U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

HAZARD INVESTIGATION

IMPROVING REACTIVE HAZARD MANAGEMENT

KEY ISSUES

REGULATORY COVERAGE

NFPA HAZARD RATING SYSTEM

MANAGEMENT SYSTEM GUIDANCE

INDUSTRY INITIATIVES

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Abstract

This hazard investigation examines reactive hazard management across the United States. Key issues are regulatory coverage, the National Fire Protection Association hazard rating system, management system guidance, and industry initiatives. This report makes recommendations to three Government agencies, seven trade associations/industry groups, and four trade unions.

The U.S. Chemical Safety and Hazard Investigation Board (CSB) is an independent Federal agency whose mission is to ensure the safety of workers and the public by preventing or minimizing the effects of chemical incidents. CSB is a scientific investigative organization; it is not an enforcement or regulatory body. Established by the Clean Air Act Amendments of 1990, CSB is responsible for determining the root and contributing causes of accidents, issuing safety recommendations, studying chemical safety issues, and evaluating the effectiveness of other government agencies involved in chemical safety. No part of the conclusions, findings, or recommendations of CSB relating to any chemical incident may be admitted as evidence or used in any action or suit for damages arising out of any matter mentioned in an investigation report (see 42 U.S.C. § 7412[r][6][G]).

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Acronyms and Abbreviations

ACC	American Chemistry Council
AFL-CIO	American Federation of Labor-Congress of Industrial Organizations
AIChE	American Institute of Chemical Engineers
AIHA	American Industrial Hygiene Association
ANSI	American National Standards Institute
API	American Petroleum Institute
APELL	Awareness and Preparedness for Emergencies at Local Level (UNEP)
ARC	Accelerating rate calorimeter (Arthur D. Little, Inc.)
ARIP	Accidental Release Information Program (EPA)
ASSE	American Society of Safety Engineers
ASTM	American Society for Testing and Materials
BLS	U.S. Bureau of Labor Statistics
BPS	Bartlo Packaging Inc.
°C	Degrees Celsius
CAAA	Clean Air Act Amendments of 1990
CAER	Community awareness and emergency response (ACC Responsible Care)
cal/g	Calorie per gram
CCPS	Center for Chemical Process Safety
CDCIR	The Community Documentation Centre on Industrial Risk (MAHB)
CFR	Code of Federal Regulations
CHETAH	Chemical Thermodynamic and Energy Release Evaluation (ASTM)
CHRIS	Chemical Hazards Response Information System (USCG)
CIMAH	Control of Industrial Major Accident Hazards (U.K.)
CIRC	Chemical Incident Reports Center (CSB)

Acronyms and Abbreviations (cont'd)

COMAH	Control of Major Accident Hazards Involving Dangerous Substances (U.K.; replaced CIMAH in 1999)
CSB	U.S. Chemical Safety and Hazard Investigation Board
CSI	Concept Sciences, Inc.
DOE	U.S. Department of Energy
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EC	European Community
EHS	Environmental health and safety
EHS	Extremely hazardous substance
EPA	U.S. Environmental Protection Agency
EPCRA	Emergency Planning and Community Right-to-Know Act
EU	European Union
°F	Degrees Fahrenheit
FMEA	Failure modes and effects analysis
GDC	General Duty Clause (OSHA)
HA	Hydroxylamine
HarsNet	Hazard Assessment of Highly Reactive Systems Thematic Network
HASTE	The European Health and Safety Database
HAZOP	Hazard and operability
HSE	Health and Safety Executive (U.K.)
HSEES	Hazardous Substances Emergency Events Surveillance (MAHB)
IAFF	International Association of Fire Fighters
IChemE	Institution of Chemical Engineers (U.K.)
ICWU	International Chemical Workers Union (now part of UFCW)
IMIS	Integrated Management Information System (OSHA)

IPD	Instantaneous power density
ISA	Instrumentation, Systems, and Automation Society
MAHB	Major Accident Hazard Bureau (European Community)
MARS	Major Accident Reporting System (MAHB)
MHIDAS	Major Hazard Incident Data Service (HSE)
MOC	Management of change
MSDS	Material safety data sheet
MSV	Management systems verification
NACD	National Association of Chemical Distributors
NAICS	North American Industry Classification System
NFIRS	National Fire Incident Reporting System
NFPA	National Fire Protection Association
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NRC	National Response Center (USCG)
NTSB	National Transportation Safety Board
OCAW	Oil, Chemical, and Atomic Workers (now part of PACE)
OSHA	Occupational Safety and Health Administration
PACE	Paper, Allied-Industrial, Chemical & Energy Workers International Union
PHA	Process hazard analysis
PSCMS	Process Safety Code Measurement System (ACC)
psi	Pound per square inch
PSI	Process safety information
PSM	Process safety management (OSHA)
QA	Quality assurance
R&D	Research and development
RDP	Responsible Distribution Process (NACD)

Acronyms and Abbreviations (cont'd)

redox	Oxidation-reduction
RMP	Risk management program (EPA)
SIC	Standard industrial classification
SOCMA	Synthetic Organic Chemical Manufacturers Association
SOP	Standard operating procedure
TCDD	Dioxin
TCP	2,4,5-Trichlorophenol
TCPA	Toxic Catastrophe Prevention Act (New Jersey)
TGA	Thermogravimetric analysis
TNO	Netherlands Organisation for Applied Scientific Research
UFCW	United Food and Commercial Workers International Union
UNEP	United Nations Environmental Programme
UNITE	Union of Needletrades, Industrial, and Textile Employees
USCG	U.S. Coast Guard
USFA	U.S. Fire Administration
USWA	United Steelworkers of America
VSP	Vent size packaging
W/mL	Watt per milliliter

Executive Summary

ES.1 Introduction

The capability of chemical substances to undergo reactions, or transformations in their structure, is central to the chemical processing industry. Chemical reactions allow for a diversity of manufactured products. However, chemical reactivity can lead to significant hazards if not properly understood and controlled.

Reactivity[1] is not necessarily an intrinsic property of a chemical substance. The hazards associated with reactivity are related to process-specific factors, such as operating temperatures, pressures, quantities handled, concentrations, the presence of other substances, and impurities with catalytic effects.

The capability of chemical substances to undergo reactions, or transformations in their structure, is central to the chemical processing industry.

Safely conducting chemical reactions is a core competency of the chemical manufacturing industry. However, chemical reactions can rapidly release large quantities of heat, energy, and gaseous byproducts. Uncontrolled reactions have led to serious explosions, fires, and toxic emissions. The impacts may be severe in terms of death and injury to people, damage to physical property, and effects on the environment. In particular, incidents at Napp Technologies in 1995 and Morton International in 1998 raised concerns about reactive hazards to a national level. These and other incidents across the United States[2] underscore the need to improve the management of reactive hazards.

A variety of legal requirements and regulations govern the hazards associated with highly hazardous chemicals (including reactive chemicals), among which are regulations of the Occupational Safety and Health Administration (OSHA) and the U.S. Environmental Protection Agency (EPA).

Reactivity is not necessarily an intrinsic property of a chemical substance.

OSHA develops and enforces standards to protect employees from workplace hazards. In the aftermath of the Bhopal tragedy,[3] OSHA was concerned about the possibility of a catastrophe at chemical plants in the United States. Its own investigations in the mid-1980s indicated a need to look beyond existing standards.

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[1] See Appendix A, Glossary, for a definition of "reactivity" and numerous other technical terms.

[2] For example: BPS Inc., West Helena, Arkansas (1997), with three fatalities; Condea Vista, Baltimore, Maryland (1998), with five injured; Whitehall Leather Company, Whitehall, Michigan (1999), with one fatality; and Concept Sciences, Inc., Allentown, Pennsylvania (1999), with five fatalities and 14 injured.

[3] On December 4, 1984, approximately 40 metric tons of methyl isocyanate was accidentally released in Bhopal, India. This reactive incident resulted in an estimated 2,000 deaths within a short period (Lees, 1996; App. 5).

Bhopal and a series of other major incidents underscored the need for increased attention to process safety management; OSHA began to develop a standard that would incorporate these principles. A proposed standard was published in 1990. Additionally, the Clean Air Act Amendments (CAAA) of 1990 required OSHA to promulgate a standard to protect employees from the hazards associated with releases of highly hazardous chemicals, including reactive chemicals.

In 1992, OSHA promulgated its Process Safety Management (PSM) Standard (29 CFR 1910.119). The standard covers processes containing individually listed chemicals that present a range of hazards, including reactivity, as well as a class of flammable chemicals. Reactive chemicals were selected from an existing list of chemicals identified and rated by the National Fire Protection Association (NFPA) because of their instability rating of "3" or "4" (on a scale of 0 to 4).[4, 5]

CAAA also required EPA to develop regulations to prevent the accidental release of substances, including reactives, that could have serious effects on the public or the environment. In 1996, EPA promulgated its Accidental Release Prevention Requirements: Risk Management Programs (RMP; 40 CFR 68) in response to the congressional mandate. Although this standard established new measures with regard to public notification, emergency response, and accident reporting, its requirements for managing process safety are similar to those of the OSHA PSM Standard. For purposes of this regulation, EPA identified covered substances based on toxicity and flammability–but not chemical reactivity.

Professional and trade associations such as the American Institute of Chemical Engineers (AIChE), the American Chemistry Council (ACC), the Synthetic Organic Chemical Manufacturers Association (SOCMA), and the National Association of Chemical Distributors (NACD) provide voluntary chemical process safety guidance to their members.

[4] OSHA used the 1975 version of NFPA 49, Hazardous Chemicals Data.

[5] An NFPA instability rating of "4" means that materials in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures. A rating of "3" means that materials in themselves are capable of detonation or explosive decomposition or explosive reaction, but require a strong initiating source or must be heated under confinement before initiation.

In 1985, AIChE established the Center for Chemical Process Safety (CCPS) in response to the Bhopal tragedy. Manufacturers, government, and scientific research groups sponsor CCPS, which has published extensive industry guidance in the area of process safety technology and management. CCPS recently produced a safety alert on reactive hazards, and a more comprehensive product is under development.

ACC and SOCMA each have programs to promote good practices among member companies in the area of chemical process safety. Similarly, NACD promotes good distribution practices and dissemination of information to end-use customers on the proper handling of chemical products.

This report, *Hazard Investigation: Improving Reactive Hazard Management,* by the U.S. Chemical Safety and Hazard Investigation Board (CSB), examines chemical process safety in the United States–specifically, hazardous chemical reactivity. Its objectives are to:

- Determine the impacts of reactive incidents.
- Examine how industry, OSHA, and EPA currently address reactive hazards.
- Determine the differences, if any, between small, medium, and large companies with regard to reactive chemical policies, practices, in-house reactivity research, testing, and process engineering.
- Analyze the appropriateness of, and consider alternatives to, industry and OSHA use of the NFPA instability rating system for process safety management.
- Develop recommendations for reducing the number and severity of reactive incidents.

ES.2 Investigative Process

. . . an "incident" is defined as a sudden event involving an uncontrolled chemical reaction–with significant increases in temperature, pressure, or gas evolution–that has caused, or has the potential to cause, serious harm to people, property, or the environment.

In conducting this investigation, CSB completed the following tasks:

- Analyzed reactive incidents by collecting and reviewing available data.
- Surveyed current reactive hazard management practices in industry.
- Visited companies to observe reactive hazard management practices.
- Analyzed regulatory coverage of reactive hazards.
- Met with stakeholders to discuss the problem and approaches to improve the management of reactive hazards.
- Conducted a public hearing at which further stakeholder inputs were solicited on key findings and preliminary conclusions from the hazard investigation.

The data analysis included evaluating the number, impact, profile, and causes of reactive incidents. CSB examined more than 40 data sources (e.g., industry and governmental databases and guidance documents; safety/loss prevention texts and journals; and industry association, professional society, insurance, and academic newsletters), focusing on incidents where the primary cause was related to chemical reactivity.

For the purposes of this investigation, an "incident" is defined as a sudden event involving an uncontrolled chemical reaction–with significant increases in temperature, pressure, or gas evolution–that has caused, or has the potential to cause, serious harm to people, property, or the environment.

Through a survey of select small, medium, and large companies, information was gathered about good practices for reactive hazard management within the chemical industry. CSB also visited chemical industry facilities that have implemented programs for managing reactive hazards.

ES.3 Key Findings

1. The limited data analyzed by CSB include 167 serious incidents in the United States involving uncontrolled chemical reactivity from January 1980 to June 2001. Forty-eight of these incidents resulted in a total of 108 fatalities. The data include an average of six injury-related incidents per year, resulting in an average of five fatalities annually.
2. Nearly 50 of the 167 incidents affected the public.[6]
3. Over 50 percent of the 167 incidents involved chemicals not covered by existing OSHA or EPA process safety regulations.[7]
4. Approximately 60 percent of the 167 incidents involved chemicals that either are not rated by NFPA or have "no special hazard" (NFPA "0").[8] Only 10 percent of the 167 incidents involved chemicals with NFPA published ratings of "3" or "4."
5. For the purpose of the OSHA PSM Standard, NFPA instability ratings have the following limitations with respect to identifying reactive hazards:
   - They were originally designed for initial emergency response purposes, not for application to chemical process safety.
   - They address inherent instability only, not reactivity with other chemical substances (with the exception of water) or chemical behavior under nonambient conditions.
   - NFPA Standard 49[9]–on which the OSHA PSM-listed highly reactive chemicals are based–covers only 325 chemical substances, a very small percentage of the chemicals used in industry.[10]

The limited data analyzed by CSB include 167 serious incidents in the United States involving uncontrolled chemical reactivity from January 1980 to June 2001.

Approximately 60 percent of the 167 incidents involved chemicals that either are not rated by NFPA or have "no special hazard". . .

NFPA Standard 49–on which the OSHA PSM-listed highly reactive chemicals are based–covers only 325 chemical substances . . .

[6] "Public impact" is defined as known injury, offsite evacuation, or shelter-in-place.

[7] OSHA PSM Standard (29 CFR 1910.119) and EPA Accidental Release Prevention Requirements: Risk Management Programs (RMP) Under the Clean Air Act, Section 112(r)(7) (40 CFR 68).

[8] An NFPA instability rating of "0" means that a material in itself is normally stable, even under "fire" conditions.

[9] NFPA 49, Hazardous Chemicals Data (1975 Edition).

[10] The Chemical Abstracts Service maintains data on over 200,000 chemicals that are listed under national and international regulations.

- The OSHA PSM Standard lists 137 highly hazardous chemicals–only 38 of which are considered highly reactive based on NFPA instability ratings of "3" or "4."
- The NFPA ratings were established by a system that relies, in part, on subjective criteria and judgment.

The OSHA PSM Standard lists 137 highly hazardous chemicals–only 38 of which are considered highly reactive based on NFPA instability ratings of "3" or "4."

6. As a result of the joint EPA-OSHA chemical accident investigation of the Napp Technologies incident in April 1995, a recommendation was made to consider adding more reactive chemicals to their respective lists of chemicals covered by process safety regulations. To date, neither EPA nor OSHA process safety regulations have been modified to better cover reactive hazards.
7. Reactive hazards are diverse. The reactive incident data analyzed by CSB included:
   - Over 40 different chemical classes (i.e., acids, bases, monomers, oxidizers, etc.), with no single dominating class.
   - Several types of hazardous chemical reactivity, with 36 percent attributed to chemical incompatibility, 35 percent to runaway reactions, and 10 percent to impact-sensitive or thermally sensitive materials.
   - A diverse range of chemical process equipment–including reaction vessels, storage tanks, separation equipment, and transfer equipment. Storage and process equipment (excluding chemical reaction vessels) accounts for over 65 percent of the equipment involved; chemical reaction vessels account for only 25 percent.

Incident data collected by OSHA and EPA provide no functional capability to track reactive incidents so as to analyze incident trends and develop preventive actions at a national level.

8. Reactive incidents can result in a variety of consequences, including fires and explosions (42 percent of incidents) as well as toxic gas emissions (37 percent).
9. No one comprehensive data source contains the data needed to adequately understand root causes and lessons learned from reactive incidents or other process safety incidents.
10. Incident data collected by OSHA and EPA provide no functional capability to track reactive incidents so as to analyze incident trends and develop preventive actions at a national level.

11. Causes and lessons learned are reported in only 20 percent of the 167 incidents. (Industry associations, government agencies, and academia typically do not collect this information.) However, more than 60 percent of the incidents for which some causal information was available involved inadequate practices for identifying hazards or conducting process hazard evaluations; nearly 50 percent involved inadequate procedures for storage, handling, or processing of chemicals.[11]

12. Over 90 percent of the incidents analyzed by CSB involved reactive hazards that are documented in publicly available literature accessible to the chemical processing and handling industry.[12]

Over 90 percent of the incidents analyzed by CSB involved reactive hazards that are documented in publicly available literature accessible to the chemical processing and handling industry.

13. Although several computerized tools[13] and literature resources are available to identify reactive hazards, surveyed companies do not generally use them. In some cases, these tools provide an efficient means of identifying reactive hazards without the need for chemical testing.

14. Surveyed companies share chemical data of a general nature for most chemicals (e.g., material safety data sheets [MSDS]) and good handling practices for some. However, detailed reactive chemical test data, such as thermal stability data–which can be valuable in identifying reactive hazards–are not typically shared.

15. Approximately 70 percent of the 167 incidents occurred in the chemical manufacturing industry. Thirty percent involved a variety of other industrial sectors that store, handle, or use chemicals in bulk quantities.

16. Only limited guidance on the management of reactive hazards throughout the life cycle of a chemical manufacturing process[14] is currently available to industry through professional societies,

[11] The summation of causal factor statistics exceeds 100 percent because each major incident can, and often does, have more than one cause.

[12] See Section 6.1 for a list of selected literature.

[13] National Oceanic and Atmospheric Administration (NOAA), The Chemical Reactivity Worksheet; American Society for Testing and Materials (ASTM), CHETAH; and Bretherick's Database of Reactive Chemical Hazards.

[14] A recently initiated CCPS project, Managing Reactive Chemical Hazards, may address this gap in industry guidance.

standards organizations, government agencies, or trade associations. There are significant gaps in the following:

- Unique aspects of reactive hazards that should be examined during process hazard analysis (PHA), such as the need for reactive chemical test data, and methods to identify and evaluate worst case scenarios involving uncontrolled reactivity.
- Integration of reactive hazard information into process safety information, operating procedures, training, and communication practices.
- Review of the impact on reactive hazards due to proposed changes in chemical processes.
- Concise guidance targeted at companies engaged primarily in the bulk storage, handling, and use of chemicals to prevent inadvertent mixing of incompatible substances.

17. Several voluntary industry initiatives, such as the ACC Responsible Care and the NACD Responsible Distribution Process (RDP), provide guidance on process safety management for chemical manufacturers and distributors. However, no voluntary industry initiatives list specific codes or requirements for reactive hazard management.

18. The EPA RMP regulation and the European Community's Seveso II directive both exempt covered processes from some regulatory provisions, if the facility documents the absence of catastrophic damage from process accidents under reasonable worst case conditions. (The State of New Jersey is also considering similar action in proposed revisions of its Toxic Catastrophe Prevention Act [TCPA] regulations.)

ES.4 Conclusions

1. Reactive incidents are a significant chemical safety problem.
2. The OSHA PSM Standard has significant gaps in coverage of reactive hazards because it is based on a limited list of individual chemicals with inherently reactive properties.
3. NFPA instability ratings are insufficient as the sole basis for determining coverage of reactive hazards in the OSHA PSM Standard.
4. The EPA Accidental Release Prevention regulations have significant gaps in coverage of reactive hazards.
5. Using lists of chemicals is an inadequate approach for regulatory coverage of reactive hazards. Improving reactive hazard management requires that both regulators and industry address the hazards from combinations of chemicals and process-specific conditions rather than focusing exclusively on the inherent properties of individual chemicals.
6. Reactive incidents are not unique to the chemical manufacturing industry. They also occur in many other industries where chemicals are stored, handled, or used.
7. Existing sources of incident data are not adequate to identify the number, severity, and causes of reactive incidents or to analyze incident frequency trends.
8. There is no publicly available database for sharing lessons learned from reactive incidents.
9. Neither the OSHA PSM Standard nor the EPA RMP regulation explicitly requires specific hazards, such as reactive hazards, to be examined when analyzing process hazards. Given that reactive incidents are often caused by inadequate recognition and evaluation of reactive hazards, improving reactive hazard management requires examining relevant factors (e.g., rate and quantity of heat and gas generated) within a process hazard analysis.

The OSHA PSM Standard has significant gaps in coverage of reactive hazards because it is based on a limited list of individual chemicals with inherently reactive properties.

Improving reactive hazard management requires that both regulators and industry address the hazards from combinations of chemicals and process-specific conditions rather than focusing exclusively on the inherent properties of individual chemicals.

Existing sources of incident data are not adequate to identify the number, severity, and causes of reactive incidents or to analyze incident frequency trends.

10. The OSHA PSM Standard and the EPA RMP regulation do not explicitly require the use of multiple sources when compiling process safety information.

11. Publicly available resources[15] are not always used by industry to assist in identifying reactive hazards.

12. There is no publicly available database to share reactive chemical test information.

13. Current good practice guidelines on how to effectively manage reactive hazards throughout the life cycle[16] of a chemical manufacturing process are neither complete nor sufficiently explicit.

14. Given the impact and diversity of reactive hazards, optimum progress in the prevention of reactive incidents requires both enhanced regulatory and nonregulatory programs.

[15] The Chemical Reactivity Worksheet (NOAA), CHETAH (ASTM), and Bretherick's Database of Reactive Chemical Hazards.

[16] "Life cycle" refers to all phases of a chemical manufacturing process–from conceptualization, process research and development (R&D), engineering design, construction, commissioning, commercial operation, and major modification to decommissioning.

ES.5 Recommendations

Occupational Safety and Health Administration (OSHA)

1. Amend the Process Safety Management (PSM) Standard, 29 CFR 1910.119, to achieve more comprehensive control of reactive hazards that could have catastrophic consequences.

   - Broaden the application to cover reactive hazards resulting from process-specific conditions and combinations of chemicals. Additionally, broaden coverage of hazards from self-reactive chemicals. In expanding PSM coverage, use objective criteria. Consider criteria such as the North American Industry Classification System (NAICS), a reactive hazard classification system (e.g., based on heat of reaction or toxic gas evolution), incident history, or catastrophic potential.

   - In the compilation of process safety information, require that multiple sources of information be sufficiently consulted to understand and control potential reactive hazards. Useful sources include:

     - Literature surveys (e.g., *Bretherick's Handbook of Reactive Chemical Hazards, Sax's Dangerous Properties of Industrial Materials*).

     - Information developed from computerized tools (e.g., CHETAH [ASTM], The Chemical Reactivity Worksheet [NOAA]).

