ESSENTIAL PRACTICES FOR

Managing Chemical Reactivity Hazards

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Preface

For over 40 years, the American Institute of Chemical Engineers (AIChE) has been involved with process safety and loss prevention in the chemical, petrochemical, hydrocarbon processing and related industries. AIChE publications are information resources for chemical engineers and other professionals to better understand the causes of process incidents and offer ways to prevent them. The Center for Chemical Process Safety (CCPS), a directorate of AIChE, was established in 1985 to develop and disseminate information for use in promoting the safe operation of chemical facilities and processes with the objective of preventing chemical process incidents. CCPS activities are supported by the funding and technical expertise of over 80 corporations. Several government agencies and nonprofit and academic institutions also participate in CCPS endeavors.

With the support and direction of its advisory and management boards, CCPS established a multifaceted program to address the need for process safety technology and management systems to reduce potential exposures to the public, the environment, personnel and facilities. Over the past several years, CCPS has extended its publication program to include a "Concept Series" of books. These books are focused on more specific topics than the longer, more comprehensive *Guidelines* series and are intended to complement them. With the issuance of this title, CCPS has published 80 books.

In 1989, CCPS published the landmark *Guidelines for the Technical Management of Chemical Process Safety*. This publication, *Essential Practices for Managing Chemical Reactivity Hazards,* has been developed to provide companies, organizations and individuals guidance relating to management systems and hazard assessment protocols. This guidance is directed toward the safe handling, processing and storing of chemicals that might become involved in uncontrolled chemical reactions, either in fixed facilities or in transport containers. This publication provides some examples and recommendations for effective methods and practices for managing the hazards related to uncontrolled chemical reactions. The objective of the publication is to provide guidance, to any facility with chemical reactivity hazards, on ways to effectively address the difficult challenge of preventing loss, injury or environmental harm from uncontrolled chemical reactions. This publication is not intended to provide the only guidance on how to safely manage chemical reactivity hazards, but it does represent the result of a consensus of the development committee representing a number of chemical companies and consulting organizations.

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Abbreviations and Acronyms

ACC	American Chemistry Council
AIChE	American Institute of Chemical Engineers
APTAC	Automatic Pressure Tracking Adiabatic Calorimeter
ARC®	Accelerating Rate Calorimeter; Accelerating Rate Calorimetry
ARSST	Advanced Reactive Systems Screening Tool
ASTM	American Society for Testing and Materials
CANUTEC	Canadian Transportation Emergency Centre
CAS	Chemical Abstracts Service
CCPS	Center for Chemical Process Safety
CDC	Centers for Disease Control and Prevention (U.S.)
CFR	Code of Federal Regulations (U.S.)
CHEMTREC®	Chemical Transportation Emergency Center
CHETAH	Chemical Thermodynamic and Energy Release Program
CIRC	Chemical Incidents Report Center
CSB	U.S. Chemical Safety and Hazard Investigation Board
DCS	Distributed Control System
DIERS	Design Institute for Emergency Relief Systems
DOT	Department of Transportation
DPT	Decomposition Pressure Test
DSC	Differential Scanning Calorimeter; Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EPCRA	Emergency Planning and Community Right to Know Act

EPA	U.S. Environmental Protection Agency
HarsNet	Thematic Network on Hazard Assessment of Highly Reactive Systems
HAZOP	Hazard and Operability [Study]
HSE	UK Health and Safety Executive
IChemE	Institution of Chemical Engineers (UK)
ICSC	International Chemical Safety Card
IET	Insulated Exotherm Test
IPL	Independent Protection Layer
IPCS	International Programme on Chemical Safety
ISO	International Organization for Standardization (Geneva, Switzerland)
LEPC	Local Emergency Planning Committee
LOPA	Layer of Protection Analysis
MIC	Methyl Isocyanate
MIE	Minimum Ignition Energy
MOC	Management of Change
MSDS	Material Safety Data Sheet
NA	Not Applicable
NACD	National Association of Chemical Distributors
NFPA	National Fire Protection Association (U.S.)
NIOSH	National Institute for Occupational Safety and Health (U.S.)
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration (U.S.)
OSHA	U.S. Occupational Safety and Health Administration
PHA	Process Hazard Analysis
PSI	Process Safety Information
PSM	Process Safety Management
RCRA	Resource Conservation and Recovery Act
RMP	Risk Management Plan/Program
RSST	Reactive System Screening Tool
SADT	Self-Accelerating Decomposition Temperature
SETIQ	Sistema de Emergencias en Transporte para la Industria Quimica (Mexico)
SOCMA	Synthetic Organic Chemical Manufacturers Association

