with more observations?

Feedback Changes Behaviors



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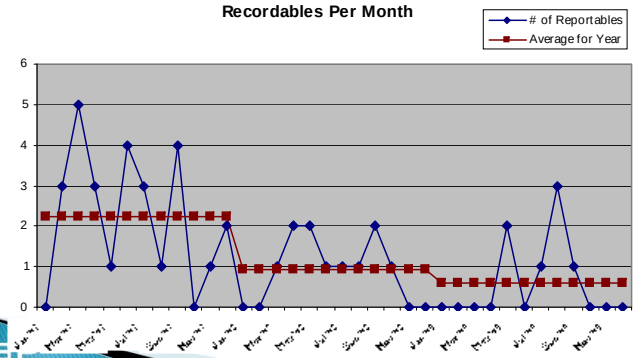
Fewer injuries!

Changed Behaviors Reduce Accidents



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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.

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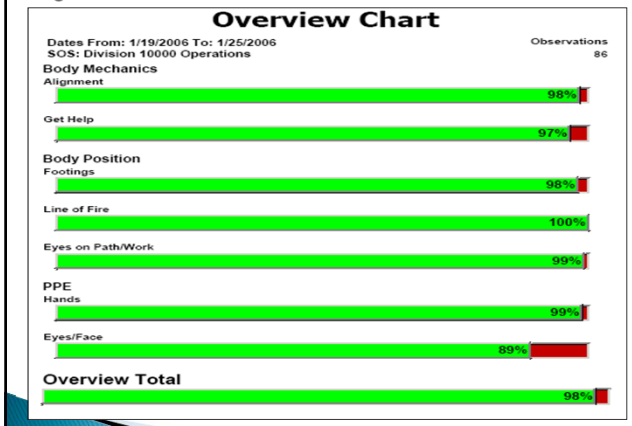
An example of a "Green/Red" Chart from the Observations of a Division at Sandia



Key: Safe Concern

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Why Implement Behavior Based Safety?

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

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/Management supported

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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.

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The 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.

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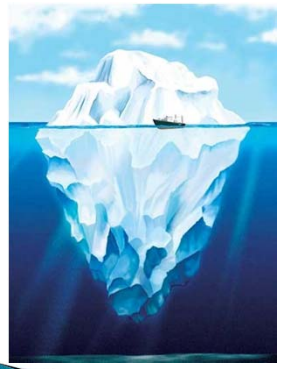
Why Implement Behavior Based Safety?



Remember:

The Iceberg Theory

For every accident, there are many "near misses" that go unnoticed.

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