     - Chemical reactivity test data produced by employers or obtained from other sources (e.g., differential scanning calorimetry, thermogravimetric analysis, accelerating rate calorimetry).

     - Relevant incident reports from the plant, the corporation, industry, and government.

     - Chemical Abstracts Service.

- Augment the process hazard analysis (PHA) element to explicitly require an evaluation of reactive hazards. In revising this element, evaluate the need to consider relevant factors, such as:
  - Rate and quantity of heat or gas generated.
  - Maximum operating temperature to avoid decomposition.
  - Thermal stability of reactants, reaction mixtures, byproducts, waste streams, and products.
  - Effect of variables such as charging rates, catalyst addition, and possible contaminants.
  - Understanding the consequences of runaway reactions or toxic gas evolution.

2. Implement a program to define and record information on reactive incidents that OSHA investigates or requires to be investigated under OSHA regulations. Structure the collected information so that it can be used to measure progress in the prevention of reactive incidents that give rise to catastrophic releases.

U.S. Environmental Protection Agency (EPA)

1. Revise the Accidental Release Prevention Requirements, 40 CFR 68 (RMP), to explicitly cover catastrophic reactive hazards that have the potential to seriously impact the public, including those resulting from self-reactive chemicals and combinations of chemicals and process-specific conditions. Take into account the recommendations of this report to OSHA on reactive hazard coverage. Seek congressional authority if necessary to amend the regulation.

2. Modify the accident reporting requirements in RMP*Info to define and record reactive incidents. Consider adding the term "reactive incident" to the four existing "release events" in EPA's current 5-year accident reporting requirements (Gas Release,

Liquid Spill/Evaporation, Fire, and Explosion). Structure this information collection to allow EPA and its stakeholders to identify and focus resources on industry sectors that experienced the incidents; chemicals and processes involved; and impact on the public, the workforce, and the environment.

National Institute of Standards and Technology (NIST)

Develop and implement a publicly available database for reactive hazard test information. Structure the system to encourage submission of data by individual companies and academic and government institutions that perform chemical testing.

Center for Chemical Process Safety (CCPS)

1. Publish comprehensive guidance on model reactive hazard management systems. At a minimum, ensure that these guidelines cover:

   - ***For companies engaged in chemical manufacturing:*** reactive hazard management, including hazard identification, hazard evaluation, management of change, inherently safer design, and adequate procedures and training.
   - ***For companies engaged primarily in the bulk storage, handling, and use of chemicals:*** identification and prevention of reactive hazards, including the inadvertent mixing of incompatible substances.

2. Communicate the findings and recommendations of this report to your membership.

American Chemistry Council (ACC)

1. Expand the Responsible Care Process Safety Code to emphasize the need for managing reactive hazards. Ensure that:
   - Member companies are required to have programs to manage reactive hazards that address, at a minimum, hazard identification, hazard evaluation, management of change, inherently safer design, and adequate procedures and training.
   - There is a program to communicate to your membership the availability of existing tools, guidance, and initiatives to aid in identifying and evaluating reactive hazards.
2. Develop and implement a program for reporting reactive incidents that includes the sharing of relevant safety knowledge and lessons learned with your membership, the public, and government to improve safety system performance and prevent future incidents.
3. Work with NIST in developing and implementing a publicly available database for reactive hazard test information. Promote submissions of data by your membership.
4. Communicate the findings and recommendations of this report to your membership.

Synthetic Organic Chemical Manufacturers Association (SOCMA)

1. Expand the Responsible Care Process Safety Code to emphasize the need for managing reactive hazards. Ensure that:
   - Member companies are required to have programs to manage reactive hazards that address, at a minimum, hazard identification, hazard evaluation, management of change, inherently safer design, and adequate procedures and training.

- There is a program to communicate to your membership the availability of existing tools, guidance, and initiatives to aid in identifying and evaluating reactive hazards.

2. Develop and implement a program for reporting reactive incidents that includes the sharing of relevant safety knowledge and lessons learned with your membership, the public, and government to improve safety system performance and prevent future incidents.
3. Work with NIST in developing and implementing a publicly available database for reactive hazard test information. Promote submissions of data by your membership.
4. Communicate the findings and recommendations of this report to your membership.

National Association of Chemical Distributors (NACD)

1. Expand the existing Responsible Distribution Process to include reactive hazard management as an area of emphasis. At a minimum, ensure that the revisions address storage and handling, including the hazards of inadvertent mixing of incompatible chemicals.
2. Communicate the findings and recommendations of this report to your membership.

International Association of Fire Fighters (IAFF)

Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE)

The United Steelworkers of America (USWA)

Union of Needletrades, Industrial, and Textile Employees (UNITE)

United Food and Commercial Workers International Union (UFCW)

American Society of Safety Engineers (ASSE)

American Industrial Hygiene Association (AIHA)

Communicate the findings and recommendations of this report to your membership.

1.0 Introduction

Safely conducting chemical reactions is a core competency of the chemical industry.[1] However, chemical reactions can become uncontrolled, rapidly releasing large quantities of heat, energy, and gaseous byproducts. As highlighted below, uncontrolled reactions have led to serious explosions, fires, and toxic emissions.

In April 1995, an explosion and fire at Napp Technologies, in Lodi, New Jersey, killed five employees, injured several others, destroyed a majority of the facility, significantly damaged nearby businesses, and resulted in the evacuation of 300 residents from their homes and a school (USEPA-OSHA, 1997). Additionally, firefighting generated chemically contaminated water that ran off into a river. Property damage exceeded $20 million.

Two years later, an explosion and fire at Bartlo Packaging (BPS Inc.), in West Helena, Arkansas, killed three firefighters and seriously injured another. Hundreds of residents, including patients at a local hospital, were either evacuated or sheltered-in-place (USEPA-OSHA, 1999). Property damage was extensive. Major roads were closed; and Mississippi River was traffic halted for nearly 12 hours.

An incident in April 1998 at Morton International, Inc., in Paterson, New Jersey, resulted in nine injuries (see Section 1.4). Residents in a 10- by 10-block area around the plant sheltered-in-place for up to 3 hours, and an estimated 10,000 gallons of contaminated water ran off into a nearby river (USCSB, 2000). Six months later, an explosion and fire at Condea Vista, in Baltimore, Maryland, injured five and caused $14 million in damages (USCSB, 2001).

In February 1999, an explosion at Concept Sciences, Inc. (CSI), in Allentown, Pennsylvania, killed five persons, including one worker at an adjacent business (USCSB, 2002a). Fourteen persons, including six firefighters, were injured. The facility was completely destroyed, and several other businesses in the vicinity suffered significant property damage. The blast also shattered windows of homes in a nearby residential area. In June 1999, a toxic release at Whitehall Leather in Whitehall, Michigan, killed one employee (NTSB, 2000).

[1] See Appendix A, Glossary, for definition of technical terms.

Each of these incidents involved an uncontrolled chemical reaction. They vividly illustrate the tragic potential of reactive hazards and offer compelling reasons to improve reactive hazard management.

1.1 Objectives

This report . . . supports the CSB goal of increasing awareness of reactive hazards and reducing the occurrence of reactive incidents.

The U.S. Chemical Safety and Hazard Investigation Board (CSB) conducted this investigation of reactive hazard management in the United States to:

- Determine the impacts of reactive incidents.
- Examine how industry, the Occupational Safety and Health Administration (OSHA), and the U.S. Environmental Protection Agency (EPA) currently address reactive hazards.
- Determine the differences, if any, between small, medium, and large companies with regard to reactive chemical policies, practices, in-house reactivity research, testing, and process engineering.
- Analyze the appropriateness of, and consider alternatives to, industry and OSHA use of the National Fire Protection Association (NFPA) instability rating system for process safety management.
- Develop recommendations for reducing the number and severity of reactive incidents.

This report, *Improving Reactive Hazard Management,* supports the CSB goal of increasing awareness of reactive hazards and reducing the occurrence of reactive incidents.

1.2 Scope

In addressing reactive hazard management in the United States, this investigation focuses on:

- Chemical manufacturing–from raw material storage through chemical processing to product storage.
- Other industrial activities involving bulk chemicals, such as storage/ distribution, waste processing, and petroleum refining.

Industrial activities involving transportation, pipelines, laboratories, minerals extraction, mining, explosives manufacturing, pyrotechnic manufacturing, or military uses are not considered.

1.3 Investigative Process

The chemical industry evaluates the reactivity of a substance in a variety of ways. With input from key stakeholders, CSB developed the following definition of a reactive incident (synonymous with "reactive chemical incident"):

> A sudden event involving an uncontrolled chemical reaction–with significant increases in temperature, pressure, or gas evolution–that has caused, or has the potential to cause, serious harm to people, property, or the environment.[2]

Using this definition, CSB analyzed data to attempt to determine the number, impact, profile, and causes of reactive incidents.

Hazards arising from reactive chemicals are covered by a variety of legal requirements and regulations, including regulations of OSHA and EPA. CSB examined these authorities and regulations to determine how reactive hazards are currently addressed.

Through site visits and a survey of select small, medium, and large companies (Appendices B and C)–and literature reviews of industry guidance documents–CSB gathered information on the strengths and limitations of reactive hazard management practices within the chemical industry. Industry facilities with programs for managing reactive hazards were selected for the site visits.

With input from key stakeholders, CSB [defined] a reactive incident [as]: A sudden event involving an uncontrolled chemical reaction–with significant increases in temperature, pressure, or gas evolution–that has caused, or has the potential to cause, serious harm to people, property, or the environment.

[2] The use of the term "sudden" is intended to imply that reactive incidents–though they may be slow to develop because of reactive chemistry effects over an extended time–have sudden consequences.

1.4 Background

On April 8, 1998, a runaway reaction during the production of Automate Yellow 96 dye initiated a sequence of events that led to an explosion and fire at the Morton International, Inc., plant in Paterson, New Jersey. On the day of the incident, flammable materials were released as the result of an uncontrolled rapid temperature and pressure rise in a 2,000-gallon kettle in which *ortho*-nitrochlorobenzene and 2-ethylhexylamine were being reacted. Nine employees were injured in the explosion and fire, including two seriously. Potentially hazardous materials were released into the community, and the physical plant was extensively damaged.

A CSB hazard investigation examines numerous incidents to better understand the nature and causes of a generic safety problem.

The CSB Morton investigation showed that inadequate evaluation and communication of reactive hazards was one important factor in the root and contributing causes of the incident (USCSB, 2000). During the course of the investigation, stakeholders requested further investigation into reactive hazards–particularly in light of similar incidents since 1995.

Occasionally, in the course of investigating incidents, CSB is alerted to significant safety problems that are beyond the scope of any one particular incident investigation. The Morton investigation validated stakeholder concerns that reactive hazards merited a more systemic analysis. Therefore, CSB recommended in its report that a hazard investigation be conducted to study issues associated with the management of reactive hazards. A CSB hazard investigation examines numerous incidents to better understand the nature and causes of a generic safety problem.

1.5 Stakeholder Involvement

CSB sought input from various stakeholders to gain insight into differing approaches on how to improve reactive hazard management. CSB staff met with industry, regulatory agencies, professional safety organizations, trade associations, trade unions, and public advocacy groups.

The following stakeholders contributed to this investigation:

- American Chemistry Council (ACC).
- Center for Chemical Process Safety (CCPS).
- Environmental Defense.
- U.S. Environmental Protection Agency (EPA).
- International Association of Fire Fighters (IAFF).
- National Association of Chemical Distributors (NACD).
- National Fire Protection Association (NFPA).
- Occupational Safety and Health Administration (OSHA).
- Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE).
- Synthetic Organic Chemical Manufacturers Association (SOCMA).
- The Chlorine Institute, Inc.
- The United Steelworkers of America (USWA).
- Union of Needletrades, Industrial, and Textile Employees (UNITE).
- United Food and Commercial Workers International Union (UFCW).
- Working Group on Community Right-to-Know.

1.6 Public Hearing

CSB convened a public hearing on May 30, 2002, at the Paterson, New Jersey, City Hall to communicate findings and conclusions from this hazard investigation and to gather input from interested parties prior to making final recommendations and issuing a final report.

The following questions were published in the *Federal Register* and were the main focus of the public hearing:

- Is there a need to improve coverage of potentially catastrophic reactive hazards under the OSHA Process Safety Management (PSM) Standard? If so, what approaches should be pursued?
    - What criteria could be used in the context of process safety regulations to classify chemical mixtures as "highly hazardous" due to chemical reactivity?
    - Should there be a minimum regulatory requirement for reactive hazard identification and evaluation that apples to all facilities engaged in chemical manufacturing?
    - What are alternative regulatory approaches?
- For processes already covered under the OSHA PSM Standard, do the safety management requirements of the standard adequately address reactive hazards? If not, what should be added or changed?
- Does the EPA Risk Management Program (RMP) regulation provide sufficient coverage to protect the public and the environment from the hazards of reactive chemicals? If not, what should be added or changed?
- What nonregulatory actions should OSHA and EPA take to reduce the number and severity of reactive chemical incidents?

Additional issues:

- Suggested improvements to industry guidance or initiatives (e.g., Responsible Care [ACC], Responsible Distribution Process [RDP; NACD]) to reduce the number and severity of reactive chemical incidents.
- Suggested improvements for sharing reactive chemical test data, incident data, and lessons learned.
- Other nonregulatory initiatives that would help prevent reactive incidents.

CSB staff presented the investigation findings and preliminary conclusions to the Board. The public hearing agenda also included panels representing industry, labor, the State of New Jersey, and technical experts in the field of chemical process safety. In addition, the hearing included eyewitness testimony from victims of reactive incidents. Former Senator Frank Lautenberg (D-NJ) and Senator Jon Corzine (D-NJ) gave statements of support for the hazard investigation. Representatives from OSHA and EPA declined an invitation to participate.

Following the hearing, a 30-day period was opened to receive written public comments. All information gathered at the hearing and written comments were carefully considered before Board approval of the final report.

2.0 Understanding Reactive Hazards

Reactive hazards are briefly defined and characterized below. However, neither Section 2.0 nor this report in its entirety is intended to substitute for any of the more extensive guides and references on this topic or to eliminate the need for expert analysis in dealing with reactive hazards.

2.1 Definition

Process safety management of reactive hazards involves the systematic identification, evaluation, and control of hazardous chemical reactivity at all phases of the process life cycle–from research and development (R&D) to pilot plant, commercial operation, change management, and decommissioning. It encompasses many types of industrial chemical operations–from storage and handling to chemical manufacturing and waste processing.

Process safety management of reactive hazards involves the systematic identification, evaluation, and control of hazardous chemical reactivity at all phases of the process life cycle . . .

CCPS (1989) defines a "hazard" as a chemical or physical condition that has the potential to cause harm to human life, property, or the environment. A "reactive hazard" has the potential to lead to a reactive incident (see Section 1.3).

There are several types of hazardous chemical reactivity. A reactive hazard may involve:

- ***Impact-sensitive or thermally sensitive materials*** (i.e., self-reactive chemicals): When subjected to heat or impact, these chemicals may rapidly decompose, resulting in a potentially explosive release of energy.
- ***Runaway reactions*** (i.e., self-reactive chemicals or mixtures): In an out-of-control reaction involving a chemical or chemical mixture, the rate at which heat is generated exceeds the rate at which it is removed through cooling media and surroundings.
- ***Chemical incompatibility between two or more substances:*** These hazards occur when a chemical is suddenly mixed or comes into contact with another chemical, resulting in a violent reaction.

Among governmental regulations, voluntary guidelines, or trade association codes of practice, there is no standard approach to classifying hazardous chemical reactivity. A variety of methods are used to address self-reactivity (e.g., decomposition reactions and some polymerization reactions) and chemical incompatibility.

A reactive chemical may include any pure substance or mixture that has the capability to cause a reactive incident.

For the purposes of this investigation–rather than adopting any single definition of a "reactive chemical"–CSB focuses on the broadest range of practices to identify reactive hazards and to manage the risk of reactive incidents. A reactive chemical may include any pure substance or mixture that has the capability to cause a reactive incident. CSB defines a reactive incident as a sudden event involving an uncontrolled chemical reaction–with significant increases in temperature, pressure, or gas evolution–that has caused, or has the potential to cause, serious harm to people, property, or the environment.

2.2 Characterization of Reactive Hazards

A reactive hazard exists when changes in chemical structure have the potential to generate heat, energy, and gaseous byproducts beyond that which can be safely absorbed by the immediate surroundings (Bretherick, 1999). If the rate of energy release is rapid enough and not adequately controlled, the consequences may include fires, explosions, or toxic emissions.

A reactive hazard exists when changes in chemical structure have the potential to generate heat, energy, and gaseous byproducts beyond that which can be safely absorbed by the immediate surroundings.

Numerous types of chemical reactions pose potential hazards. Literature and incident data highlight the hazards of common industrial reactions, such as polymerization, decomposition, acid-base, oxidation-reduction (redox), and reactions with water. Polymerization and decomposition can be classified as "self-reactions" because they often involve just one chemical substance. However, other substances acting unexpectedly–such as catalysts or contaminants–are often required to promote even these reactions. "Chemical incompatibility" requires that two or more substances come into contact. A reactive hazard may involve further, more complicated behavior when an intended chemical reaction releases enough heat and energy to initiate a second unintended reaction, usually a chemical decomposition.

Therefore, chemical reactivity is not necessarily an intrinsic property of a single chemical substance. The severity of reactive hazards is influenced by process-specific factors, such as operating temperatures, pressures, quantities handled, chemical concentrations, impurities with catalytic effects, and compatibility with other chemicals onsite.

Section 6.0 and Appendix D discuss good practices and guidelines for reactive hazard management.

. . . chemical reactivity is not necessarily an intrinsic property of a single chemical substance. The severity of reactive hazards is influenced by process-specific factors . . .

3.0 Profile and Causes of Reactive Incidents

The purpose of the CSB data search and analysis was to better understand the impact of reactive incidents by evaluating their number, severity, and causes. Five recent reactive incidents–which illustrate the diversity of reactive hazards–are highlighted as case studies throughout Section 3.0.

3.1 Data Sources and Methods

CSB searched over 40 data sources for incidents that met its definition of a reactive incident (see Sections 1.3 and 2.1). The data search focused on recent incidents (since 1980) where the primary cause was related to chemical reactivity; however, the 1980 cutoff is not intended to diminish the important lessons learned from prior incidents. The search covered both chemical manufacturing (i.e., raw material storage, chemical processing, and product storage) and other industrial activities involving bulk chemicals, such as storage/ distribution, waste processing, and petroleum refining.[3] For purposes of this incident search, only reactive incidents that caused serious consequences[4] were examined.

Sources of incident data include a variety of public-domain databases, technical literature, and news accounts (Appendix E). Sources are categorized in Appendix E as "reviewed only" if incident data did not meet the CSB definition of "reactive incident."

[3] Incidents involving transportation, pipelines, laboratories, minerals extraction, mining, explosives manufacturing, pyrotechnic manufacturing, or military uses are beyond the scope of this investigation, in addition to events involving simple combustion (i.e., rapid reaction of fuel [liquid, vapor, or dust] with oxygen in air).

[4] Serious consequences are injuries or fatalities, significant property damage, environmental contamination, and offsite evacuation or shelter-in-place.

CASE STUDY

Napp Technologies Inc.

On April 21, 1995, a fire and explosion at Napp Technologies in Lodi, New Jersey, killed five employees and destroyed the facility (Figure 1). The plant was conducting a toll blending operation to produce a commercial gold precipitation agent. The chemicals involved were water reactive (i.e., aluminum powder, a combustible metal in the form of finely divided particles; and sodium hydrosulfite, a combustible solid).

During the process operation, water was introduced into the blender, probably as a result of a mechanical failure. Operators noticed the production of heat and the release of foul-smelling gas. During an emergency operation to offload the blender of its reacting contents, the material ignited and a deflagration occurred. The most likely cause of this incident was the inadvertent introduction of water into water-reactive materials (USEPA-OSHA, 1997).

NFPA rates aluminum powder as "1" and sodium hydrosulfite as "2" for reactivity. Therefore, these chemicals are not included on the OSHA PSM list and are not regulated under that standard. The product of the mixture of aluminum powder and sodium hydrosulfite–a gold precipitation agent–is not rated by NFPA. However, a material safety data sheet (MSDS) on the chemical from the company contracting with Napp to produce the material gave it an NFPA rating of "3."

The Napp incident raises questions regarding use of the NFPA rating system as the sole basis for regulating reactive hazards (see Section 5.1.4).

Photo not available for website.

Rich Gigli, The Bergen Record

Figure 1. Case Study: Fire and explosion, Napp Technologies Inc. cosmetics and pharmaceuticals plant, Lodi, New Jersey, April 21, 1995.

3.2 Data Limitations

The statistics provided in Section 3.3 on the number and severity of reactive incidents are grave; however, existing sources of incident data are inadequate to identify the frequency and causes of reactive incidents. The following limitations affected CSB analysis of incident data:

- No single data source provides a comprehensive collection of chemical incidents from which to retrieve or track reactive incident data.
- Incident data collected by OSHA and EPA provide no functional capability to track the occurrence of reactive incidents with serious worker or public impacts;[5] such data are a valuable resource for analyzing incident trends and developing prevention actions at a national level.
- No one comprehensive data source contains the data needed to adequately understand root causes and lessons learned from reactive incidents or other process safety incidents.[6] Table 1 lists the limitations of some public databases.
- It is difficult to identify causes and lessons learned in existing sources of process safety incident data because industry associations, government agencies, and academia generally do not collect this information.
- Data sources contained incomplete and sometimes inaccurate incident information–for example, on number of injuries and community impacts. Descriptions of incidents and causal information were sometimes vague and incomplete.
- There are limited Federal or state requirements to report incidents unless they involve specific consequences.

No single data source provides a comprehensive collection of chemical incidents from which to retrieve or track reactive incident data.

Incident data collected by OSHA and EPA provide no functional capability to track the occurrence of reactive incidents with serious worker or public impacts . . .

There are limited Federal or state requirements to report incidents unless they involve specific consequences.

[5] Research indicates that the OSHA Integrated Management Information System (IMIS) identified 70 percent of the reactive incidents reported in Section 3.3, but none were tracked as "reactive incidents." Only 25 percent of the reactive incidents that occurred from June 1994 through June 1999 were reported to EPA. These reports are contained in the RMP 5-year accident histories sent to EPA prior to the June 1999 deadline for initial submissions.

[6] Only one publicly available database is designed to provide such information. The Accident Database from the Institution of Chemical Engineers (IChemE) contains lessons learned for 25 percent of 12,000 incidents.