UK	United Kingdom
UN	United Nations
U.S.	United States [of America]
VSP	Vent Sizing Package
VSP2	Vent Sizing Package, version 2

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Introduction and Overview

1

A **chemical reactivity hazard**, as the term is used in this publication, is a situation with the *potential* for an *uncontrolled chemical reaction* that can result directly or indirectly in serious harm to people, property or the environment. The uncontrolled chemical reaction might be accompanied by a temperature increase, pressure increase, gas evolution or other form of energy release. It need not be explosive to result in serious harm. For example, gases evolved from a chemical reaction can be flammable, toxic, corrosive, hot, or can pressurize an enclosure to the point of rupture.

Chemical reactivity hazards have also been called *reactive hazards, reactive chemical hazards* and *chemical reaction hazards*. *Chemical reactivity* is analogous to other material hazards such as toxicity, corrosivity, flammability and dust explosibility. Chemical reactivity hazards are posed not only by *self-reacting materials* such as organic peroxides and polymerizing monomers, but also by uncontrolled *chemical interactions* (e.g., incompatibilities), even between substances that may not be generally considered *reactive chemicals.* Hence, a chemical reactivity hazard may not be a simple, intrinsic property of a material. The potential for an uncontrolled chemical reaction can take many forms, involving one or more intrinsic material properties as well as the conditions under which the material or materials are used. This is reflected in one of the conclusions reached by an investigation into chemical reactivity hazards conducted by the U.S. Chemical Safety and Hazard Investigation Board:

> 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 focus exclusively on the inherent properties of individual chemicals. (CSB 2002b)[1]

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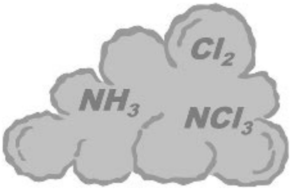
[1] All references are listed together in the References section of this publication.

Damaging fires are uncontrolled chemical reactions, so fire hazards involving ordinary flammable and combustible materials could be included in the above definition of chemical reactivity hazards. However, this publication seeks to supplement basic fire prevention and protection measures by addressing how to successfully manage other chemical reactivity hazards in the work environment. Consequently, the use of the term "chemical reactivity hazards" in this publication will not include explosion, fire and dust explosibility hazards involving the burning of flammable and combustible materials in air. Storage and use of commercial explosives is also outside the scope of this publication.

As indicated above, chemical reactivity hazards are manifested in two ways. *Self-reacting materials* can cause loss or injury by decomposing, polymerizing or rearranging in an uncontrolled manner, even without being combined with other materials. *Chemical interactions* have the potential for loss or injury consequences, if conditions are such that an uncontrolled chemical reaction can take place. This includes situations where chemical reactions are intended to occur (e.g., batch reactions) but something goes wrong such as a temporary loss of agitation. It also includes situations where no chemical reaction is intended, but incompatible materials are combined or mixtures are subjected to heating or other conditions that lead to an uncontrolled chemical reaction. These chemical interactions can involve materials as common as air (combined with spontaneously combustible materials or peroxide formers), water (combined with water-reactive materials), and ordinary combustible materials such as wood, cloth, or cardboard (combined with oxidizers).

Many materials in common business and household use, such as cleaners and solvents, can pose chemical reactivity hazards. The potential often exists for them to be combined with other materials with which they will chemically react, or to self-react such as to decompose when sufficiently heated. For example, numerous incidents occur every year as a result of chlorine bleach being combined with ammonia-based cleaners. The reaction between these materials generates heat, evolves toxic vapors, and under certain conditions can form highly explosive nitrogen trichloride (NCl_3).



As mentioned in a CCPS Safety Alert (CCPS 2001a), chemical reactivity is a highly desirable trait that permits numerous useful materials to be synthesized. It also allows products to be made under relatively moderate conditions of pressure and temperature, saving energy and reducing the physical risks of high-temperature or high-pressure equipment. However, the same properties that make chemical reactivity so useful also pose hazards to health and property. Reactions are not confined to intended and controlled situations.

This publication is for people who design, manage, operate, or support facilities that store, handle, or process materials posing chemical reactivity hazards. To help determine whether a chemical reactivity hazard is present, a "Preliminary Screening Method for Chemical Reactivity Hazards" has been provided (Chapter 3). Example programs are given from leading companies, and previous incidents involving chemical reactivity hazards are highlighted.

Do I Even* Have *a Chemical Reactivity Hazard?

Chapter 3 provides a screening tool to help determine whether chemical reactivity hazards are present that need to be managed and controlled.