Table 1
Limitations of Common Public Databases

Data Source (a)	Description	Years Searched	Strengths	Limitations
USCG NRC	Data on release notifications of oil and hazardous substance reports to NRC or EPA	1982-Present	Extensive range of incidents, including those resulting in a chemical release from a reactive incident Include all states and localities	Knowledge of incident limited at time of notification, leading to possible inaccuracies No requirement to follow up on reports to improve data quality Relies on company compliance to notify (or third party) Notification requirement is driven by release of specified chemical above reportable quantity **Not designed to be a lessons-learned database**
OSHA IMIS	Records of workplace inspections, including those prompted by accidents where a worker is injured	1984-Present	Information from OSHA field inspections More accurate description of impacts on employees and contractors Keyword indexing allows for easy search and retrieval	Not comprehensive, limited to incidents selected by OSHA Inspections without abstracts cannot be keyword searched; causal information unavailable Designed to assist compliance enforcement, not to report on incident causes Limited information from "State-Plan" states **Not designed to be a lessons-learned database**
EPA RMP*Info	Data about chemical releases resulting in specific impacts covered under RMP regulation	1994-Present	Information about major events involving specific listed chemicals More accurate data on impacts, causal factors, and corrective actions Includes all states and localities	Not comprehensive, limited to events resulting in major harm for a select group of chemicals None of selected chemicals were listed due to reactivity No requirements to include extensive description of incidents, including causes and lessons learned Checklist approach limits respondent's choices (no indicator for incidents resulting from reactive hazards) **Not designed to be a lessons-learned database**

Table 1 (cont'd)

Data Source (a)	Description	Years Searched	Strengths	Limitations
EPA ARIP	Responses to questionnaires from facilities that have had significant releases; purpose is to learn about causes and consequences of hazardous material incidents	1986-Present	Supplements NRC reports for more significant events Additional information on causal factors, consequences, and company safety programs Data are easily analyzed for common causes Includes all states and localities	Survey relies on voluntary compliance Not comprehensive; limited to select cases Checklist approach limits value of information to understand root cause **Not designed to be a lessons-learned database**
IChemE Accident Database	Reports about chemical incidents around the world from official government sources, news media, and company reports	1980-Present	Scope is beyond incidents reported to or investigated by regulatory agencies or first responders Contains lessons learned from 3,000 incidents	Only one-fourth of the 12,000 incidents contain lessons-learned information
HSE MHIDAS	Information from public domain sources worldwide, nearly 7,000 incidents	1985-Present	Scope is beyond incidents reported to or investigated by regulatory agencies or first responders Includes domestic and international incidents	No extensive description of incidents, including causes and lessons learned
USFA NFRIS	Response data submitted by local fire departments	1980-Present	Includes fire and explosion incidents with no/little release, incidents resulting in property damage only, and near-misses if fire department was called	Limited state participation Represents limited information available to fire department at time of response Checklist approach limits respondent choices **Not designed to be a lessons-learned database**
CSB CIRC	Initial reports about chemical incidents worldwide from official government sources, news media, and eyewitnesses	1998-Present	Scope is beyond incidents reported to or investigated by regulatory agencies or first responders Includes domestic and international incidents	Not comprehensive, only select incidents included Limited time span Frequent reliance on media accounts limits the depth of initial reports **Not designed to be a lessons-learned database**

(a) ARIP=Accidental Release Information Program; CIRC=Chemical Incident Reports Center; HSE=Health and Safety Executive, United Kingdom; IChemE=Institution of Chemical Engineers; IMIS=Integrated Management Information System; MHIDAS=Major Hazard Incident Data Service; NFIRS=National Fire Incident Reporting System; NRC=National Response Center; RMP=Risk Management Program; USCG=U.S. Coast Guard; USFA=U.S. Fire Administration.

CASE STUDY

Bartlo Packaging Inc.

This incident occurred on May 8, 1997 (Figure 2). BPS–a bulk storage and distribution facility in West Helena, Arkansas–was repackaging an organic pesticide, AZM50W. As the substance was being offloaded into a warehouse, employees noticed smoke coming from the building. City emergency response personnel were notified.

A team of four West Helena firefighters was attempting to locate the source of the smoke when an explosion occurred. A collapsing cinderblock wall killed three of the firefighters, and one was injured.

The most likely causes of the incident were the decomposition of bulk sacks of the pesticide, which had been placed too close to a hot compressor discharge pipe, and the release of flammable vapors (USEPA-OSHA, 1999).

This case history illustrates that severe reactive incidents can occur even at companies engaged in the simple storage and handling of chemicals. The facility was not covered by OSHA PSM, and AZM50W does not have an NFPA rating.

Photo not available for website.

Rick McFarland, Arkansas Democrat-Gazette

Figure 2. Case Study: Fire and explosion, BPS Inc. chemical storage facility, West Helena, Arkansas, May 8, 1997; agricultural chemicals.

The results of the CSB incident data analysis are acknowledged as representing only a sampling of recent reactive incident data. This limitation precludes CSB from drawing statistical conclusions on incidence rates or inferring trends in the number or severity of incidents. However, despite these limitations, the data can be used to illustrate the profile and causes of reactive incidents.

3.3 Assessment of Reactive Incidents

Reactive incidents can severely affect workers and the public, as well as cause major economic losses and environmental damage. The limited data available to CSB includes 167 incidents over nearly 22 years, as summarized in Figure 3.

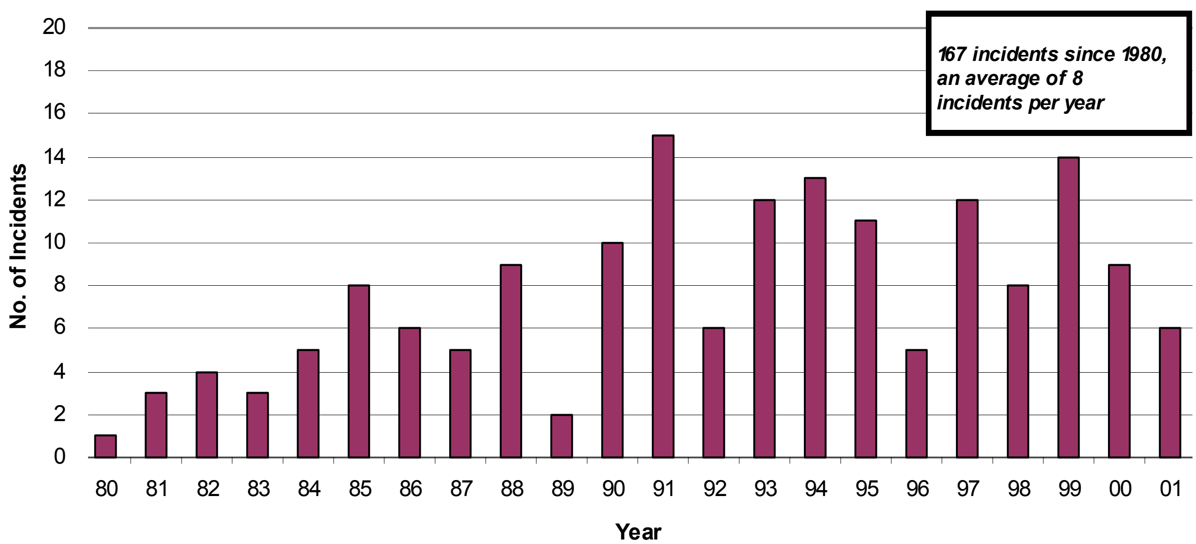

Figure 3. Total incidents by year, 1980–2001.

3.3.1 Injuries and Fatalities

Of the 167 reactive incidents, 48 caused a total of 108 fatalities. Since 1980, CSB data show an average of six injury-related incidents per year, resulting in an average of five fatalities per year. Table 2 provides data on 12 incidents with three or more fatalities (see also Figures 4 and 5). Appendix F presents a 5-year summary of U.S. Bureau of Labor Statistics data on occupational fatalities.

Table 2
Incidents With Three or More Fatalities

Location	Date	Fatalities
ARCO Chemical, Channelview, TX (a)	07/05/90	17
Albright and Wilson, Charleston, SC	06/17/91	9
IMC Fertilizer/Angus Chemical, Sterlington, LA	05/01/91	8
NAPP Technologies, Lodi, NJ	04/21/95	5
Concept Sciences, Hanover Township, PA	02/19/99	5
Terra Industries, Port Neal, IA	12/13/94	4
Bastian Plating, Auburn, IN	06/28/88	4
Plastifax, Gulfport, MS	06/02/82	3
Merck, Barceloneta, Puerto Rico	06/12/86	3
Shell Chemical, Belpre, OH	05/27/94	3
BPS Inc., West Helena, AR	05/08/97	3
BP Amoco, Augusta, GA	03/13/01	3

(a) Although this incident involved combustion, an *uncontrolled peroxide decomposition reaction* created an oxygen-enriched atmosphere in a tank containing flammable liquids. This incident does not meet the “simple combustion” exclusion in the CSB reactive incident definition because it involved combustion in an oxygen-enriched atmosphere rather than oxygen in air.

Photo not available for website.

Jeff Bundy, Omaha World-Herald

Figure 4. Explosion, Terra Industries farm fertilizer plant, Port Neal, Iowa, December 13, 1994; Midwest Power generating station to the south.

Photo not available for website.

Matt Detrick, The Columbus Dispatch

Figure 5. Fire and explosion, Shell Chemical Company plastics plant and chemical storage tank area, Belpre, Ohio, May 27, 1994; styrene and diesel fuel.

3.3.2 Consequences

In addition to causing injuries and fatalities to plant personnel and the public, reactive incidents can also result in environmental harm and equipment damage. These impacts may be due to fires, explosions, hazardous liquid spills, toxic gas releases, or any combination of such (Figure 6). Fires and explosions are the most frequent occurrence in CSB data, followed by toxic gas releases.

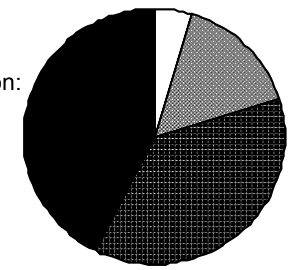

Figure 6. Categorization of consequences of incidents.

3.3.3 Property Damage

At least a dozen incidents in the CSB data resulted in property damage alone exceeding $10 million, with three cases in which loss exceeded $100 million (Figure 7).[7] These numbers do not include further financial losses due to business interruption or lost market share.

3.3.4 Public Impact

Reactive incidents primarily cause onsite impacts, such as worker fatalities and injuries–and severe business impacts, including lost production and property damage. However, a significant number of incidents have led to public impacts,[8] which include public harm (injury or fatality), offsite evacuation, or shelter-in-place.

Nearly 50 of the 167 incidents in the CSB data affected the public. At least eight of the 12 reactive incidents listed in Table 2 had public impacts. One of these incidents (CSI) resulted in a public fatality.

[7] Property loss figures are quoted for the year in which they were incurred. The numbers in Figure 7 are not scaled to represent constant dollar valuation of loss.

[8] The definition of public impact is based on the criteria for reporting offsite incidents in the EPA RMP regulation (40 CFR 68). "Public" includes anyone except employees or contractors at the facility.

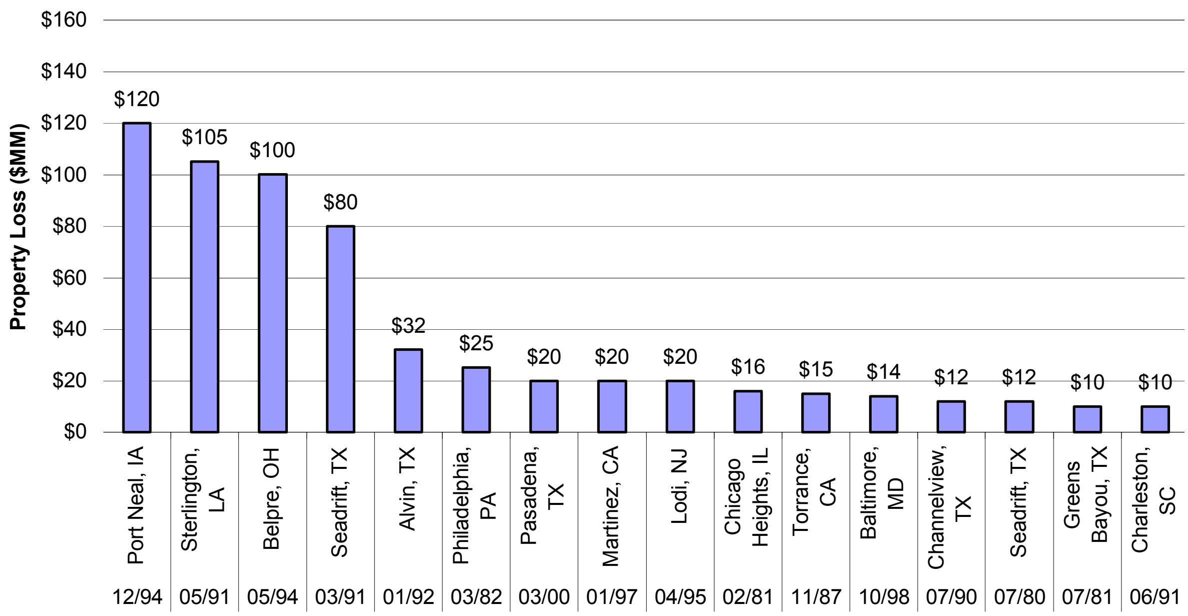

Figure 7. Incidents resulting in large property losses.

3.4 Profile of Affected Industries

Analysis of CSB data shows that reactive incidents are not unique to the chemical manufacturing industry (Figure 8). Although about 70 percent of the 167 incidents occurred in the chemical manufacturing industry, the remaining 30 percent occurred in other industries that use bulk quantities of chemicals–such as waste processing and petroleum refining.

The BPS incident (see case study) is an example of a severe reactive incident at a nonchemical manufacturing site. The fire and explosion at Chief Supply Corporation also occurred at a nonchemical manufacturing facility (Figure 9).

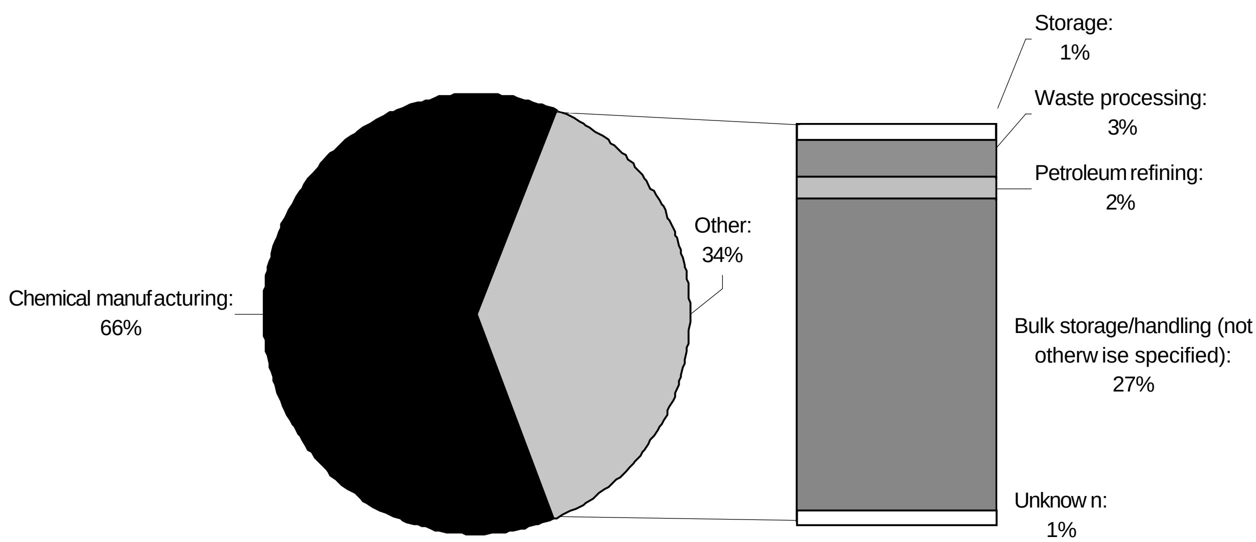

Figure 8. Industry profile, 1980-2001.

Photo not available
for website.

Steve Pingry, Tulsa World

Figure 9. Fire and explosion, Chief Supply Corporation, Stone Bluff, Oklahoma, March 26, 1997; hazardous waste storage of petroleum-based products.

CASE STUDY

Whitehall Leather Company

On June 4, 1999, the inadvertent mixing of two incompatible chemicals caused a toxic gas release at Whitehall Leather Company in Whitehall, Michigan (Figure 10). One person was killed, and another was injured.

A truck driver arrived at the facility to deliver a load of sodium hydrosulfide solution. The delivery took place on the night shift. During prior deliveries on this shift, the shift supervisor had received only “pickle acid.” (The material commonly known onsite as pickle acid was actually ferrous sulfate.) He assumed that the sodium hydrosulfide was pickle acid and directed the truck driver to unload at the facility’s pickle acid tank.

Hydrogen sulfide gas was produced when the sodium hydrosulfide solution was unloaded into the ferrous sulfate tank. The truck driver was exposed to the gas and died; one Whitehall Leather employee was injured (NTSB, 2000).

The Whitehall Leather case demonstrates that reactive hazards other than thermal runaways in reactors–such as inadvertent mixing of incompatible materials–can cause severe reactive incidents. Neither ferrous sulfate nor sodium hydrosulfide is rated by NFPA, and neither compound is an OSHA PSM-listed chemical.

Figure 10. Case Study: Muskegon County Hazardous Materials Response team, chemical reaction during cargo transfer, Whitehall Leather Company plant, Whitehall, Michigan, June 4, 1999; sodium hydrosulfide and ferrous sulfate solutions.

Photo not available for website.

Lisa Medendorp, The Muskegon Chronicle

3.5 Profile of Reactive Incidents

3.5.1 Chemical Classes

The CSB data analysis shows that reactive incidents are not limited to any one chemical nor to a few classes of chemicals. Table 3 lists common chemical classes involved in the 167 incidents. None of these classes represent a majority of incidents in the CSB data.

The CSB data analysis shows that reactive incidents are not limited to any one chemical nor to a few classes of chemicals.

Table 3
Classes of Chemicals Involved in Reactive Incidents

Chemical Class	No. of Incidents (a)
Acid	38
Oxidizer	20
Monomer	15
Water	14
Base	12
Organic peroxide	12
Hypochlorite	10
Alcohol	8
Hydrocarbon	7
Inorganic/metal	6
Hydrosulfite	6
Other	79

(a) Some incidents involved more than one class of chemicals.

Over 90 percent of the 167 incidents analyzed by CSB involved reactive hazards that are documented in literature available to the chemical processing industry.

3.5.2 Type of Reactions

A range of chemical reactions can cause reactive incidents. Over 90 percent of the 167 incidents analyzed by CSB involved reactive hazards that are documented in literature available to the chemical processing industry (see Section 6.1). The various types of reactions indicate the diversity of chemistry involved. For example, an explosion at a Georgia-Pacific resin factory–involving formaldehyde, phenol, and sulfuric acid–was caused by an exothermic runaway reaction (Figure 11). The BP Amoco incident described in the fifth case study, which appears at the end of Section 3.0, was caused by a slow endothermic reaction that released gases.

Photo not available for website.

Mike Munden, AP Photo/The Columbus Dispatch

Figure 11. Explosion, Georgia-Pacific resin factory, Columbus, Ohio, September 10, 1997; production of formaldehyde and resin bonding agents.

Nearly 75 percent of the incidents from the CSB data were caused by one of the following types of reactions:

- Decomposition (26 percent).
- Acid/base (11 percent).
- Water reactive (10 percent).
- Polymerization (10 percent).
- Oxidation (6 percent).
- Decomposition initiated by another reaction (5 percent).
- Oxidation-reduction (4 percent).
- Chlorination, catalytic cracking, halogenation, hydrolysis, and nitration (each 1 percent).

Information was insufficient to determine type of reaction for the remaining 23 percent of incidents.

3.5.3 Type of Equipment

A reactive incident can occur in most equipment used to store, handle, manufacture, and transport chemicals. The CSB data show that incidents occur in a variety of chemical processing and storage equipment–including reactors, storage tanks, and bulk storage drums (Figure 12). Twenty-five percent of the incidents involved reactor vessels; 22 percent, storage equipment (e.g., tanks, rail cars, and designated storage areas); 22 percent, other process equipment (e.g., holding tanks, mixers, and dryers); 13 percent, waste, separation, and transfer equipment; and 10 percent, bulk storage drums. No particular equipment accounted for 8 percent of the data.

A reactive incident can occur in most equipment used to store, handle, manufacture, and transport chemicals.

These data contradict the common perception that a majority of reactive incidents involve chemical reactor vessels. Chemical processing and storage equipment (excluding reactors) and bulk storage drums account for over 65 percent of the equipment involved in reactive incidents. The case histories highlighted throughout Section 3.0 are examples of reactive incidents that did not occur in reaction vessels.

The case histories highlighted throughout Section 3.0 are examples of reactive incidents that did not occur in reaction vessels.

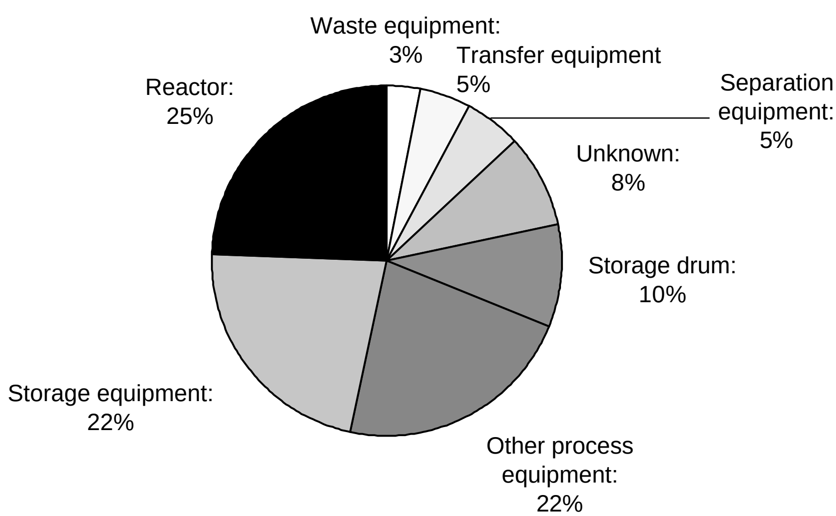

Figure 12. Equipment involved in incidents, 1980-2001.

CASE STUDY

Concept Sciences, Inc.

An explosion during the distillation of a solution of aqueous hydroxylamine (HA) and potassium sulfate killed four CSI employees and an employee of an adjacent business on February 19, 1999 (Figure 13; USCSB, 2002a). Fourteen people were injured. The CSI facility, in Hanover Township, Pennsylvania, was destroyed. Several buildings in the industrial park were damaged, and windows were broken in nearby residences.

On the day of the incident, CSI was in the process of producing its first full-scale batch of 50 wt-percent HA. After the distillation process was shut down, the HA contained in one of the process tanks explosively decomposed. The last recorded concentration of the HA solution in the tank was 86 wt-percent. HA has been shown to explosively decompose at high concentrations (i.e., 85 wt-percent; Koseki and Iwata, 2001).

The CSB investigation determined that CSI did not adequately evaluate the hazards of HA during process development. The explosive decomposition hazard of HA was not adequately translated into CSI's process design, operating procedures, mitigation measures, or precautionary instructions for operators.

This incident demonstrates the need for effective reactive hazard management throughout the many phases of the process life cycle–including development, design, construction, and startup. Furthermore, the offsite fatality dramatically illustrates that reactive incidents can affect the public. HA is not a listed chemical under the EPA RMP regulation. It is an OSHA PSM-listed chemical and has an NFPA rating of "3."

Photo not available for website.

Tom Volk, The Morning Call

Figure 13. Case Study: Explosion, Concept Sciences, Inc., February 19, 1999; hydroxylamine manufacturing.

3.6 Common Reactive Hazards and Causal Information

Identifying common types of associated hazards and causes is an essential element of understanding the reactive incident problem.

CSB data analysis identified three common types of reactive hazards:
- ***Chemical incompatibility***
- ***Runaway reaction***
- ***Impact or thermally sensitive materials.***

3.6.1 Reactive Hazards

A common perception is that reactive incidents are primarily the result of runaway reactions. In fact, analysis of data from the 167 incidents suggests that other types of reactive hazards should also be of concern. CSB data analysis identified three common types of reactive hazards (see Appendix A for definitions):

- Chemical incompatibility
- Runaway reaction
- Impact or thermally sensitive materials.

Of the 167 incidents, 36 percent are attributed to chemical incompatibility, 35 percent to runaway reactions, and 10 percent to impact or thermally sensitive materials. The hazard is unknown for 19 percent of the incidents.

. . . more than 60 percent of reactive incidents for which some causal information was available involved inadequate management systems for identifying or evaluating hazards.

3.6.2 Causal Information

Causal[9] data are reported for only 37 of the 167 incidents. Analysis of this limited set of data revealed that more than 60 percent of reactive incidents for which some causal information was available involved inadequate management systems for identifying or evaluating hazards (Table 4). In the CSI incident, even though the reactive hazard was known, an inadequate hazard evaluation was performed. Nearly 50 percent of the causal data also point to inadequate procedures for the safe storage, handling, or processing of chemicals (e.g., Whitehall Leather and BPS).

[9] The term "cause" within this section refers to inadequate process safety management practices. The causal information presented is not intended to be considered as root causes; no consistent root cause analysis methods were identified within the data.

Table 4
Analysis of Causal Information (a)

Causes	**No. of Incidents** (b)
Inadequate hazard identification	9
Inadequate hazard evaluation	16
Inadequate procedures for storage/handling of reactive chemicals	17
Inadequate training for storage/handling of reactive chemicals	10
Inadequate management of change (MOC) system to identify/evaluate reactivity hazards	6
Inadequate process design for reactive hazards	6
Inadequate design to prevent human error	9
Inadequate company-wide communication of hazards	5
Inadequate emergency relief system design	3
Inadequate safe operating limits	3
Inadequate near miss/incident investigation	2
Inadequate inspection/maintenance/monitoring of safety critical devices in reactive chemical service	2
Previously unknown reactive hazards	1

(a) Causal data are reported for 37 of the 167 incidents.

(b) Total greater than 37 because each incident may have more than one cause.

CASE STUDY

BP Amoco Polymers, Inc.

On March 13, 2001, three persons were killed as the result of a vessel failure and fire at the BP Amoco Polymers plant in Augusta, Georgia (USCSB, 2002b). The facility produces plastics.

Startup operations in a process to produce Amodel–a nylon-family polymer–were suspended due to problems with equipment in a finishing line. During the aborted startup attempt, polymer was discarded into the polymer catch tank, a waste collection vessel (Figure 14). Cooling effects created a layer of hardened plastic 3 to 5 inches thick along the entire inner wall of the vessel, blocking all normal and emergency vents.

However, the material in the core of the vessel remained hot and molten. It continued to react and decompose, generating gas that could not escape. Over several hours, the catch tank became pressurized. The failure occurred as workers attempted to open a cover on the vessel.

The CSB investigation determined that BP Amoco was unaware of the hazardous reaction chemistry of the polymer because of inadequate hazard identification during process development. This lack of awareness is a commonly cited cause of reactive incidents within the CSB data. The BP Amoco incident also involved an endothermic (or heat consuming) reaction rather than the more commonly recognized exothermic (or heat producing) runaway chemical reaction.

Figure 14. Case Study: Thermal decomposition, BP Amoco Polymers, Inc., March 13, 2001.

4.0 NFPA Hazard Rating System

CSB analyzed incident data in terms of the chemicals published in NFPA Standards 49 and 325 (1994; 2001a). The data show that only about 10 percent of the 167 known incidents involved chemicals that are rated NFPA "3" or "4"; "not rated" or "0" accounts for nearly 60 percent of the data (Figure 15). (Both the BPS and the Morton incidents involved chemicals that were not rated by NFPA.)

The OSHA PSM Standard lists 137 highly hazardous chemicals–only 38 of which are considered to be highly reactive based on NFPA ratings "3" or "4"[10] (as defined in NFPA Standard 704 [2001b]).

Public and labor union concerns as the result of a number of reactive incidents have caused OSHA to consider PSM revisions. One alternative OSHA identified through a petition from unions

The OSHA PSM Standard lists 137 highly hazardous chemicals–only 38 of which are considered to be highly reactive based on NFPA ratings "3" or "4" . . .

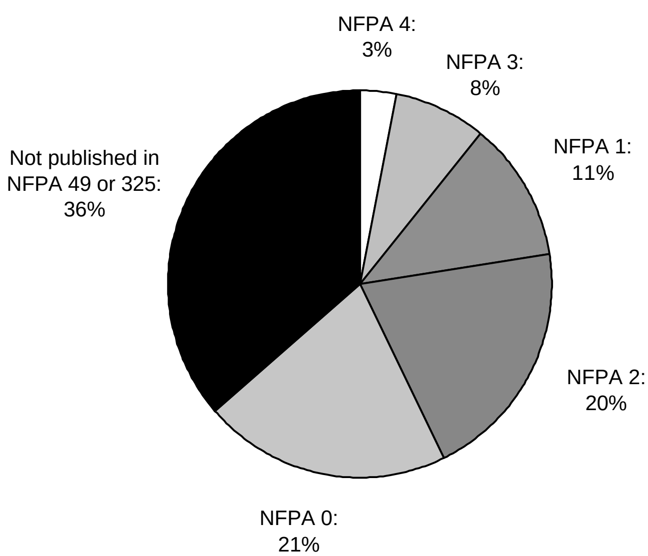

Figure 15. NFPA instability rating analysis (formerly reactivity rating) of incident data, 1980–2001.

[10] The PSM chemical list is based on ratings in the 1975 edition of NFPA 49. Six of the 137 PSM chemicals are listed twice. An NFPA instability rating of "4" means that materials in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures (13 of 131 PSM-listed chemicals have an NFPA "4" reactivity). A rating of "3" means that materials in themselves are capable of detonation or explosive decomposition or explosive reaction, but require a strong initiating source or must be heated under confinement before initiation (25 of 131 PSM-listed chemicals have an NFPA "3" reactivity).

The instability rating . . . was not intended to be used to measure reactivity, but rather to measure the "inherent" instability of a pure substance or product under conditions expected for product storage.

(Section 5.1.3) is to add the remaining NFPA "3" and "4" chemicals and all NFPA "1" and "2" chemicals to the PSM list. However, this approach addresses less than half of the chemicals involved in the 167 incidents examined by CSB.

NFPA developed Standard 704 as a tool for identification and evaluation of potential hazards during emergency response, not for application to chemical process safety. The instability rating is a part of this standard. It was not intended to be used to measure reactivity, but rather to measure the "inherent" instability of a pure substance or product under conditions expected for product storage. The instability rating does not measure the tendency of a substance or compound to react with other substances or any other process-specific factors, such as operating temperature, pressure, quantity handled, chemical concentration, impurities with catalytic effects, and compatibility with other chemicals onsite.

NFPA 704 is a voluntary standard. Table 5 lists the five degrees of hazard defined in NFPA 704. This hazard rating system primarily relies on qualitative criteria and judgment to assign chemical instability ratings, which may vary considerably from company-to-company. The instability rating system was so named in 1996 to clarify its intent; it was formerly known as the reactivity rating system. NFPA 49 lists the ratings for 325 chemicals–representing only a very small percentage of the chemicals used in industry.[11]

The more recent editions of NFPA 704 provide some objective criteria (Table 5) for assignment of ratings. The degree of instability hazard is ranked based on "ease, rate, and quantity of energy release" of the substance (NFPA, 2001b). Onset temperature, instantaneous power density (IPD; Hofelich et al., 1997),[12] and–in the case of water-reactive substances–the energy of reaction upon mixing are the parameters considered. Onset temperature was added in the 1990 edition of the standard, and the latter two criteria were added in 1996. These criteria are not intended to replace the primarily

[11] The Chemical Abstracts Service maintains data on over 200,000 chemicals that are listed under national and international regulations.

[12] IPD is calculated as the mathematical product of the energy of decomposition/reaction and the initial rate of reaction, determined at 482 degrees Fahrenheit (°F; 250 degrees Celsius [°C]).

Table 5
NFPA-Defined Degrees of Instability Hazard

NFPA Instability No.	Stability Criteria	Typically Includes	Water Reactivity Criteria (a)	Instantaneous Power Density Criteria (b)
4	Materials that in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures	Materials that are sensitive to localized thermal or mechanical shock at normal temperatures and pressures	Not applicable	Greater than 1,000 W/mL
3	Materials that in themselves are capable of detonation or explosive decomposition or explosive reaction, but require a strong initiating source or must be heated under confinement before initiation	Materials that are sensitive to thermal or mechanical shock at elevated temperatures and pressures	Materials that react explosively with water without heat or confinement; heat of mixing greater than 600 cal/g	Less than 1,000 but greater than 100 W/mL
2	Materials that readily undergo violent chemical change at elevated temperatures and pressures	Materials that exhibit an exotherm at temperatures less than 200^{o}C and materials that polymerize vigorously and evolve heat	Materials that react violently with water or form potentially explosive mixtures with water; heat of mixing less than 600 but greater than 100 cal/g	Less than 100 but greater than 10 W/mL
1	Materials that in themselves are normally stable, but can become unstable at elevated temperatures and pressures	Materials that exhibit an exotherm at temperatures greater than 200^{o}C but less than 500^{o}C	Materials that react vigorously with water, but not violently; heat of mixing less than 100 but greater than 30 cal/g	Less than 10 but greater than 0.01 W/mL
0	Materials that in themselves are normally stable, even under fire conditions	Materials that exhibit an exotherm at temperatures greater than 500^{o}C when tested by differential scanning calorimetry (DSC)	Materials that do not react with water; heat of mixing less than 30 cal/g	Less than 0.01 W/mL

Source: NFPA 704 (2001b).

(a) cal/g = calories per gram
(b) WmL = watts per milliliter

qualitative nature of the rating system, but to be used as a hazard recognition aid. Where data are available, NFPA currently prefers ratings based on IPD.

NFPA 49 is no longer issued in the NFPA Fire Code set, and the standard is no longer updated;[13] however, Standard 704 was updated in 2001. NFPA 49 information is available in the *Fire Protection Guide to Hazardous Materials* (NFPA, 2001a).

. . . the rating system is insufficient for use as the sole basis of determining reactivity for regulatory lists because it considers only one facet of chemical reactivity.

NFPA confirmed the intent of NFPA 704 and the instability rating system through correspondence with CSB staff. The committee clarified that the rating system is insufficient for use as the sole basis of determining reactivity for regulatory lists because it considers only one facet of chemical reactivity. NFPA staff reiterated this position in testimony given at the CSB public hearing on reactive chemical safety on May 30, 2002.

[13] Revision of NFPA 49 was withdrawn as a committee project in 1998.

5.0 Regulatory Analysis

5.1 OSHA

5.1.1 Overview

CSB found significant gaps in process safety regulations designed to protect workers from highly hazardous chemicals, including reactive hazards. OSHA standards cover the hazards of some classes of substances, such as flammable and combustible liquids; however, no OSHA standard specifically addresses reactive hazards.

OSHA standards cover the hazards of some classes of substances, such as flammable and combustible liquids; however, no OSHA standard specifically addresses reactive hazards.

Two OSHA standards are designed to protect employees from acute chemical hazards resulting from reactive incidents–including fires, explosions, and toxic releases.

- The Hazard Communication Standard (29 CFR 1910.1200) requires chemical manufacturers to evaluate chemicals produced or handled in their workplace and to communicate the associated hazards via labels and MSDSs. The standard also requires all employers to provide information to employees about the hazardous chemicals to which they could be exposed.
- The PSM Standard (29 CFR 1910.119) requires employers to prevent or minimize the consequences of catastrophic releases of highly hazardous chemicals, including highly reactive chemicals.

Numerous other OSHA regulations apply to the chemical industry in general, but are not specific to reactive hazards. Where no specific OSHA standards apply, the General Duty Clause (GDC; Section 5[a][1] of the 1970 Occupational Safety and Health Act) creates a legal obligation for an employer to address a known hazard, including a reactive hazard.

5.1.2 Process Safety Management

The CSB incident data were analyzed to determine whether the chemicals involved were considered "highly hazardous" under the OSHA PSM Standard. For the purposes of analyzing the data, CSB determined if a chemical was covered by the PSM Standard by identifying whether it was listed in PSM or was covered as a flammable chemical by OSHA definition.[14]

All 167 incidents were included in the analysis, even if the incident predated the promulgation of PSM:

- For 30 percent of the incidents, the chemicals were covered under PSM.
- For 50 percent of the incidents, the chemicals were not PSM covered.

It could not be determined whether PSM-covered chemicals were involved in the remaining 20 percent of incidents.

CSB was unable to determine from the incident data if a process was PSM covered.[15]

5.1.2.1 Development of PSM Standard

Following a series of very serious chemical accidents in the 1980s, OSHA began to develop the PSM Standard. The proposed standard was published in 1990, the same year that Congress enacted the Clean Air Act Amendments (CAAA).

Section 304 of CAAA required OSHA to promulgate a chemical process safety standard to protect employees from hazards associated with accidental releases of highly hazardous chemicals in the workplace. It further required that OSHA develop and apply the standard to a list of highly hazardous chemicals. Congress specified that highly hazardous chemicals included "toxic, flammable, highly reactive, and explosive substances."

OSHA relied on several established lists–including those from the New Jersey Toxic Catastrophe Prevention Act (TCPA), the Delaware Extremely Hazardous Substances Risk Management Act, the

[14] Processes covered by the OSHA PSM Standard due to the presence of flammable substances may, in fact, have significant reactive hazards as well. An example is a polymerization reaction involving the flammable chemical 1,3-butadiene. Such processes are required to address all chemical hazards, including reactive hazards.

[15] The CSB analysis is limited by incomplete knowledge of chemical concentrations, quantities, or other covered chemicals in the same process–all of which are relevant in determining whether a process is regulated under the PSM Standard.

European Community Seveso Directive (82/501/EEC), and NFPA Hazardous Chemicals Data (NFPA 49)–to develop its list of highly hazardous chemicals. OSHA chose to list the chemicals classified as reactive category "3" or "4" in NFPA 49 (1975 edition).

The PSM Standard lists 131 distinct chemicals with toxic or reactive properties.[16] It includes 25 chemicals with an NFPA rating of "3" and 13 chemicals with an NFPA rating of "4." The PSM Standard applies to processes that involve listed chemicals at or above threshold quantities and to processes with flammable liquids or gases onsite in one location, in quantities of 10,000 pounds or more. Companies that manufacture explosives and pyrotechnics are also required to comply with the standard.

. . . the PSM Standard has significant gaps in coverage of reactive hazards because it is based on a limited list of individual chemicals with inherently reactive properties.

The OSHA list has not been updated since the promulgation of PSM in 1992. It does not reflect changes in the list of chemicals and their ratings made by NFPA in 1991 and 1994.

It is evident that the PSM Standard has significant gaps in coverage of reactive hazards because it is based on a limited list of individual chemicals with inherently reactive properties.

5.1.2.2 Process Safety Information and Process Hazard Analysis

The OSHA PSM Standard is a performance-oriented standard that requires the employer to prevent catastrophic releases from covered processes by executing a 14-element safety program. All processes with highly hazardous chemicals are required to have a management system that addresses each element of the standard.

Two commonly cited causes of reactive incidents . . . are inadequate understanding of reactive chemistry or inadequate hazard evaluation.

As supported by the CSB incident data, two elements are particularly relevant to reactive hazards–Process Safety Information (PSI; 29 CFR 1910.119 [d]) and Process Hazard Analysis (PHA; 29 CFR 1910.119 [e]). Two commonly cited causes of reactive incidents, as shown by the data, are inadequate understanding of reactive chemistry or inadequate hazard evaluation (Section 3.0; Table 4).

[16] Six of the 137 chemicals on the PSM list are not distinct (i.e., are listed under a synonym).

The PSM Standard requires that the following information be contained within the PSI element–physical data, reactivity data, corrosivity data, thermal and chemical stability data, and hazardous effects of potential inadvertent mixing of different materials. The standard does not specifically define what is to be included in any of these data categories, the level of detail required, or the method of compilation.[17] It does, however, stipulate that an MSDS can be used to compile the data to the extent that it contains the information required. In a Hazard Information Bulletin, OSHA cautioned that MSDSs do not always contain information about hazards from mixing or blending chemicals (OSHA, 1996).

Under the PHA element, the PSM Standard requires that the employer conduct process hazard analysis, which OSHA defines as "an organized and systematic effort to identify and analyze the significance of potential hazards associated with the processing or handling of highly hazardous chemicals." The analysis must identify the hazards of the process and necessary safeguards; however, the standard does not explicitly define requirements for addressing reactive hazards.

5.1.3 General Duty Clause

The OSHA GDC states:

> Each employer shall furnish to each of his [sic] employees employment and a place of employment which are free from recognized hazards that are causing or are likely to cause death or serious physical harm to his [sic] employees.

In the event that there is no OSHA standard to address a hazard, OSHA may use the GDC to enforce a legally binding requirement on an employer or to impose a fine.

[17] Incident data in Section 3.0 illustrate that reactive hazards are broader than the hazardous effects of potential inadvertent mixing of different materials.

To substantiate a GDC violation, several criteria must be met,[18] including:

- A condition or activity in the employer's workplace presents a hazard to employees.
- The cited employee or the employer's industry recognizes the hazard.
- The hazard is likely to cause death or serious physical harm.
- There is a feasible means of eliminating or materially reducing the hazard.

. . . no industry consensus standard has been identified for the management of reactive hazards in support of a GDC citation.

Among other forms of evidence, employer or industry recognition of a hazard may be demonstrated by a consensus standard (NFPA, American National Standards Institute [ANSI], American Petroleum Institute [API], American Society for Testing and Materials [ASTM], etc.). Industry standards may also be used to identify feasible means of reducing the hazard. However, no industry consensus standard has been identified for the management of reactive hazards in support of a GDC citation.[19]

5.1.4 Other PSM Initiatives

As a result of the joint EPA-OSHA chemical accident investigation of the Napp Technologies incident in April 1995, a recommendation was made by both agencies to consider adding more reactive chemicals to their respective lists of chemicals covered by process safety regulations (USEPA-OSHA, 1997). To date, however, neither EPA nor OSHA has modified process safety regulations to better cover reactive hazards.

[18] OSHA response to CSB interrogatory for the reactive chemical hazard investigation, June 6, 2001.

[19] OSHA response to CSB interrogatory for the reactive chemical hazard investigation, June 6, 2001.

Following the Napp incident, six labor unions[20] petitioned OSHA for emergency revision of the PSM Standard, stating that it failed to cover reactive chemicals. In a followup letter, the labor unions asked OSHA to consider the following issues in any revision of the standard:

- Addition of NFPA category "1" and "2" reactives to the list of highly hazardous chemicals.
- Hazard evaluation, including the conditions for use of highly hazardous chemicals.
- Adequacy of the NFPA ratings process.
- Synchronization of the OSHA PSM and the EPA RMP lists; and expansion of worker/union involvement.

In February 1996, the Chemical Manufacturers Association (now ACC) and API submitted a letter to OSHA responding to issues raised by the labor unions. The letter indicated ACC support of PSM as an effective standard. It also reflected the opinion that expanding PSM in the ways proposed would greatly increase compliance costs without substantial benefits and that a large amount of the additional cost would fall on small businesses. ACC and API identified several alternatives for regulating reactives, but concluded that each presented technical difficulties, significant cost, and minimal benefit. For these reasons, both trade groups opposed any revisions to the PSM Standard.

OSHA did not undertake an emergency revision of the PSM Standard in response to the labor unions' petition. In October 1997, OSHA and EPA issued a joint chemical accident investigation report on the Napp Technologies incident. Among the recommendations was that OSHA and EPA review the lists of substances subject to the PSM Standard and RMP regulation to determine whether reactive substances should be added (USEPA-OSHA, 1997).

[20] Union of Needletrades, Industrial, and Textile Employees (UNITE); United Steelworkers of America (USWA); Oil, Chemical, and Atomic Workers (OCAW); American Federation of Labor-Congress of Industrial Organizations (AFL-CIO); International Association of Fire Fighters (IAFF); and International Chemical Workers Union (ICWU). In 1999, OCAW merged with the United Paperworkers International Union to form the Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE). In 1996, ICWU merged with the United Food and Commercial Workers International Union (UFCW).

The OSHA regulatory agenda published on May 14, 2001, indicated that it intended to reconsider the reactives issue that year. However, in the regulatory agenda published on December 3, 2001, OSHA withdrew from consideration changes to the PSM Standard. A May 21, 2002, letter from John Henshaw, Assistant Secretary of Labor for OSHA, to CSB stated that issues related to reactives–though dropped from the current regulatory agenda–would be reconsidered and possibly raised in future regulatory agendas.

OSHA . . . stated that issues related to reactives–though dropped from the current regulatory agenda–would be reconsidered and possibly raised in future regulatory agendas.

5.2 EPA

5.2.1 Overview

Similar to OSHA, EPA has no regulations specifically targeted to reactive hazard management. However, some legal requirements cover limited aspects of reactivity. The EPA RMP and GDC are two such requirements, as discussed in more detail below. EPA has made no decision on how to address reactivity because it has not yet identified a technically sound method for determining reactive substances.[21]

. . . EPA has no regulations specifically targeted to reactive hazard management.

CSB incident data were analyzed with respect to coverage under the EPA RMP regulation:

- For 20 percent of the incidents, the chemicals were covered under RMP.
- For 60 percent of the incidents, the chemicals were not RMP listed.

It could not be determined whether RMP-listed chemicals were involved in the remaining 20 percent of incidents.

The 1990 CAAA required EPA to promulgate regulations to prevent the accidental release of substances that could cause death, injury, or serious adverse effects to human health or the environment. Congress directed EPA to regulate at least 100 substances and to take into account several factors when developing a chemical list, including

[21] EPA response to CSB interrogatory for the reactive chemical hazard investigation, May 31, 2001.

"toxicity, reactivity, volatility, dispersibility, combustibility, or flammability of the substance, and amount of the substance."

5.2.2 Accidental Release Prevention Requirements

EPA promulgated the Accidental Release Prevention Requirements (40 CFR 68), which contain the list of regulated chemicals and requirements for facilities possessing more than a threshold quantity of a listed chemical in an individual process. Covered facilities are required to implement a risk management program and submit a risk management plan to EPA.

When developing the list of substances, EPA considered only the inherent characteristics of a chemical that indicate a severe threat due to exposure. Well-defined criteria were used for toxicity and flammability. However, because of the complexities of site-specific factors and process conditions, EPA was unable to determine any inherent characteristic as an indicator of reactivity. EPA concluded that there was "insufficient technical information for developing criteria for identifying reactive substances."[22] Consequently, the January 1994 RMP list of 130 chemicals does not contain any substances listed due to reactive hazards.

Unlike OSHA's use of criteria for covering classes of chemicals, such as the criterion for flammable substances as a class, EPA has used only chemical lists for the RMP regulation. The authority provided by Congress in the CAAA for EPA to develop the Accidental Release Prevention Requirements is explicit on the use of a "List of Substances" (Section 112[r][3]) to identify the covered chemicals.

The list of RMP-regulated chemicals has not been revised since the October 1997 recommendation by the EPA-OSHA joint chemical accident investigation team to review the lists of substances subject to the RMP regulation and PSM Standard to determine whether reactive chemicals should be added.

[22] EPA Response to CSB interrogatory for the reactive chemical hazard investigation, May 31, 2001.

RMP requires covered processes to have a hazard assessment, a prevention program, and an emergency response program. The hazard assessment must evaluate the accidental release of regulated substances, including the worst case scenario. RMP contains requirements for prevention of accidental releases, which include the same basic elements as the OSHA PSM Standard. Therefore, the limitations described in Section 5.1.2.2 with respect to process safety information and process hazard analysis also apply to RMP.

. . . the EPA RMP has significant gaps in coverage of reactive hazards.

It is evident that the EPA RMP has significant gaps in coverage of reactive hazards.

5.2.3 General Duty Clause

The EPA GDC is a statutory requirement found in Section 112(r)(1) of the 1990 CAAA. It reads as follows:

> The owners and operators of stationary sources producing, processing, handling or storing [a chemical in 40 CFR 68 or any other EHS] have a general duty [in the same manner and to the same extent as the OSHA GDC] to identify hazards which may result from such releases using appropriate hazard assessment techniques, to design and maintain a safe facility taking such steps as are necessary to prevent releases, and to minimize the consequences of accidental releases which do occur.

GDC applies to all stationary sources (fixed facilities) that handle, produce, process, or store regulated substances or extremely hazardous substances (EHS).[23] It obligates facilities to identify and safely manage all hazards, including reactive hazards. Similar to OSHA, EPA can use its GDC enforcement authority to create legally binding requirements or enforce actions for hazards that have not been properly identified or managed.

[23] The Senate Report on the 1990 CAAA stated that EHS includes substances specifically listed under EPA's Accidental Release Prevention Requirements (40 CFR 68) and substances listed under Section 302 of the Emergency Planning and Community Right-to-Know Act (EPCRA). The definition also includes substances not necessarily listed that–due to their toxicity, reactivity, flammability, volatility, or corrosivity–may cause death, injury, or property damage as a result of short-term exposure upon release to the air.

EPA has used GDC order authority in only one situation for reactive hazards.

The EPA GDC is not limited solely to hazards addressed by industry standards; however, there are no standards for management of reactive hazards that can be used to enforce a general duty on industry.

GDC enforcement authority can be used in either a proactive (before an incident) or a reactive (after an incident) manner. EPA can use its order authority (CAA Section 112[r][9]) to enforce GDC in a case where it finds the possibility of imminent and substantial endangerment. EPA has used GDC order authority in only one situation for reactive hazards.

6.0 Management System Guidance

Inadequate process safety management practices are often cited as the cause of reactive incidents, as discussed in Section 3.0 (Table 4). Incident data underscore the critical importance of successfully implementing the following key elements throughout the life cycle[24] of a manufacturing process:

- ***Hazard identification:*** structured approach to identifying and understanding the reactive hazards of chemicals used alone or in combination.
- ***Hazard evaluation:*** system for investigating reactive hazards, assessing the potential consequences of uncontrolled reactions, and establishing a safe design and operating basis.
- ***Management of change (MOC):*** procedure to re-evaluate reactive hazards when changes occur throughout the life cycle of a chemical process.
- ***Personnel training and procedures:*** program that includes written operating procedures and consideration of the potential for human error in reactive systems.

CSB staff found a considerable amount of technical guidance for chemists and process engineers on how to identify reactive hazards during the R&D and design phases. This guidance covers chemical manufacturing processes and storage/handling.

However, only limited guidance is available on the following aspects of reactive hazard management:

- Use of reactive test data, including data from the reactive hazard evaluation.
- Use of a protocol to identify reactive hazards (e.g., checklist or specific guidewords).
- Application of a chemical interaction matrix.
- Identification and evaluation of worst case scenarios involving uncontrolled reactivity.

[24] "Life cycle" refers to all phases of a chemical manufacturing process–from conceptualization, process R&D, engineering design, construction, commissioning, commercial operation, and major modification to decommissioning.

- Integration of reactive hazard information into process safety information, operating procedures, training, and communication practices.
- Evaluation of reactive hazards during MOC procedures.

Companies engaged primarily in the bulk storage, handling, and use of chemicals are particularly in need of concise guidance on preventing the inadvertent mixing of incompatible substances.

Companies engaged primarily in the bulk storage, handling, and use of chemicals are particularly in need of concise guidance on preventing the inadvertent mixing of incompatible substances.

Additionally, as discussed earlier, though several computerized tools and literature resources are available to identify reactive hazards, the surveyed companies generally do not use them. Also, they typically do not share detailed reactive chemical test data.

6.1 Hazard Identification

Understanding and identifying reactive hazards is a key component of process knowledge.

Understanding and identifying reactive hazards is a key component of process knowledge. It is often the first activity in managing reactive hazards and may occur early in product research or in process development. Ineffective hazard identification is commonly cited as a cause of reactive incidents. Where some causal information is available from CSB's data search,[25] about 25 percent of incidents are attributed to this factor.

The identification of reactive hazards is a prerequisite to conducting a hazard evaluation and developing safe design, operation, and maintenance practices (CCPS, 1992; pp. 9, 12). A variety of reactive hazard identification methods are currently used, including literature searches and screening tests (CCPS, 1995a, 1995b; HSE, 2000; Barton and Rogers, 1997). No one technique is appropriate for all circumstances.

[25] Causal information is available in approximately 20 percent of the incidents identified by CSB.

6.1.1 Existing Sources of Data

Relevant sources of information for reactive hazard data include the following, as noted throughout this report and listed in Section 11.0:

- *Bretherick's Handbook of Reactive Chemical Hazards*.
- U.S. Coast Guard (USCG) Chemical Hazard Response Information System (CHRIS) Database.
- NFPA 49, Hazardous Chemicals Data.
- NFPA *Fire Protection Guide to Hazardous Materials*.
- *Sax's Dangerous Properties of Industrial Materials*.
- National Oceanic and Atmospheric Administration (NOAA) The Chemical Reactivity Worksheet.
- Pohanish and Greene's *Rapid Guide to Chemical Incompatibilities*.
- ASTM Chemical Thermodynamic and Energy Release Program (CHETAH).

Responses to the CSB industry survey[26] indicate that most companies consult a variety of information sources as a first step in compiling data on reactive hazards. However, respondents prefer literature sources and expert opinion over computerized tools such as CHETAH, The Chemical Reactivity Worksheet, or Bretherick's Database of Reactive Chemical Hazards.

Computer programs can be used to predict the thermal stability of compounds, reaction mixtures, or potential chemical incompatibilities. In some cases, they provide an efficient means of identifying reactive hazards without chemical testing. Survey responses show that five of nine companies consider computer-based tools "not valuable." Only two of the surveyed companies use The Chemical Reactivity Worksheet.[27]

[26] Appendix B describes the CSB industry survey.

[27] The survey did not seek to determine whether the participants had used the tools and concluded that they were of little value, or whether they had only a limited understanding of the potential benefits.

CSB data show that hazard information was available in existing literature for over 90 percent of the reactive incidents.

6.1.2 Chemical Incompatibility

In many cases, it is not possible to identify hazards through intrinsic chemical properties because they may be caused by the interaction of process chemicals . . .

Approximately 36 percent of incidents in the CSB data are related to chemical incompatibility. CCPS guidelines for chemical reactivity emphasize the need to systematically examine possible chemical incompatibilities and describe the use of interaction matrices (CCPS, 1995a, p. 7; 1995b, p. 108).[28, 29] This guidance applies to chemical manufacturers as well as to other industries.

In many cases, it is not possible to identify hazards through intrinsic chemical properties because they may be caused by the interaction of process chemicals, either inadvertent or intentional. Such hazards are commonly encountered at facilities primarily engaged in the bulk storage, handling, and use of chemicals. There is limited guidance on segregation and isolation of incompatible substances, handling water- or air-reactive chemicals, training, and MOC.

Seven of nine respondents use chemical interaction matrices to identify potential chemical incompatibilities. Most use a binary matrix (i.e., the mixing of only two chemical components at a time). Respondents indicated that literature and expert opinion are important sources of data for the matrix.

Five of the seven respondents who use a matrix also use chemical testing results as a data source. A similar number review the matrix during qualitative hazard evaluation studies (i.e., hazard and operability [HAZOP] studies, "what-if," checklist, etc.).

CCPS (1995a; pp. 46-49) provides only limited discussion on when to conduct an incompatibility study or how to apply the results during a hazard evaluation. It suggests that the PHA team review the interaction matrix, but does not provide detailed guidance on this subject (CCPS, 1995b; p. 111).

[28] An interaction matrix indicates whether the combination of two or more materials yields an undesired consequence (see ASTM E2012-99, Standard Guide for Preparation of Binary Chemical Compatibility Chart).

[29] Section 6.1.1 lists data sources for developing an interaction matrix.

6.1.3 Thermal Hazards

From the data collected by CSB, 35 percent of the 167 incidents are attributed to runaway reaction hazards. CCPS (1995a, Ch. 2; 1995b, Ch. 3), HSE (2000; pp. 15-28), and IChemE (Barton and Rogers, 1997; pp. 20-45) offer guidance on methods for identifying thermal hazards such as runaway reactions. In *Guidelines for Safe Storage and Handling of Reactive Materials,* CCPS (1995b; p. 58) outlines a materials assessment strategy for hazard identification that applies recognition aids along with expert judgment and experience. The guidelines suggest evaluation of each substance stored or handled onsite.

6.1.4 Chemical Reactivity Testing

When there are gaps in literature or expert knowledge of reactive hazards, industry good practice guidelines (e.g., CCPS, 1995a; p. 13) recommend chemical testing prior to scaleup of a chemical manufacturing process. Chemical reactivity testing can be used either to aid in hazard identification during product research or to evaluate hazards during capital projects. Most survey participants view chemical testing as a valuable part of the hazard identification process. Appendix G presents more detailed information on testing.

Chemical reactivity testing can be used either to aid in hazard identification during product research or to evaluate hazards during capital projects.

The survey participants were asked about their reactivity testing programs. Three of five companies visited by CSB use expert opinion to examine the need for testing. Seven of nine use a mix of in-house and contracted testing capabilities. Two respondents rely on literature surveys and expert opinion instead of chemical testing. Only two of 10 respondents to a recent SOCMA survey[30] use reactive chemical test data to identify hazards. (SOCMA membership includes many small- and medium-sized companies.)

[30] SOCMA conducted a survey of reactive hazard management practices among its 300 member companies during the April 2001 Responsible Care conference. The survey consisted of a two-page questionnaire distributed at a working session on reactive chemical safety. Ten companies responded. A copy of the survey report was provided to CSB.

Guidance on when to conduct testing is not consistent. When designing processes for conducting chemical reactions, CCPS (1995a; p. 13) suggests that all materials be subject to screening tests, even if no reactivity concerns are identified in the literature search and expert judgment. In other guidance, CCPS (1995b; p. 85) states that in designing storage and handling systems for reactive materials, prior experience, theoretical evaluations, and expert opinion may be used to determine the need for screening tests.

One company visited by CSB had compiled a database of over 60,000 reactive chemical test results.

6.1.5 Accessibility of Chemical Reactivity Test Data

Although no dedicated data repository for reactive chemical test results is generally available to industry or the public, the chemical industry has generated a substantial amount of test data. One company visited by CSB had compiled a database of over 60,000 reactive chemical test results.

CSB investigators determined that the surveyed companies share data of a general nature for most chemicals (i.e., data typically found on an MSDS) and good handling practices for some. However, this typically does not include reactive chemical test data. Several reasons were given for the absence of substantial data sharing, including:

- Potential liability concerns.
- Need for expert interpretation of reactivity data.
- Reluctance to share trade secrets or confidential business information.

The feasibility of a publicly available test database has not yet been studied by industry or government.

Currently, there is no mechanism to effectively share reactive chemical test data throughout industry. The feasibility of a publicly available test database has not yet been studied by industry or government. Reactive chemical experts at one company visited by CSB expressed an interest in working with the National Institute of Standards and Technology (NIST) to develop such a database.

6.2 Hazard Evaluation

More than 40 percent of the 167 incidents from the CSB data search, where some causal information is available,[31] are attributed to inadequate hazard evaluation. In several cases, the hazard was known, but its potential magnitude was not–nor was the potential severity of the consequence. In other cases, the hazard evaluation did not properly identify initiating events.

IChemE acknowledges that "there is no standard procedure for evaluating chemical reaction hazards" (Barton and Rogers, 1997; p. 120). The CSB survey further highlights the variety of approaches to reactive hazard evaluation; companies rely to varying degrees on quantitative and qualitative evaluation methods.

6.2.1 Quantitative Methods

A prerequisite to any process hazard evaluation is adequate knowledge of the chemistry. Prior to specifying safe design and operating requirements, identified hazards must be evaluated to understand what can go wrong and the potential consequences. CCPS (1995a, p. 17; 1995b, p. 94) and IChemE (Barton and Rogers, 1997; p. 28) provide guidance on parameters for reactive hazard evaluation. Quantitative modeling techniques and calorimetry data are sometimes required along with extensive process-specific information.[32]

Both HSE (2000; p. 34) and IChemE (Barton and Rogers, 1997; p. 107) emphasize the need to identify a worst case scenario involving uncontrolled reaction to ensure that safety systems are designed and maintained to provide adequate protection under all postulated circumstances. When identifying the worst case, IChemE provides

[31] Causal information is available in approximately 20 percent of the incidents identified by CSB.

[32] Good practice guidelines illustrate how these parameters are typically examined for both normal and postulated abnormal conditions, such as variations in reactant quantity, concentration, agitation, sequence, time, failure of utilities, and instrumentation. Qualitative hazard evaluation protocols are not well suited for such complex chemical phenomena (e.g., the severity of an uncontrolled reaction under a loss of electrical power may not be apparent without sufficient test data).

a general recommendation to evaluate any scenario not protected by high integrity shutdown systems.[33] However, there is little guidance on how to systematically identify and evaluate a worst case scenario involving uncontrolled reaction.

6.2.2 Qualitative Methods

Chemical reactivity information is gathered from data searches, calculations, and reactivity testing. Qualitative hazard evaluation is one commonly used approach to assessing process hazards, including reactive hazards (CCPS, 1992).

Several qualitative approaches can be used to identify hazardous reaction scenarios, including process hazard analysis, checklists, chemical interaction matrices, and an experience-based review. CCPS (1995a; p. 176) describes nine hazard evaluation procedures to identify hazardous reaction scenarios–checklists, Dow fire and explosion indices, preliminary hazard analysis, "what-if" analysis, failure modes and effects analysis (FMEA), HAZOP study, fault tree analysis, human error analysis, and quantitative risk analysis.

Existing good practice guidelines from CCPS, HSE, and IChemE do not adequately address how to manage the unique aspects of reactive hazards while performing hazard evaluations.

Although each of these methods can be useful in identifying reactive scenarios, none are designed specifically to address the reactive hazard. Existing good practice guidelines from CCPS (1992), HSE (2000), and IChemE (Barton and Rogers, 1997) do not adequately address how to manage the unique aspects of reactive hazards while performing hazard evaluations.

The CSB survey identified examples of modified or hybrid techniques to identify reactive hazard scenarios and ensure the implementation of adequate safeguards. For example, companies conducting reactions in batch chemical reactors often conduct HAZOP studies by evaluating deviations from procedural steps as opposed to deviations from intended equipment design. One company uses a "what-if" PHA protocol specifically designed to address reactivity hazards.

[33] Instrumentation, Systems, and Automation Society (ISA) Standard 84, Application of Safety Instrumented Systems for the Process Industries, outlines the principles of high integrity shutdown systems.

Most survey respondents indicated that they perform reactive hazard evaluation studies during specific life-cycle phases of a process or product. These phases include process development, commercial process design, periodic re-evaluation, and before proposed modifications. The protocol for hazard evaluation of reactive systems varies from company-to-company. At a minimum, all surveyed companies use qualitative hazard evaluation.[34]

Industry guidance from CCPS (1995a; 1995b), HSE (2000), and IChemE (Barton and Rogers, 1997) contains little information on how and when to apply reactive chemical test data during a process hazard analysis. During site visits, CSB investigators encountered PHA teams that use test data to evaluate reactive hazards. In combination with input on reactive chemistry, the test data are used to assist in evaluating appropriate safe operating limits and potential consequences of an uncontrolled reaction.

For reactive processes, MOC applies to increases or decreases in process temperature, and to changes in raw material specifications, concentration, process time, and materials of construction.

This practice supports the CSB observation that effective process hazard analysis for a reactive system is essentially more "data driven" than conventional process hazard analysis given the technical complexity of the reactive hazard. Three of the five visited companies use reactivity test data when conducting process hazard analysis; two use qualitative hazard evaluation methods only.

6.3 Management of Change

MOC is a systematic procedure for reviewing potential hazards of proposed changes to facilities. It applies to all hazardous materials regardless of reactivity; however, there are specific considerations for reactive hazards. Inadequate MOC procedures are a contributing cause of several reactive incidents described in Section 3.0.

For reactive processes, MOC applies to increases or decreases in process temperature, and to changes in raw material specifications, concentration, process time, and materials of construction (HSE, 2000; p. 41). CCPS (1995a, p. 6; 1995b, p. 197) explains that chemical testing may be required to identify and evaluate new hazards from process changes.

[34] Qualitative hazard evaluation is commonly referred to as "process hazards analysis," or PHA, which is used in OSHA PSM.

Overall, there is a lack of specific guidance on how to evaluate reactive hazards during the MOC procedure. Existing guidelines from CCPS (1995a; 1995b), IChemE (Barton and Rogers, 1997), and HSE (2000) do not address how to maintain and update reactive hazard evaluation as part of the change approval procedure–nor do they address what type of change to process chemistry or product formulation necessitates a review and possible update of the reactive hazard evaluation.

6.4 Personnel Training and Procedures

Personnel training and performance–as a management systems element–focuses on development of process knowledge and documentation, including clearly defined technical information and operating procedures (CCPS, 1989).

Incident data in Section 3.0 show that more than half of the reactive incidents, where some causal information is available, are attributed to inadequate operating procedures and training. These data illustrate the challenge of effectively communicating a practical, working knowledge of an often complex array of chemical and process information.

. . . reactive hazard management requires a working knowledge of the complex intersection of chemical properties and process-specific conditions.

Personnel who work with reactive chemicals must understand the hazards they face and take precautions to ensure safety (HSE, 2000; p. 42). Training is required for both technical personnel (e.g., process engineers, chemists) and operators and maintenance personnel. In the Morton incident, plant personnel did not have a proper understanding of reactive hazards and were unaware of the potential for a runaway reaction. The Morton case and others described in Section 3.0 show that reactive hazard management requires a working knowledge of the complex intersection of chemical properties and process-specific conditions.

Both IChemE (Barton and Rogers, 1997; p. 137) and HSE (2000; p. 42) briefly address operator training in systems that involve reactive hazards. None of the guidelines, however, address the transfer and communication of this information to technical personnel. There is little guidance on integrating reactive hazard information into operating procedures, training, and communication practices.

At one company visited by CSB, newly appointed production managers are required to demonstrate their knowledge of reactive hazards before a review committee. The basis for technical and managerial training is an established "operating discipline," an up-to-date reference of process knowledge containing technical details, operational details, and process hazard information. This approach to ensuring technical and management personnel training is unique among survey participants.

There is little guidance on integrating reactive hazard information into operating procedures, training, and communication practices.

6.5 Summary

Guidance on safety management throughout the life cycle of a process is limited. CCPS (1989; 1994) provides a framework for a systems-based approach to managing chemical process safety. No organization provides comprehensive guidance on technical and management practices for reactive hazards that applies to all phases of the process life cycle, though CCPS (1995b; pp. 193-202) briefly describes how these management principles apply to reactive hazards.

Good management practices include not only hazard identification and evaluation early in R&D, but also issues such as MOC throughout the life of the chemical manufacturing process. The existing body of knowledge is largely focused on technical topics, such as calorimetry testing, engineering design, scaleup, and emergency venting. CCPS currently has a project underway that addresses technical and management practices for reactive hazards.

Good management practices include not only hazard identification and evaluation early in R&D, but also issues such as MOC throughout the life of the chemical manufacturing process. The existing body of knowledge is largely focused on technical topics . . .

7.0 Industry Initiatives

Voluntary industry initiatives supplement regulatory requirements. The chemical industry has voluntarily undertaken several initiatives to provide guidance on chemical process safety, including processes involving reactive hazards. However, at present, no industry initiatives list specific codes or requirements for managing reactive hazards.

. . . at present, no industry initiatives list specific codes or requirements for managing reactive hazards.

7.1 Responsible Care Process Safety Code

Approximately 70 percent of incidents in CSB data occurred in the chemical manufacturing industry. Both ACC and SOCMA have programs to promote good practices among their member companies in the area of chemical process safety.[35] In 1989, ACC developed the Responsible Care Process Safety Code[36] to prevent fires, explosions, and accidental chemical releases. The code and its accompanying resource guidelines include a series of recommended safety management practices.

Responsible Care is intended to apply throughout the life cycle of a process–from conception and design through construction and startup, and continuing with long-term operation of the facility. The safety practices are divided into four areas, as listed in Table 6. Although many practices are similar to requirements of the OSHA PSM Standard, the Responsible Care Process Safety Code includes such additional elements as accountability, multiple safeguards, and performance measurement.

The ACC and SOCMA bylaws obligate member companies to participate in Responsible Care, which includes making good faith efforts to implement the program elements. Companies are required to undergo a self-evaluation process; a third-party management systems verification (MSV) audit is optional.

[35] Currently, ACC has approximately 190 member and partner companies, representing 1,700 facilities. SOCMA–with 300 member companies, representing 2,000 facilities– has been a Responsible Care Partner Association since 1990.

[36] Approximately 30 chemical industry associations are Responsible Care Partner Associations.

Table 6
ACC Responsible Care Safety Management Practices

Management Leadership in Process Safety	
1	Commitment
2	Accountability
3	Performance Measurement
4	Incident Investigation
5	Information Sharing
6	Community Awareness and Emergency Response (CAER) Integration
Process Safety Management of Technology	
7	Design Documentation
8	Process Hazards Information
9	Process Hazard Analysis
10	Management of Change
Process Safety Management of Facilities	
11	Siting
12	Codes and Standards
13	Safety Reviews
14	Maintenance and Inspection
15	Multiple Safeguards
16	Emergency Management
Managing Personnel for Process Safety	
17	Job Skills
18	Safe Work Practices
19	Initial Training
20	Employee Proficiency
21	Fitness for Duty
22	Contractors

7.1.1 Guidance on Implementation

ACC has published a resource guide to aid member companies in implementing the Responsible Care Process Safety Code (ACC, 1989). Although the guide provides suggestions on how to continually improve process safety, it does not prescribe how to comply with the code. It does not list specific requirements for reactive hazard management, but does require management systems to be developed–several of which could apply to reactive hazards as determined by member companies.

Currently, ACC highlights reactive hazard management only in the following areas:

- Management Practice 7, Design Documentation, which emphasizes the need to develop and retain process description, chemistry, and "reaction data."
- Management Practice 8, Process Hazards Information, which describes the need to maintain current, accessible information on material characteristics, including "reactivity."

Management Practice 12, Codes and Standards, discusses the need to identify, use, and comply with voluntary and consensus standards where applicable.

The ACC Process Safety Code Management System . . . contains data on type of incident, . . . number of injuries, etc., for 1,500 facilities–but no data on causes of incidents or lessons learned.

ACC member companies are required to establish company-specific goals against which progress is measured toward the common vision of no accidents, injuries, or harm to the environment. An example of one such goal is to limit the annual number of process safety incidents below a target level.

Member companies submit annual reports to ACC on process safety incidents that meet specific criteria.[37] The ACC Process Safety Code Measurement System (PSCMS), established in 1996, contains data on type of incident (i.e., fire, explosion, toxic gas), number of injuries, etc., for 1,500 facilities–but no data on causes of incidents or lessons learned.

PSCMS is primarily designed as a metric for tracking industry performance on process safety incidents; it is not intended to be a lessons-learned database. However, if expanded to include causes and lessons learned and if more widely distributed, the data could be useful in preventing similar incidents.

[37] The criteria include any fire or explosion causing more than $25,000 in property damage; an episodic loss of containment incident of a chemical in excess of the threshold quantities listed in 40 CFR 355.40, Appendix A; an episodic loss of containment incident involving more than 5,000 pounds of a flammable substance; or any fire, explosion, or chemical release that involves one or more fatalities or serious injuries.

7.1.2 SOCMA Guidance

The *Guide to Process Safety* is designed to help with implementation of the Responsible Care Process Safety Code (SOCMA, 1999). The guide presents voluntary, proactive initiatives for the continuous improvement of process safety performance.

The SOCMA process safety committee informally shares information on incidents at member facilities, but it does not offer a formal incident reporting mechanism such as the ACC PSCMS.

7.2 Responsible Distribution Process

Approximately 30 percent of incidents in CSB data occurred at industrial facilities that use or consume chemicals in bulk quantities.

Reactive incidents are not unique to the chemical manufacturing industry. Approximately 30 percent of incidents in CSB data occurred at industrial facilities that use or consume chemicals in bulk quantities.

NACD is an association of chemical distributor companies that purchase and take title of chemical products from manufacturers.[38] Member companies process, formulate, blend, repackage, warehouse, transport, and market chemical products to industrial customers. NACD has developed the Responsible Distribution Process (RDP), which is similar in concept to the ACC Responsible Care code.

As a condition of NACD membership, each chemical distribution company is required have an active safety management program designed to continuously improve safety and reduce incidents. The RDP code has been in place since 1991 and includes risk management, compliance review and training, carrier selection, handling and storage, job procedures and training, waste management, emergency response and public preparedness, community outreach, and product stewardship.

[38] NACD has approximately 300 member companies and distributes to 750,000 industrial customers.

NACD (2002) has published an RDP implementation guide to assist member companies in developing programs. The RDP code requires a self-evaluation and a third-party onsite MSV audit. In the last 3 years, NACD has expelled 20 companies because of noncompliance.

The RDP code does not contain explicit requirements for reactive hazard management, though several elements may apply. For example, the handling and storage element requires:

> . . . procedures for loading and unloading chemicals at the member company's facilities that result in protection of personnel, a reduction in emissions to the environment, and ensure[s] that chemicals are loaded and unloaded into and out of proper storage facilities.

This element implicitly applies to reactive hazards in terms of inadvertent mixing of incompatible materials.

The RDP handling and storage element also requires "a program for providing manufacturer guidance and information to customers, warehouses, terminals and carriers on procedures for loading, unloading, and storing chemicals." Again, this element implicitly applies to the communication of good practices for reactive hazards–from the manufacturer to the end use customer. The product stewardship element of RDP includes similar requirements.

8.0 Alternatives for Improving Regulatory Coverage

There is considerable debate over the need to extend regulatory coverage of reactive hazards. Testimony provided at the CSB public hearing on May 30, 2002, and elsewhere indicates a general consensus that there are concerns with the number and range of reactive hazards covered under the OSHA PSM Standard and EPA RMP regulation (e.g., addressing reactive mixtures of substances as well as single substances). However, there is no consensus on how the problems should be addressed–by regulatory means, by voluntary efforts such as the ACC Responsible Care program, or by a combination of approaches.

There are significant differences in the laws authorizing the OSHA PSM Standard and the EPA RMP regulation. Because EPA specifically lists substances covered under RMP and does not establish classes of substances, this report separately discusses alternatives for OSHA (Section 8.1) and EPA (Section 8.2). Section 8.3 briefly discusses regulatory relief absent catastrophic consequences, and Section 8.4 suggests improvements within the requirements of the existing PSM Standard and RMP regulation to enhance hazard identification and hazard evaluation.

One approach to improving management of reactive hazards is to extend OSHA PSM coverage to a class of "highly reactive substances," similar to the way the existing standard defines a class of "flammable liquids or gases."

8.1 OSHA PSM

8.1.1 Highly Reactive Substance Classification

One approach to improving management of reactive hazards is to extend OSHA PSM coverage to a class of "highly reactive substances," similar to the way the existing standard defines a class of "flammable liquids or gases." "Highly reactive substances" would include single components as well as multicomponent substances; coverage would apply to all chemical processes (as defined by OSHA PSM). For example, a criterion based on the heat of reaction would specify coverage if the quantity exceeded a certain level (e.g., 100 cal/g); or, alternatively, multiple criteria such as heat of reaction and total pressure could be applied.

With relevant criteria, the highly reactive substance classification would cover the most likely process deviations and inadvertent mixing scenarios leading to injury; however, it may not take into account all process-specific conditions, such as inadvertent mixing of unexpected chemicals or addition of an unexpected catalyzing agent.

Highly reactive substance classification could also include regulatory relief, as discussed in Section 8.3.

A performance-based system–rather than a list of "reactive chemicals"–is suggested as another alternative for extending regulatory coverage of reactive hazards.

8.1.2 Hazard Evaluations

A performance-based system–rather than a list of "reactive chemicals"–is suggested as another alternative for extending regulatory coverage of reactive hazards. Such a system would consider the risk of reactive chemicals, site-specific (extrinsic) factors such as siting and proximity, and conditions that create potentially reactive situations. Objective criteria such as the North American Industry Classification System (NAICS) codes, accident history, or number of employees could be used to establish coverage.

If the hazard evaluation demonstrates the possibility of a catastrophic consequence, the process has regulatory coverage.

The process hazard analysis required by OSHA PSM is an example of a performance-based approach; it allows for a variety of hazard analysis methodologies. A performance-based system requires experts to identify and evaluate all relevant reactive hazards of a process and to determine the complexity of the hazards analysis. If the hazard evaluation demonstrates the possibility of a catastrophic consequence, the process has regulatory coverage. This approach to hazard evaluation allows for both a comprehensive analysis and flexibility in implementation; however, if applied to reactive hazards, it requires expertise for implementation and regulatory evaluation.

8.1.3 "Safety Case"

A safety case approach along the lines of the Seveso[39] requirements is another possible alternative for determining regulatory coverage. The safety case requires a detailed explanation of why a process is safe to operate. Again, objective criteria such as NAICS codes, thermodynamic properties, or some combination of those criteria previously discussed are used to establish coverage.

The safety case requires a detailed explanation of why a process is safe to operate.

The concept of a safety case comes from the European Union/European Community (EU/EC) Seveso Directive (82/501/EC) and, in particular, regulations that the United Kingdom and other member states used to implement it. United Kingdom regulations (Control of Industrial Major Accident Hazards [CIMAH], 1984; replaced by Control of Major Accident Hazards Involving Dangerous Substances [COMAH] in 1999) require that major hazardous facilities produce a safety report or safety case.[40]

In Europe, the requirement for a safety case is initiated by a list of chemicals and a class of flammables. Like the hazard evaluation approach (Section 8.1.2), experts identify the reactive hazards of the process; if analysis shows that the proposed process is safe, it may be excluded from additional regulatory requirements.

. . . if analysis shows that the proposed process is safe, it may be excluded from additional regulatory requirements.

The objective of a safety case is to demonstrate to the regulatory authority that a company is fully aware of the hazards associated with its operations and that they are conducted in a safe manner, such that employees and the public are not exposed to undue risks. The regulatory authority must examine the safety case and communicate the results of its examination to the facility, usually within a "reasonable period of time."

[39] On July 9, 1976, in Meda, Italy, near Seveso, a chemical reactor incident caused a release of dioxin (TCDD), which is a highly toxic chemical. The regulatory requirements developed as a result of this incident are referred to as the Seveso Directive.

[40] The concept of a safety case exists within the context of a licensing regime. Licensing mechanisms exist in the United States, but compliance with workplace safety requirements is not a prerequisite for license.

The safety case may be prescriptive or performance based. Although this approach is comprehensive, if applied to reactive hazards, it requires that regulatory agencies have expertise to assess the adequacy of the analysis.

8.2 EPA RMP

Significant differences in the laws authorizing the OSHA PSM Standard and the EPA RMP regulation may affect the means by which EPA can revise coverage of processes containing reactive hazards. EPA maintains that it is required to specifically list substances covered under RMP and cannot establish classes of substances. For this reason, EPA individually lists flammables, rather than adopting the "class" approach to flammables used by OSHA.

Two states have successfully implemented or are considering a list-based approach to address coverage of reactive hazards that affect the public. Delaware uses the same overpressurization criterion as OSHA for determining the quantity of a listed substance that is covered. New Jersey is expected to include the criterion in its revision of the Toxic Catastrophe Prevention Act (TCPA).

To most effectively improve reactive hazard management, OSHA and EPA coverage should be more compatible. EPA should seek the authority needed to allow it to address reactive hazards in a manner compatible with any revised OSHA approach.

8.3 Regulatory Relief Absent Catastrophic Consequences

Physical processing conditions affect both the rate at which energy is released from an "intended reaction" and the potential damage. For this reason, many processes–which could be otherwise covered–may not present a catastrophic risk to workers under reasonable worst case scenarios.

Moreover, even if the reaction "runs away," there may be no catastrophic injury to workers because the process is designed to handle reasonable worst case scenarios or offers effective passive mitigation measures, such as containment, diking, blast walls, and adequate emergency relief systems.

Regulations could encourage inherently safer design and mitigation by granting exemptions where such measures are proven to prevent catastrophic incidents.

8.4 Improvements in OSHA PSM and EPA RMP Requirements

8.4.1 Process Safety Information

The PSI element of both the OSHA PSM Standard and the EPA RMP regulation can be improved by requiring the inclusion of all existing information on chemical reactivity. Examples of such information are chemical reactivity test data, such as DSC, thermogravimetric analysis (TGA), or accelerating rate calorimetry (ARC); and relevant incident reports from the plant, the corporation, industry, and government. OSHA and EPA should require the facility to consult such resources as *Bretherick's Handbook of Reactive Chemical Hazards* (1999), *Sax's Dangerous Properties of Industrial Materials* (Lewis, 1996), and computerized tools (e.g., CHETAH, The Chemical Reactivity Work Sheet).

The PSI element of both the OSHA PSM Standard and the EPA RMP regulation can be improved by requiring the inclusion of all existing information on chemical reactivity.

8.4.2 Process Hazard Analysis

In both the OSHA PSM Standard and the EPA RMP regulation, the PHA element does not currently specify the factors that must be considered to effectively manage reactive hazards. Present requirements should be augmented to explicitly require an evaluation of such factors as rate and quantity of heat generated; maximum operating temperature to avoid decomposition; thermostability of reactants, reaction mixtures, byproduct waste streams, and products; effect of charging rates, catalyst addition, and possible contaminants; and understanding the consequences of runaway reactions or toxic gas evolution.

8.4.3 Reporting Requirements

. . . mandatory submission of the reports would increase available data and thus improve the capability of identifying or tracking reactive incidents.

OSHA PSM-covered facilities are required to investigate "each incident which resulted in, or could reasonably have resulted in a catastrophic release of a highly hazardous chemical in the workplace" (29 CFR 1910.119[m][1]). At the conclusion of an incident investigation, the company is required to prepare a report on the factors that contributed to the incident. At present, OSHA does not require submittal of these incident reports. However, mandatory submission of the reports would increase available data and thus improve the capability of identifying or tracking reactive incidents.

8.5 Regulatory Initiatives Under Review by New Jersey

The New Jersey Department of Environmental Protection and Energy is presently considering amendment of its TCPA to establish coverage of reactive hazards that might affect the public. The State has asked for stakeholder input on the following proposition (paraphrased):

> Processes having a reactive hazard with a heat of reaction of 100 calories per gram will be regulated under the NJ TCPA when the quantity of reactive hazard contained in the process equals or exceeds the threshold quantity calculated to result in a 2.3 psi overpressure wave endpoint at a distance of 100 meters or a lesser distance to the source boundary.

New Jersey is also considering whether it should have varying compliance requirements for covered processes. Less stringent requirements are proposed for covered processes where the reactive hazard substance is only stored in shipping containers and handled, with no emptying or filling. The State is proposing that a covered process could escape regulation under TCPA if the facility provides evidence that the reactive hazard substance is not capable of producing an explosion or deflagration overpressure.

9.0 Conclusions

1. Reactive incidents are a significant chemical safety problem.
2. The OSHA PSM Standard has significant gaps in coverage of reactive hazards because it is based on a limited list of individual chemicals with inherently reactive properties.
3. NFPA instability ratings are insufficient as the sole basis for determining coverage of reactive hazards in the OSHA PSM Standard.
4. The EPA Accidental Release Prevention regulations have significant gaps in coverage of reactive hazards.
5. Using lists of chemicals is an inadequate approach for regulatory coverage of reactive hazards. Improving reactive hazard management requires that both regulators and industry address the hazards from combinations of chemicals and process-specific conditions rather than focusing exclusively on the inherent properties of individual chemicals.
6. Reactive incidents are not unique to the chemical manufacturing industry. They also occur in many other industries where chemicals are stored, handled, or used.
7. Existing sources of incident data are not adequate to identify the number, severity, and causes of reactive incidents or to analyze incident frequency trends.
8. There is no publicly available database for sharing lessons learned from reactive incidents.
9. Neither the OSHA PSM Standard nor the EPA RMP regulation explicitly requires specific hazards, such as reactive hazards, to be examined when analyzing process hazards. Given that reactive incidents are often caused by inadequate recognition and evaluation of reactive hazards, improving reactive hazard management requires examining relevant factors (e.g., rate and quantity of heat and gas generated) within a process hazard analysis.
10. The OSHA PSM Standard and the EPA RMP regulation do not explicitly require the use of multiple sources when compiling process safety information.

NFPA instability ratings are insufficient as the sole basis for determining coverage of reactive hazards in the OSHA PSM Standard.

Reactive incidents are not unique to the chemical manufacturing industry. They also occur in many other industries where chemicals are stored, handled, or used.

Current good practice guidelines on how to effectively manage reactive hazards throughout the life cycle of a chemical manufacturing process are neither complete nor sufficiently explicit.

11. Publicly available resources[41] are not always used by industry to assist in identifying reactive hazards.
12. There is no publicly available database to share reactive chemical test information.
13. Current good practice guidelines on how to effectively manage reactive hazards throughout the life cycle[42] of a chemical manufacturing process are neither complete nor sufficiently explicit.
14. Given the impact and diversity of reactive hazards, optimum progress in the prevention of reactive incidents requires both enhanced regulatory and nonregulatory programs.

[41] The Chemical Reactivity Worksheet (NOAA), CHETAH (ASTM), and Bretherick's Database of Reactive Chemical Hazards.

[42] "Life cycle" refers to all phases of a chemical manufacturing process–from conceptualization, process R&D, engineering design, construction, commissioning, commercial operation, and major modification to decommissioning.

10.0 Recommendations

Occupational Safety and Health Administration (OSHA)

1. Amend the Process Safety Management Standard (PSM), 29 CFR 1910.119, to achieve more comprehensive control of reactive hazards that could have catastrophic consequences. (2001-01-H-R1)

   - Broaden the application to cover reactive hazards resulting from process-specific conditions and combinations of chemicals. Additionally, broaden coverage of hazards from self-reactive chemicals. In expanding PSM coverage, use objective criteria. Consider criteria such as the North American Industry Classification System (NAICS), a reactive hazard classification system (e.g., based on heat of reaction or toxic gas evolution), incident history, or catastrophic potential.

   - In the compilation of process safety information, require that multiple sources of information be sufficiently consulted to understand and control potential reactive hazards. Useful sources include:

     - Literature surveys (e.g., *Bretherick's Handbook of Reactive Chemical Hazards, Sax's Dangerous Properties of Industrial Materials*).

     - Information developed from computerized tools (e.g., CHETAH [ASTM], The Chemical Reactivity Worksheet [NOAA]).

     - Chemical reactivity test data produced by employers or obtained from other sources (e.g., differential scanning calorimetry, thermogravimetric analysis, accelerating rate calorimetry).

     - Relevant incident reports from the plant, the corporation, industry, and government.

     - Chemical Abstracts Service.

   - Augment the process hazard analysis (PHA) element to explicitly require an evaluation of reactive hazards. In revising this element, evaluate the need to consider relevant factors, such as:

- Rate and quantity of heat or gas generated.
- Maximum operating temperature to avoid decomposition.
- Thermal stability of reactants, reaction mixtures, byproducts, waste streams, and products.
- Effect of variables such as charging rates, catalyst addition, and possible contaminants.
- Understanding the consequences of runaway reactions or toxic gas evolution.

2. Implement a program to define and record information on reactive incidents that OSHA investigates or requires to be investigated under OSHA regulations. Structure the collected information so that it can be used to measure progress in the prevention of reactive incidents that give rise to catastrophic releases. (2001-01-H-R2)

U.S. Environmental Protection Agency (EPA)

1. Revise the Accidental Release Prevention Requirements, 40 CFR 68, to explicitly cover catastrophic reactive hazards that have the potential to seriously impact the public, including those resulting from self-reactive chemicals and combinations of chemicals and process-specific conditions. Take into account the recommendations of this report to OSHA on reactive hazard coverage. Seek congressional authority if necessary to amend the regulation. (2001-01-H-R3)

2. Modify the accident reporting requirements in RMP* Info to define and record reactive incidents. Consider adding the term "reactive incident" to the four existing "release events" in EPA's current 5-year accident reporting requirements (Gas Release, Liquid Spill/Evaporation, Fire, and Explosion). Structure this information collection to allow EPA and its stakeholders to identify and focus resources on industry sectors that experienced the incidents; chemicals and processes involved; and impact on the public, the workforce, and the environment. (2001-01-H-R4)

National Institute of Standards and Technology (NIST)

Develop and implement a publicly available database for reactive hazard test information. Structure the system to encourage submission of data by individual companies and academic and government institutions that perform chemical testing. (2001-01-H-R5)

Center for Chemical Process Safety (CCPS)

1. Publish comprehensive guidance on model reactive hazard management systems. (2001-01-H-R6) At a minimum, ensure that these guidelines cover:
   - ***For companies engaged in chemical manufacturing:*** reactive hazard management, including hazard identification, hazard evaluation, management of change, inherently safer design, and adequate procedures and training.
   - ***For companies engaged primarily in the bulk storage, handling, and use of chemicals***: identification and prevention of reactive hazards, including the inadvertent mixing of incompatible substances.
2. Communicate the findings and recommendations of this report to your membership. (2001-01-H-R7)

American Chemistry Council (ACC)

1. Expand the Responsible Care Process Safety Code to emphasize the need for managing reactive hazards. (2001-01-H-R8) Ensure that:
   - Member companies are required to have programs to manage reactive hazards that address, at a minimum, hazard identification, hazard evaluation, management of change, inherently safer design, and adequate procedures and training.
   - There is a program to communicate to your membership the availability of existing tools, guidance, and initiatives to aid in identifying and evaluating reactive hazards.

2. Develop and implement a program for reporting reactive incidents that includes the sharing of relevant safety knowledge and lessons learned with your membership, the public, and government to improve safety system performance and prevent future incidents. (2001-01-H-R9)
3. Work with NIST in developing and implementing a publicly available database for reactive hazard test information. Promote submissions of data by your membership. (2001-01-H-R10)
4. Communicate the findings and recommendations of this report to your membership. (2001-01-H-R11)

Synthetic Organic Chemical Manufacturers Association (SOCMA)

1. Expand the Responsible Care Process Safety Code to emphasize the need for managing reactive hazards. (2001-01-H-R12) Ensure that:
   - Member companies are required to have programs to manage reactive hazards that address, at a minimum, hazard identification, hazard evaluation, management of change, inherently safer design, and adequate procedures and training.
   - There is a program to communicate to your membership the availability of existing tools, guidance, and initiatives to aid in identifying and evaluating reactive hazards.
2. Develop and implement a program for reporting reactive incidents that includes the sharing of relevant safety knowledge and lessons learned with your membership, the public, and government to improve safety system performance and prevent future incidents. (2001-01-H-R13)
3. Work with NIST in developing and implementing a publicly available database for reactive hazard test information. Promote submissions of data by your membership. (2001-01-H-R14)
4. Communicate the findings and recommendations of this report to your membership. (2001-01-H-R15)

National Association of Chemical Distributors (NACD)

1. Expand the existing Responsible Distribution Process to include reactive hazard management as an area of emphasis. At a minimum, ensure that the revisions address storage and handling, including the hazards of inadvertent mixing of incompatible chemicals. (2001-01-H-R16)
2. Communicate the findings and recommendations of this report to your membership. (2001-01-H-R17)

International Association of Fire Fighters (IAFF)

Communicate the findings and recommendations of this report to your membership. (2001-01-H-R18)

Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE)

Communicate the findings and recommendations of this report to your membership. (2001-01-H-R19)

The United Steelworkers of America (USWA)

Communicate the findings and recommendations of this report to your membership. (2001-01-H-R20)

Union of Needletrades, Industrial, and Textile Employees (UNITE)

Communicate the findings and recommendations of this report to your membership. (2001-01-H-R21)

United Food and Commercial Workers International Union (UFCW)

Communicate the findings and recommendations of this report to your membership. (2001-01-H-R22)

American Society of Safety Engineers (ASSE)	Communicate the findings and recommendations of this report to your membership. (2001-01-H-R23)
American Industrial Hygiene Association (AIHA)	Communicate the findings and recommendations of this report to your membership. (2001-01-H-R24)

By the

U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

Carolyn W. Merritt
Chair

John S. Bresland
Member

Gerald V. Poje, Ph.D.
Member

Isadore Rosenthal, Ph.D.
Member

Andrea Kidd Taylor, Dr. P.H.
Member

October 8, 2002

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APPENDIX A: Glossary

Adiabatic calorimetry: Chemical testing technique that determines the self-heating rate and pressure data of a chemical under near-adiabatic conditions. ("Adiabatic" refers to any change in which there is no gain or loss of heat.) This measurement technique conservatively estimates the conditions for, and consequences of, a runaway reaction.

Acid-base reaction: Chemical reaction involving the transfer of a hydrogen ion from an acidic substance to a basic substance.

Blast: Potentially damaging pressure or shock wave produced by an explosion.

Catalyst: Substance that usually increases the rate of a chemical reaction without changing its own composition.

Chemical incompatibility: Type of reactive hazard that occurs when a chemical is mixed or comes in contact with other chemicals, or process materials, resulting in an uncontrolled and often violent reaction.

Chemical reaction: Interaction of substances in which they undergo change of composition and properties due to changes in molecular structure of the constituent atoms or molecular fragments.

Chlorination: Reaction of substances with chlorine whereby chlorine atoms are chemically integrated into the original chemical molecule.

Contaminant: Any substance that enters a process where it is not normally found.

Decomposition: Chemical reaction that leads to the breakdown or decomposition of a chemical into smaller molecules or elements, often with the liberation of energy and product gases.

Differential scanning calorimetry (DSC): Chemical testing technique to establish approximate temperature ranges in which a substance undergoes an exothermic decomposition and to determine the energy output of those reactions; may also be used to study endothermic processes, such as melting. DCS data provide very simple and approximate reaction kinetics.

Differential thermal analysis (DTA): Chemical testing technique that produces data similar to DSC. DTA uses temperature differences to generate test results; DSC has largely replaced the DTA technique as a screening tool for chemical hazard test data.

Endothermic reaction: Chemical reaction that absorbs heat.

Explosion: Sudden release of energy that causes a blast or shock wave; may lead to personal injury or structural damage.

Exothermic reaction: Chemical reaction that liberates heat.

Halogenation: Chemical reaction of substances with a halogen–typically, fluorine, chlorine, and bromine. See "chlorination."

Hazard: Chemical or physical condition that has the potential to cause harm to human life, property, or the environment.

Hazard evaluation: Systematic process to investigate hazards, assess potential consequences, and establish a design and operating basis for safety.

Hazard and operability analysis (HAZOP): Qualitative hazard analysis technique to identify and evaluate process hazards and potential operating problems; focuses on a detailed and systematic examination of process deviations and their consequences.

Human factors: Discipline concerned with designing machines, operations, and work environment to match human capacities and limitations.

Hydrolysis: Chemical reaction of a substance with water; may lead to undesired runaway reactions and generation of gaseous molecules, such as hydrogen, hydrogen chloride, and alkanes.

Impact or thermally sensitive material: Material that decomposes rapidly when subjected to heat or impact, resulting in a potentially explosive release of energy.

Layers of protection: Multiple, redundant, or diverse safeguards to prevent an incident from occurring regardless of the initiating event or the performance of any single safeguard.

Management system: Structured, systematic method to implement an identified set of activities with assigned responsibilities and accountability.

Mixing calorimetry: Technique used to measure heat evolved upon instantaneous mixing of two or more chemicals; usually designed to be rapid (15 to 45 minutes), operating over the range of -50 to 200 degrees Celsius (°C).

Monomers: Chemicals that are the simple starting units from which polymers are made; they are reactive and sometimes unstable under ambient conditions.

Nitration: Chemical reaction of a substance in which the nitro group (-NO_2) is introduced into the molecule; often accomplished under highly reactive conditions using mixtures of nitric and sulfuric acids at high temperatures. Byproducts of the reaction may have explosive properties; if reaction control is lost, may lead to vigorous and strongly exothermic runaway reactions due to oxidation of the reactants.

Oxidation: Chemical reaction in which the oxidation state of a molecule increases due to the abstraction of electrons; often occurs when oxygen or other oxidizing material combines with the reacting substance.

Oxidation-reduction (redox): Chemical reaction in which an element loses (oxidation) or gains (reduction) an electron.

Oxidizer: Material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion.

Polymer: Large chemical molecule made up of repeating smaller units (e.g., polyethylene is a synthetic polymer made up of repeating ethylene units).

Polymerization: Chemical reaction in which one or more relatively simple molecules (monomers) combine to form a more complex compound (polymer).

Process hazard analysis: Organized effort to identify and evaluate hazards associated with chemical processes; normally involves the use of qualitative techniques to identify and assess the significance of hazards.

Process-specific factors: Conditions such as temperature, pressure, quantities handled, chemical concentrations, catalytic effects, and addition rates.

Process life cycle: All phases of a process from its conception through chemical and process research and development (R&D), engineering design, construction, commissioning, commercial operation, major modification, and decommissioning.

Public: Any person other than employees or contractors at or near a facility.

Public impact: Known injury to the public, offsite evacuation, or shelter-in-place.

Reactive incident: Sudden event involving an uncontrolled chemical reaction–with significant increases in temperature, pressure, or gas evolution–that has caused, or has the potential to cause, serious harm to people, property, or the environment.

Reactive hazard: Reactive properties and physical conditions of a single chemical or mixture that have the potential to generate heat, energy, and gaseous byproducts that have the potential to do harm.

Reactivity: Tendency of substances to undergo chemical change.

Reaction calorimetry: Chemical testing technique that determines thermodynamic and kinetic information on a desired reaction under conditions closely similar to those of a larger-scale plant; measures heat flow (production of desired process) and product generation (without knowledge of heat of reaction), and facilitates isothermal and temperature-ramped experiments.

Root cause: Primary reason why an incident occurred, developed through systematic analyses.

Runaway reaction: Reaction that is out of control because the heat generation rate exceeds the rate at which heat is removed to cooling media and surroundings.

Self-reactivity: Chemical reaction that involves only one chemical substance.

Thermal gravitational analysis (TGA): Chemical testing technique that precisely measures weight loss (due to gas-forming reactions) as a function of temperature and time.

Toll manufacturer: Facility that blends, mixes, processes, or packages chemicals.

Worst case scenario: The most severe postulated scenario involving an uncontrolled reaction.

Water reactive: Substance that reacts with water, often producing a vigorous exothermic reaction.

APPENDIX B: Surveys

B.1 Industry Survey

The U.S. Chemical Safety and Hazard Investigation Board (CSB) conducted a survey of companies that store, handle, and process chemicals. The objective of the survey was to examine current management practices with regard to reactive hazard management. Survey responses served primarily to highlight good practices, but also to point out areas for potential improvement. The survey questionnaire is posted on the CSB website at www.chemsafety.gov/info/Reactives.Survey.Final.pdf.

The survey was designed, administered, and analyzed by CSB staff with the support of EQE International, a consulting company with expertise in chemical process safety. Questions focused on the application of systematic programs, procedures, and practices for reactive chemicals management at the site level. Respondents were asked to provide details about good management practices in all phases of the manufacturing life cycle, including research and development (R&D), engineering, capital projects, commissioning, plant operations, and management of change (MOC). Where possible, respondents were asked to provide information about actual routine practices.

The nine surveyed companies volunteered to participate. Industry trade associations (American Chemistry Council [ACC], National Association of Chemical Distributors [NACD], Synthetic Organic Chemical Manufacturers Association [SOCMA]) and professional societies (Center for Chemical Process Safety [CCPS]) were asked to identify possible survey candidates–small, medium, and large sites or companies with reactive chemical hazard management programs or practices in place. As such, the survey was not intended to represent the practices of the chemical industry as a whole; in fact, the survey respondents more likely represent the “upper tier” of companies/ facilities handling reactive chemicals and managing the related hazards.

To supplement the industry survey, CSB staff conducted five selected site visits at facilities that have implemented programs for managing reactive hazards. The first-hand information gathered in these visits provided an understanding of the challenges involved in developing a systematic management program for reactive hazards.

All nine survey participants were primarily engaged in chemical manufacturing, representing synthetic organic chemicals, pharmaceuticals, specialty chemicals, fine organics, polymers, agrochemicals, and contract manufacturing. Most considered their sites to use many reactive chemicals and highly reactive chemicals. Interpretation of the term "highly reactive" was left to the participant. Seven of the nine survey respondents were member companies of ACC; four of nine were member companies of SOCMA; and five of nine were CCPS sponsors.

Considering the limitations of the industry survey–including the small number of respondents–it is important to also recognize that the conclusions are limited. Although representative small, medium, and large companies and sites were surveyed, the conclusions of this investigation do not support a differentiation among the practices of small versus large companies.

B.2 SOCMA Survey

SOCMA conducted a survey of members during its April 2001 Responsible Care Conference on Managing Reactive Chemicals. However, eight of the 10 respondents represented facilities with less than 100 employees.

APPENDIX C: Site Visits

C.1 Company Profiles

Company A is a major pharmaceutical manufacturer with worldwide operations. The U.S. Chemical Safety and Hazard Investigation Board (CSB) staff visited a site with both pilot-plant facilities and pharmaceutical manufacturing operations. The company is continually developing new and innovative chemistry, which results in frequent changes in the chemicals handled and manufacturing techniques used.

Company B is a diversified chemical manufacturing company with worldwide operations. CSB staff visited the corporate headquarters, which also houses extensive chemical manufacturing operations, including thermal hazards testing capability. CSB met with corporate staff, site manufacturing personnel, and thermal hazards chemists. The Company B testing laboratory evaluates a range of chemicals.

Company C is a small custom chemical manufacturer. Contract manufacturing accounts for its entire business. CSB staff visited a small manufacturing site with several batch chemical manufacturing operations. The nature of custom chemical manufacturing translates into very frequent changes in chemicals handled and processed.

Company D is a large pharmaceutical manufacturer with worldwide operations. CSB staff visited a pilot-plant facility and thermal hazards laboratory. Pilot-plant operations included the use of several batch chemical reactors. Like Company A, this company also frequently changes chemicals handled and manufacturing techniques.

Company E is a large chemical manufacturer with worldwide operations. CSB staff visited a medium-sized manufacturing site. Operations included storage and handling/processing of monomers, as well as extensive batch polymerization. The site uses standardized manufacturing methods and typically handles a specific set of chemicals.

C.2 Reactive Hazard Management Practices

C.2.1 Company A (Major Pharmaceutical Manufacturer)

C.2.1.1 Program Philosophy

- Reactive chemical hazard management is one element of an overall process safety program and is emphasized through thermal hazards analysis.
- Capabilities and practices are driven by the business need for rapid scaleup and high product quality.
- The corporate environmental health and safety (EHS) group provides technical resources (including expertise in reactive chemicals).
- The corporate research and development (R&D) facility has sophisticated thermal hazards capability/expertise.

C.2.1.2 Hazard Identification and Testing

- The company employs a phased approach to identify hazards, as outlined below:

Company A, Hazard Identification

Stage	Activity
Research	Literature search
Pilot plant (process development)	Screening test prior to pilot plant
Production	Additional tests as indicated by process hazard analysis (PHA)

- Scaleup to pilot plant is the key step in identifying and controlling reactivity hazards.
- A checklist approach is used to gather process safety information (PSI) prior to scaleup to pilot plant.
  - ***Basic process/chemical data:*** material safety data sheet (MSDS), special handling requirements, pressure, temperature, gaseous byproducts, and waste streams; includes a list of potentially hazardous chemical interactions.
  - ***Reaction safety:*** thermal test data, hazardous bond groups, and exothermic reactions.
  - ***Powder handling/milling:*** dust explosion issues.
- The company is beginning to use chemical interaction matrices as an input to PHA review.
- The company has a well-equipped laboratory for thermal hazards screening and sophisticated reaction calorimetry.
- Small quantities and the high cost of making the product limit the amount of material available for R&D testing.
- Differential scanning calorimetry (DSC) and dust explosion tests are usually conducted before a new chemical goes into the pilot-plant phase.
- Thermal hazards data are accessible through the company intranet.

C.2.1.3 Hazard Evaluation

- The company conducts process hazards evaluation of all new or modified products/processes.
- PHA techniques involve a combination of "what if" for unit operations and hazard and operability (HAZOP) for both equipment- and procedural-based deviations.
- Thermal hazards testing staff plays a key role on the PHA team.

- The thermal hazards laboratory, in consultation with pilot-plant engineering, typically assesses emergency venting scenarios and requirements for runaway reaction hazards.
- Over 1,300 equipment configuration changes per year account for extensive use of management of change (MOC).

C.2.1.4 Risk Reduction/Controls

- Process hazard analysis forms the basis for identifying needed controls.
- Small-scale batch equipment is typically "over designed" for multipurpose use.
- The company has in place numerous checks and balances to prevent human error; quality assurance (QA)-driven processes require validation (secondary checks/rechecks) of operator actions, sampling/analysis, etc.

C.2.1.5 Communications and Training

- The pharmaceutical industry has no official EHS trade group that develops codes of practice equivalent to Responsible Care.
- The company recognizes the need for better and more formal sharing of lessons learned and for support of an improved industry incident database.

C.2.2 Company B (Diversified Chemical Manufacturer)

C.2.2.1 Program Philosophy

- The reactives program focuses on preventing uncontrolled chemical reactions that have the potential to cause loss or injury or environmental harm.

- Reactive hazards are addressed separately and uniquely from other process safety factors.
- The reactives program involves the interaction of several diverse technical experts to study the chemistry and process, looking for risk reduction opportunities; in-house expertise is available to handle reactive chemical issues.
- The company perceives its reactives program as adding value rather than being regulatory driven.
- Value is defined as having a competitive advantage; reducing damage to the facility, property, and equipment; reducing injuries; and being accepted as a good member of the community.
- The company advocates an outside-in approach, using reviewers from outside the technology or business to help identify hazards that may have been overlooked.
- Program philosophy focuses on identifying potential accident scenarios.
- The reactives program emphasizes both self-reactivity (instability) and binary reactivity.
- The company strongly supports owner responsibility on the part of the production leader–knowing reactive chemicals and their process hazards, participating in the establishment and maintenance of corporate memory, and demonstrating a fundamental understanding of reactive chemical hazards within the facility within 90 days of any new assignment.
- Corporate guidelines require that individuals develop an understanding of reactive hazards based on data collection, hazard evaluation, training, etc.
- Corporate standards, approved by the EHS board, are established for audit/review; performance-based training; MOC, which is approved by the area production leader; and training, which addresses worst case scenarios, cardinal rules, and lines of defense.
- There are corporate guidelines for application of the reactive chemicals program, formation of a reactive chemicals team, project reviews, and chemicals testing.

- Key deliverables are capital project reviews; new production leader reviews; existing facility hazard reviews on a 3- to 5-year cycle; research facility reviews; and a formal training and awareness program.
- The company offers as key resources a global standard, how-to guidelines, testing laboratories/expertise, and computerized tools.
- The company offers multidisciplinary support through research, manufacturing, 27 technology centers, and EHS.
- Technology centers provide critical functions in establishing corporate memory, documenting findings and implementing preventive measures, submitting data to CCPS, sharing operating knowledge across the company, and establishing effective process technologies.

C.2.2.2 Hazard Identification and Testing

- Key elements of reactive hazard identification are owner-initiated review, chemistry review, review of unit operations, review of scenarios, definition of required testing, records testing, and interpretation of results for owner.
- Testing centers are geographically distributed and include contractor support.
- Testing includes screening (e.g., literature research, mixing calorimetry, thermodynamic calculations, estimation of heats of reaction, DSC, flash point calculations), quantitative assessment (e.g., accelerated rate calorimetry, specialized calorimetry), and scaleup (vent size packaging [VSP], modeling, reaction calorimetry).
- The program focuses on binary and higher levels of reactivity in addition to self-reactivity (instability).
- An incompatibility-mixing chart facilitates the prediction of reactive mixing hazards.
- The reactive testing laboratories cover fire, dust, kinetics, high energy, and thermodynamics.

C.2.2.3 Hazard Evaluation

- The company hazard review process was revised in June 1997 to combine reactive chemicals, loss prevention, distribution risk review, EHS review for safety and loss, project risk review, and technology center review.
- Each major company site has a hazard review committee to administer the standard and guideline. The committee includes representatives from process safety, chemistry, reactive chemistry, manufacturing, process engineering, pilot-plant operations, and the technology center.
- The outside-in approach brings people without specific knowledge of a process into reviews.
- Flowcharts are used for process overview; analysis of causes and consequences, lines of defense, and testing data requirements; and review of hazard checklist, schedule, and followup on recommendations.
- Review of work progress includes scenarios for inadvertent mixing, reaction loss-of-control, and instability of materials.

C.2.2.4 Risk Reduction/Controls

- The need for additional controls is identified through design standards, reactive chemicals process hazard analysis, and technology centers.

C.2.2.5 Communications and Training

- The communications/training challenge is to retain learning from incidents in corporate memory to prevent recurrence.
- The key premises of corporate memory are to never have to pay for an incident more than once, to learn from history and leverage across all plants and technologies, and to derive benefit from the experience of other companies.

- Eighty percent of incidents are due to known chemistry hazards; it has been 6 years since the company's last "unknown" chemistry incident.
- Technical centers provide small sites with access to data and technical expertise for reactive chemicals.
- The company maintains global databases for 60,000+ tests, prior incident data for 22 years, and databases of all credible reactive chemical scenarios with key lines of defense for all technologies.
- Small sites generally have little/no capability in R&D, process engineering, reactive chemical testing, and chemistry.
- A global reactive chemical newsletter is published regularly and read by over 4,000 employees worldwide.

C.2.3 Company C (Custom Chemical Manufacturer)

C.2.3.1 Program Philosophy

- Management considers reactive hazard management as a subset of process safety management.
- The company has specific procedures for reactive chemicals hazard management.
- Management takes a proactive approach in terms of Occupational Safety and Health Administration (OSHA) and U.S. Environmental Protection Agency (EPA) requirements. The company applies the Process Safety Management (PSM) Standard and the Risk Management Program (RMP) regulation to processes that normally do not require coverage (under threshold quantities) because it makes good business sense.
- Management focuses on safety-oriented programs to prevent business interruptions.
- Reactive hazards play a significant role in deciding whether to manufacture new chemicals onsite.

- Although the company has very limited safety resources onsite, management perceives safety as added value and hires individuals from organizations with a good safety culture. The management commitment to safety is clearly evident in each aspect of the safety program.
- When a customer requests production of a chemical, the steering committee reviews the inquiry and determines the initial feasibility of production; within 1 to 2 weeks, the committee renders a go-no go decision to the customer. Process safety plays a significant role in the decision process.

C.2.3.2 Hazard Identification and Testing

- The customer requesting production of a chemical provides reactive hazard information (literature reviews, thermal test data, etc.).
- If the information is insufficient to assess reactive hazards, additional data are requested, such as thermal screening test data.
- When considering development of a new process for a customer, a team is formed to assess potential hazards (including reactive) and to determine the technically feasibility of production.
- Potential hazards (flammability, corrosivity, etc.) are reviewed to identify concerns regarding the storage and handling of reactive chemicals, and information is obtained from raw material suppliers (e.g., technical bulletins). Flashpoint, DSC, or differential thermal analysis (DTA) testing is typically done by the customer.
- If potential reactive hazards are identified within a proposed process, the customer is asked to provide additional test data. The company occasionally contracts testing services.

C.2.3.3 Hazard Evaluation

- Expert opinion is essential in the hazard evaluation process.
- A hazard evaluation is performed before assessing the technical feasibility of a new process. Chemical handling/storage criteria, critical process conditions, quality measurements, thermal hazards, and post-campaign cleanup are considered in the introduction of any new process/product.
- Once a new process is identified as feasible, it goes through a process hazard analysis (usually HAZOP) to evaluate issues such as reactive chemistry.
- Hazard evaluations are conducted in a team environment that typically includes a process engineer, EHS staff, a chemist, maintenance, a production operator, and the customer.
- Design reviews are conducted to refine requirements. Hazards are introduced to plant operators following laboratory work, EHS review, capital requirements review, and process hazard analysis. Reactivity is addressed during process hazard analysis and the initial review.
- A HAZOP is performed on all new chemicals following process review, preliminary equipment review, and development of preliminary standard operating procedures (SOP). “What-if” and checklists are typically used to review a process without process design and chemistry changes.
- Process chemistry changes are evaluated for quality and EHS impacts.
- MOC and SOPs are vehicles for approving and communicating change.

C.2.3.4 Risk Reduction/Controls

- Process hazard analysis leads to risk reduction/control recommendations.
- Risk reduction/control is primarily accomplished through design measures, SOPs, and training.

C.2.3.5 Communication and Training

- Once a new chemical is introduced into the plant, employees receive on-the-job training on the new production process, which covers safe operating limits, process controls, emergency situations, etc.
- Operators have levels of expertise. The most experienced operators (level 3) generally perform the majority of the process-related functions. Entry-level operators are not assigned this work, and level 2 operators perform these functions with supervision.

C.2.4 Company D (Large Pharmaceutical Manufacturer)

C.2.4.1 Program Philosophy

- Reactive chemical hazard management is one element of an overall process safety program and is emphasized through thermal hazards evaluation.
- The program is driven by previous incidents, concern for the community, and business factors.

C.2.4.2 Hazard Identification and Testing

- Hazard identification is built into the design process.
- Testing is conducted regardless of supplier information.
- The program includes a preliminary screening test, team-based screening, reactive evaluation, and process hazard analysis.
- The reactive hazard evaluation protocol is nonprescriptive; the type and quantity of testing is based on judgment.
- National Fire Protection Association (NFPA) ratings are used for original screening; no chemicals with NFPA ratings of 3 or 4 are used at the site.

- The company has a full range of reactive chemical test equipment onsite.

C.2.4.3 Hazard Evaluation

- A complete evaluation is conducted during process development, including testing and system evaluation of process aberrations.
- A multidisciplinary team approach is used during all phases of evaluation.
- A binary interaction matrix is developed for all materials in the process, including air and rust.
- The PHA method is case dependent, focused on procedure, and required for every pilot-plant run.
- Process hazard analysis considers equipment failure, human factors–including errors of omission and commission, and previous incidents.

C.2.4.4 Risk Reduction and Controls

- Risk is identified at various stages in the process.
- Special setups are used to control risk.
- The process hazard analysis identifies operator training needs.
- Risk assessment is qualitative.

C.2.4.5 Communications and Training

- Incident data are kept in a local database and shared both site- and company-wide.
- There is no formal pharmaceutical industry trade group that dicusses safety issues.

C.2.5 Company E (Large Chemical Manufacturer)

C.2.5.1 Program Philosophy

- Reactive chemicals hazard management is part of the overall process safety program, which is applied regardless of regulatory coverage.
- Codes of practice developed at the corporate level promote standardization throughout the company.

C.2.5.2 Hazard Identification and Testing

- Reactive chemical testing is done at the corporate level.
- The company maintains a list of chemicals that are considered to be highly hazardous based on such characteristics as flash point (less than 100 degrees Fahrenheit [°F]), self reactivity, water reactivity, boiling point, and toxicity.

C.2.5.3 Hazard Evaluation

- Plants are periodically audited against rigid corporate guidelines for safe operation.
- Multidisciplinary teams conduct process hazard analyses.
- Exceptions to corporate guidelines are made by committee.
- Process hazard analyses are conducted in accordance with formal procedure, with piping and instrumentation diagrams for reference.

C.2.5.4 Risk Reduction and Controls

- The company generates a standard MSDS for all raw materials and products.
- Corporate guidelines dictate procedures for safe limits of operation and response to a runaway reaction.
- Color-coded buckets and storage locations protect against inadvertent mixing of incompatible chemicals.
- An interaction matrix is available on the intranet.

C.2.5.5 Communications and Training

The company offers comprehensive training on plant safety policies.

APPENDIX D: Resources

D.1 Guidelines

There are extensive writings on reactive hazard management. The term "guidelines" is used herein to refer to nonmandatory good practices that are developed through industry consortia, committees, professional societies, and other bodies.

CSB analysis included guidelines that focus primarily on the process safety of reactive chemicals; other good practices that might include some elements of reactive process safety were not included.

D.1.1 CCPS Guidelines Series

In 1985, the American Institute of Chemical Engineers (AIChE) established the Center for Chemical Process Safety (CCPS) to aid in the prevention or mitigation of catastrophic chemical accidents. CCPS publishes a series of Guidelines books and bulletins on good management and engineering practices, including the following on reactive hazard management:

- *Guidelines for Chemical Reactivity Evaluation and Application to Process Design,* 1995

  This publication describes the principles for evaluating chemical reactivity as an element of chemical process design. It outlines methods for identifying reaction hazards and establishing safe operating conditions. Special emphasis is placed on state-of-the-art theory and testing methods, as well as inherent safety principles. The intended audience is those involved in R&D, pilot-plant, process design, and (to a lesser degree) commercial plant operations. The guidelines focus on technical issues; they are not intended to be a manager's guide to reactive hazard management.

- *Guidelines for Safe Storage and Handling of Reactive Materials,* 1995

  This book summarizes industry practices for design and operation of reactive chemical storage and handling systems. Special emphasis is placed on the engineering design of storage and handling systems. The intended audience is primarily process engineers or others with technical responsibility–not managers. The guidelines do not cover chemical reactions, mixing, or blending.

- *Safety Alert, Reactive Material Hazards,* 2001

  This 10-page bulletin offers an introduction to reactive material hazards. It is organized around four key questions: Do you handle reactive materials? Can you have reactive interaction? What data do you need to control these hazards? What safeguards do you need to control these hazards?

D.1.2 Other Guidance

Other international publications offer guidance on reactive hazard management, such as:

- *Chemical Reaction Hazards, A Guide to Safety,* 1997

  The purpose of this guidebook, written by Barton and Rogers for the Institution of Chemical Engineers (IChemE), is to provide a basis for good practice in assessing reactive hazards. It is written for those responsible for design and operation of chemical plants. It addresses hazards from uncontrolled exothermic activity in batch and semibatch chemical reaction systems as well as associated process equipment.

- *Designing and Operating Safe Chemical Reaction Processes,* 2000

  The intent of this book, published by the Health and Safety Executive (HSE) of the United Kingdom, is to guide programs for small- and medium-sized chemical manufacturing companies using batch and semibatch manufacturing processes. Its intended audience is those directly responsible for the development, design, and operation of chemical plants and processes, particularly process chemists and process engineers. The objectives of the HSE guidance are to:

  - Increase awareness of potential reactive hazards.
  - Assist in the assessment of risks.
  - Provide a systematic approach for the design, operation, and control of chemical reactions in batch and semibatch processes.
  - Advise on safe management procedures.

- Advise on maintenance, training, and information needs to prevent and control reactive hazards.

D.2 Future Guidance

At least two efforts are currently underway to develop additional guidance in the area of reactive hazard management:

- CCPS project on the management of reactive chemical hazards

  As the result of a number of recent incidents caused by inappropriate handling of reactive chemicals, CCPS initiated a project in 2001 to develop additional management guidelines for reactive hazards. A CCPS technical steering committee documented the urgent need for comprehensive "best practice" guidelines.

  The audience is expected to be process safety professionals, engineers, chemists, and other technical personnel who generate data and design processes that involve reactive chemicals. Manufacturing personnel who operate such facilities are also expected to benefit through improved understanding of risks.

- Hazard Assessment of Highly Reactive Systems Thematic Network (HarsNet).

  HarsNet is a thematic network project sponsored by the European Commission's Industrial and Materials Technologies Program. It is coordinated through the Instituto Químico de Sarrià, with participation by government organizations, universities, major companies (e.g., Dow, BASF, and CIBA), and private testing services.

  The objectives of HarsNet are to:

  - Analyze existing methodologies and prepare guidelines for thermal hazard assessment and prevention.
  - Disseminate information and provide technical support to small- and medium-sized enterprises.

  HarsNet maintains that reactive chemical testing and analysis is too complex for most small- and medium-sized companies because of the wide spectrum of processes and equipment involved. The project seeks to provide an industry guide for estimating the thermal hazard of a chemical synthesis without sophisticated testing and analysis.

D.3 ASTM Codes and Standards

The American Society for Testing and Materials (ASTM) is a not-for-profit organization that provides a forum for the development and publication of voluntary consensus standards for materials, products, systems, and services.[1] One ASTM committee (E27) develops standardized physical and chemical test methods on the hazard potential of chemicals, including but not limited to reactive hazards. The committee has developed standard analytical methods for calorimetry studies in addition to a standard guide for determining binary chemical compatibility (ASTM, 2000).

ASTM also distributes the computer program CHETAH (Chemical Thermodynamic and Energy Release Evaluation), a tool for predicting both thermodynamic properties and certain reactive hazards associated with a pure chemical, a mixture of chemicals, or a chemical reaction.

D.4 Select Resources on Reactive Hazards

A variety of tools and resources are available to aid in the recognition of reactive hazards. Table D-1 provides a list and brief description of selected literature resources and computerized tools.

[1] ASTM standards are developed voluntarily and used voluntarily. They become legally binding only when a government body makes them so or when they are cited in a contract.

Table D-1
Select Resources on Reactive Hazards

Title	Contents	Source
Bretherick's Handbook of Reactive Chemicals	Summaries of reactivity, incompatibility, and other dangerous properties of individual substances either alone or in combination; case histories	Butterworth-Heinemann
Sax's Dangerous Properties of Industrial Materials	Summaries of reactivity, incompatibility, and other dangerous properties; applicable standards and recommendations; hazard rating	VanNostrand Reinhold (Lewis)
Rapid Guide to Chemical Incompatibilities	Summaries of known effects of dangerously reactive substances	Wiley and Sons (Pohanish and Greene)
The Chemical Reactivity Worksheet	Database of reactivity information for more than 4,000 common chemicals; includes information on special hazards of each chemical and whether a chemical reacts with air, water, or other materials; predicts the reactivity between two chemicals	National Oceanic and Atmospheric Administration (NOAA)
CASREACT	Database of abstracts related to reaction chemistry, including hazard/safety information	American Chemical Society (Chemical Abstracts Service)
Chemical Hazards Response Information System (CHRIS)	Database on chemical and physical properties; guides to compatibility of chemicals	U.S. Coast Guard (USCG)
Material Safety Data Sheets (MSDS)	Data on chemical and physical properties, and other dangerous properties	Chemical manufacturer
Guidelines for Chemical Reactivity Evaluation and Application to Process Design	Fundamentals for identification and evaluation of reactive hazards	CCPS
Guidelines for Safe Storage and Handling of Reactive Materials	Design of storage and handling systems for reactive chemicals	CCPS
Reactive Material Hazards, What You Need to Know	Introduction to reactive issues	CCPS
Safety and Runaway Reactions	Articles on reactive hazards	Institute for Systems Informatics and Safety
Chemical Reaction Hazards, A Guide to Safety	Fundamentals of reactive hazards	IChemE (Barton and Rogers)
Designing and Operating Safe Chemical Reaction Processes	Safe design and operation of plants and processes for chemical reactions	HSE
Safety of Reactive Chemicals and Pyrotechnics	Evaluation of reactive hazards and case histories	Elsevier (Yoshida, Wada, and Foster)

Table D-1 (cont'd)

Title	Contents	Source
CRC Handbook of Chemistry and Physics	Data on chemical properties, especially thermochemistry, kinetics, and molecular structure	CRC Press (Lide)
Encyclopedia of Chemical Technology	Articles on chemical manufacturing of either single substances or groups of substances	Wiley and Sons (Kirk-Othmer)
Chemistry of Hazardous Materials	Fundamentals of hazardous properties	Brady, Prentice-Hall (Meyer)
Ashford's Dictionary of Industrial Chemicals	Hazardous properties of particular chemicals	Wavelength Publications
A Comprehensive Guide to the Hazardous Properties of Chemical Substances	Chemical structure of compounds and hazardous properties	Wiley and Sons (Patnaik)
Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens	Data on chemical properties and chemical incompatibility	William Andrew Publishing
Hazardous Chemicals Desk Reference	Chemical property data on safe handling and storage, applicable standards and recommendations, hazard rating	Wiley and Sons (Lewis)
NFPA 491M Manual of Hazardous Chemical Reactions	Data on hazardous chemical reactions	National Fire Protection Association (NFPA)
NFPA 43B Storage of Organic Peroxide Formulations	Hazards of peroxides	NFPA
NFPA 49 Hazardous Chemicals Data	Chemical hazard information, including reactivity data	NFPA
NFPA 325 Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids	Chemical hazard information, including reactivity ratings	NFPA
NFPA 430 Storage of Liquid and Solid Oxidizers	Hazards of oxidizers	NFPA

APPENDIX E:
Hazard Investigation Data Sources

Title	Source	CSB Action
Process Safety Incident Database	Center for Chemical Process Safety (CCPS)/American Institute of Chemical Engineers (AIChE)	Proprietary - unavailable
National Response Center (NRC) Data	U.S. Coast Guard (USCG)	Retrieved information
Integrated Management Information System (IMIS)	Occupational Safety and Health Administration (OSHA)	Retrieved information
The Accident Database	Institution of Chemical Engineers (IChemE)	Retrieved information
Accidental Release Information Program (ARIP)	U.S. Environmental Protection Agency (EPA)	Retrieved information
RMP*Info (Five-Year Accident History Data)	EPA	Retrieved information
Major Hazard Incident Data Service (MHIDAS)	Health and Safety Executive, United Kingdom (HSE)	Retrieved information
Chemical Incident Reports Center (CIRC)	U.S. Chemical Safety and Hazard Investigation Board (CSB)	Retrieved information
Fire Incident Data Organization Database	National Fire Protection Association (NFPA)	Retrieved information
Reports of Chemical Safety Occurrences at U.S. Department of Energy (DOE) facilities	DOE	Retrieved information
Process Safety Code Measurement System	American Chemistry Council (ACC)	Reviewed only
National Fire Incident Reporting System	U.S. Fire Administration (USFA)	Reviewed only
TNO Process Safety and Dangerous Goods (FACTS)	Netherlands Organisation for Applied Scientific Research	Reviewed only
Major Accident Reporting System (MARS)	European Communities Major Accident Hazard Bureau (MAHB)	Reviewed only
Mary Kay O'Connor Process Safety Center Database	Texas A&M University	Reviewed only
Hazardous Substances Emergency Events Surveillance (HSEES)	MAHB	Reviewed only
The Community Documentation Centre on Industrial Risk	MAHB	Reviewed only

Title	Source	CSB Action
Awareness and Preparedness for Emergencies at Local Level (APELL)	United Nations Environmental Programme (UNEP)	Reviewed only
Acute Hazardous Events Database	EPA	Reviewed only
Census of Fatal Occupational Injuries	U.S. Bureau of Labor Statistics	Reviewed only
Process Safety Database	American Petroleum Institute (API)	Reviewed only
The European Health and Safety Database (HASTE)	European Foundation for the Improvement of Living and Working Conditions	Reviewed only
Various Chlorine Related Incident Reports	Chlorine Institute	Retrieved information
Hazardous Materials Incident Reports	National Transportation Safety Board (NTSB)	Retrieved information
Fire Incident Reports	NFPA	Retrieved information
Annual Loss Prevention Symposium (CD ROM)	CCPS	Retrieved information
Bretherick's Handbook of Reactive Chemical Hazards, 6th Ed.	Butterworth-Heinemann	Retrieved information
Loss Prevention in the Process Industries	F. P. Lees	Retrieved information
Large Property Damage Losses in the Hydrocarbon Chemical Industries, A Thirty-Year Review, 18th Ed.	Marsh and McLennan	Retrieved information
NAPP Technologies Chemical Accident Investigation Report	EPA/OSHA	Retrieved information
Prevention of Reactive Chemical Explosions	EPA	Retrieved information
How to Prevent Runaway Reactions	EPA	Retrieved information
Tosco Avon Refinery Chemical Accident Investigation Report	EPA	Retrieved information
Surpass Chemical Company Chemical Accident Investigation Report	EPA	Retrieved information
Incidents in the Chemical Industry Due to Thermal Runaway Reactions	Barton and Nolan	Retrieved information

Title	Source	CSB Action
Lessons From Disaster	T. Kletz	Reviewed only
What Went Wrong?	T. Kletz	Reviewed only
Chemical Process Safety, Lessons Learned from Case Histories	R. Sanders	Reviewed only
Explosions in the Process Industries	IChemE	Reviewed only
Chemical Reaction Hazards, A Guide to Safety, 2nd Ed.	IChemE	Reviewed only
NFPA 491 Guide for Hazardous Chemical Reactions	NFPA	Reviewed only
Proceedings of the 2nd International Symposium on Runaway Reactions, Pressure Relief Design, and Effluent Handling	CCPS	Reviewed only
Occurrence and Impact of Unwanted Chemical Reactions, Journal of Loss Prevention in the Process Industries	B. Rasmussen	Reviewed only
Origins of Unwanted Reactions, Report M-2631	B. Rasmussen	Reviewed only
Unwanted Chemical Reactions in the Chemical Process Industry	B. Rasmussen	Reviewed only
Intl. Conference and Workshop on Process Industry Incidents	CCPS	Reviewed only
Chemical Reaction Hazards and the Risk of Thermal Runaway	HSE	Reviewed only
Safety of Reactive Chemicals and Pyrotechnics, Industrial Safety Series, Volume 5	Yoshida et al.	Reviewed only
Safety and Runaway Reactions	Mitchison and Snyeder	Reviewed only
Safety of Chemical Batch Reactors and Storage Tanks	Benuzzi and Zaldivar	Reviewed only

APPENDIX F: Statistical Review of Occupational Fatalities

The U.S. Chemical Safety and Hazard Investigation Board (CSB) reviewed Bureau of Labor Statistics (BLS) data (1996–2000) on occupational fatalities to determine the significance of the reactive incident problem in the context of chemical process safety.[1] Table F-1 summarizes this information.

As described in Section 3.1, CSB data represent only a sampling of reactive incidents and should not be directly compared to BLS data, which offer a more complete accounting of occupational fatalities. Nonetheless, CSB data provide an indication that a significant number of fatalities from process safety incidents involve reactive hazards.

Table F-1
Review of Occupational Fatalities

Year	1996	1997	1998	1999	2000	Total
Total occupational fatalities	6,112	6,218	6,026	6,023	5,915	30,294
Fatalities in the chemical manufacturing industry (a)	40	62	91	78	41	272
Fatalities in the chemical manufacturing industry due to fire, explosion, and toxic releases (b)	16	23	46	46	16	147
Fatalities from reactive incidents in data collected by CSB	2	8	0	10	1	21
Fatalities from reactive incidents in the chemical manufacturing industry in data collected by CSB	0	3	0	7(c)	1	11

(a) Chemical manufacturing industry (SIC Division D Group 28).
(b) Incidents that resulted in fires, explosions, and toxic releases are assumed to be process safety incidents.
(c) In addition to occupational fatalities, there was also one public fatality from a reactive incident during 1999.

[1] CSB analyzed BLS fatality data only within SIC Division D Group 28 (chemical manufacturing and allied products). Thus, the data presented in Table F-1 are conservative and do not include fatalities that occurred to contractors or to personnel in other industries, such as petroleum refining, rubber products, or paper products. Contractor fatalities are documented within BLS according to the services the contract company provides. For example, in the ARCO incident there were 17 fatalities– five ARCO employees (a chemical manufacturer under SIC Group 28) and 12 contractors (who had been working at the facility for several years). The fatalities to the ARCO employees were recorded under SIC Division D Group 28. However, the 12 contractor fatalities were not attributed to the chemical manufacturing industry; they were grouped under the construction SIC. Thus, these 12 contractor fatalities would not have been included in our analysis of BLS data.

APPENDIX G: Identifying Hazards Using Chemical Reactivity Testing

This appendix, which briefly illustrates how testing can be an integral part of a reactive hazard management system, is provided to facilitate the discussion of alternative criteria for improving regulatory coverage in Section 8.0. It does not describe in detail testing methods, theory, or practical application. Further information on these topics is provided in Grewer (1994), CCPS (1995a; 1995b), IChemE (Barton and Rogers, 1997), and HSE (2000). The Glossary (Appendix A) briefly defines each analytical test.

Screening is typically used to indicate when more detailed testing is necessary. The Center for Chemical Process Safety (CCPS, 1995b; p. 90) explains that the objective of thermal stability screening is to obtain data on the possibility of exothermic (heat generating) reaction for mixtures or self-reaction for single substances. Screening calorimeters measure the energy produced by a reaction and the temperature at which energy is liberated. Differential screening calorimetry (DSC) is considered to be the primary screening test, though differential thermal analysis (DTA) is also used. Thermogravimetric analysis (TGA) can be used to screen for stability at high temperature through precise weight loss measurements.

Screening techniques are relatively cost-effective and require only a small chemical sample; however, they do not measure gas evolution or maximum pressure rise. A material is generally considered to be thermally stable if the temperature at which energy from reaction is first observed is at least 100 degrees Celsius (°C) above the maximum operating temperature of a process event under upset conditions (CCPS, 1995b; p. 93).

CCPS recommends more sensitive and sophisticated methods if screening calorimetry shows thermal instability at or near the temperature range of large-scale storage or processing (CCPS, 1995b; p. 94). The next logical choice is adiabatic calorimetry,[1] which uses

[1] In this context, the term "adiabatic" refers to calorimetry conducted under conditions that minimize heat losses to the surrounding environment to better simulate conditions in the plant, where bulk quantities of stored or processed material tend to minimize cooling effects. This class of calorimetry includes the accelerating rate calorimeter (ARC), from Arthur D. Little, Inc., and PHI-TEC from Hazard Evaluation Laboratory Ltd.

a larger sample and more advanced technology. This technique is more sensitive to detecting the onset temperature[2] for exothermic reactions, adiabatic temperature rise, and rate of reaction; it can also measure pressure rise in a closed vessel, an important parameter in reaction scaleup. Compared to screening calorimetery, this sophisticated technique more accurately measures the overall energy of reaction, though the tests tend to be more costly and time intensive.

A common theme of industry guidelines is that every test result must be individually interpreted because of limitations and variations in conditions, and the complexity of the instrument. Factors such as sample size, container material, and heating rate can greatly affect results. Therefore, personnel with appropriate training and experience should be consulted both before testing and for interpretation of results.

CCPS offers guidance on when to conduct testing for hazard identification. When designing processes for conducting chemical reactions, CCPS (1995a; p. 13) suggests that all materials be subject to screening tests even if no reactivity concerns are identified in the literature search or by expert judgment. In other guidance, CCPS (1995b; p. 85) states that that prior experience, theoretical evaluations, and expert opinion may be used to determine whether screening tests are necessary in designing storage and handling systems for reactive materials.

One of the factors that may be important in this determination is the possible rate of reaction. Theoretical evaluations can determine a large potential energy of reaction, but they do not determine how fast or slow that energy can be released. The rate of reaction can be the critical factor in determining the severity of the reactive hazard (CCPS, 1995b; p. 86). When such uncertainties arise, an expert opinion may be needed to determine whether chemical testing is necessary.

Five of nine respondents to the CSB survey frequently use both screening and more sophisticated approaches, including adiabatic

[2] Onset temperature is the lowest temperature at which the test first observes an exothermic (heat liberating) reaction.

calorimetry, to determine the thermal stability or compatibility of process materials. Seven of nine respondents use screening alone for chemical reactivity testing. The most often used testing objectives are:

- To determine the onset temperature of a runaway reaction using calorimetry.
- To determine thermal stability using screening tests.
- To determine gas evolution and maximum pressure rise.