1.1. Purpose

The purpose of this publication is to contribute to a continued reduction in the number and severity of incidents involving uncontrolled chemical reactions in the workplace. The objective of this publication is to convey the essentials of managing chemical reactivity hazards—those elements that are necessary, but not always sufficient, to avoid or mitigate chemical reactivity incidents. Implementing these elements should result in a management system that will, on an ongoing basis:

1. **Commit** to managing chemical reactivity hazards throughout the entire facility lifetime.
2. **Identify** all chemical reactivity hazards.
3. **Understand** the situations that can cause uncontrolled reactions.
4. **Reduce** hazards where feasible, resulting in an inherently safer facility.
5. **Prevent** chemical reactivity incidents by designing, constructing, operating and maintaining the facility in such a way that all chemical reactivity hazards are contained and controlled.
6. **Mitigate** (reduce the severity of) incidents that may occur despite prevention efforts.

Somewhat different organizational structures may be needed for managing different kinds of chemical reactivity hazards. As defined in Section 1.3, three general situations involving chemical reactivity hazards are as follows:

- **Storage, Handling and Repackaging** (e.g., warehousing or tank storage, with no combining of different materials and no chemical reaction intended)
- **Mixing and Physical Processing** (e.g., combining, formulating, crushing, blending, screening, drying, distillation, absorption, or heating with no chemical reaction intended)
- **Intentional Chemistry** (e.g., batch or continuous reaction processes).

The effort required to identify and fully understand all chemical reactivity hazards is likely to be greater in a facility where intentional chemistry is practiced, as compared to a warehouse that stores reactive chemicals. Although this Concept Book applies to all three of the general situations listed above, intentional chemistry, due to its complexity, will also require the use of additional resources. Other resources such as Barton and Rogers (1997), CCPS (1995a, 1999a), ESCIS (1993), Grewer (1994), and HSE (2000) more fully address various aspects of managing intentional chemistry. Nevertheless, companies practicing intentional chemistry should find the essential management practices presented here to be applicable and beneficial.

1.2. Need

Chemical reactivity hazards have been involved in some of the most severe industry incidents in history:

- The 1976 runaway reaction at Seveso, Italy that resulted in the contamination of several square miles of land with dioxin
- The 1984 methyl isocyanate release in Bhopal, India that resulted in 2000 fatalities
- The 2001 massive ammonium nitrate explosion near Toulouse, France that led to 30 fatalities, 2500 injuries, damage to nearly a third of the city of Toulouse, and the permanent closing of the facility. Figure 1.1 shows the crater formed by the blast.

Other incidents in which uncontrolled chemical reactions have affected employees and the surrounding public are listed in Section 1.3. These incidents have brought new awareness of the potential for uncontrolled chemical reactions to cause severe injuries and losses.

This Concept Book seeks to fulfill a need for a document that gives details of practices that are essential to safely managing chemical reactivity hazards. Although it is presented primarily in the context of the U.S. and European industrial and regulatory arenas, the practices outlined in the

Figure 1.1. **Crater formed by explosion near Toulouse, France** (Reuters).

publication should be applicable to any facility worldwide where chemical reactivity hazards exist.

As an example of how chemical reactivity hazards are governmentally regulated, the U.S. Occupational Safety and Health Administration (OSHA) Process Safety Management Standard, 29 CFR 1910.119 (OSHA 1992), includes a number of "highly reactive" materials in its list of regulated chemicals. The handling of one or more of these substances above its threshold quantity at a fixed facility in the U.S. requires a process safety management (PSM) program to be in place. The management practices in this publication can be incorporated into existing company PSM programs where chemical reactivity hazards are present.

Other U.S. federal regulations that may have some relation to managing chemical reactivity hazards (acronyms are defined on pages xi–xiii) include the EPA RMP Rule (40 CFR Part 68), EPCRA Sections 311 and 312, RCRA, and the OSHA Hazard Communication Standard (29 CFR 1910.1200). Although the EPA RMP Rule does not explicitly cover chemical reactivity hazards, a number of the chemicals covered by the RMP Rule have significant reactivity properties as well as toxic or flammable hazards. General duty clauses are included in both OSHA (OSH Act 1970) and Clean Air Act legislation that relate, respectively, to providing a safe workplace and preventing accidental releases of extremely hazardous substances. EPA (2000) has provided guidance on the implementation of the general duty clause in Section 112(r)(1) of the Clean Air Act.

In Europe, the Seveso II Directive [96/082/EEC] applies to facilities handling threshold quantities or greater of listed "dangerous substances," including a number of chemicals classified as reactive. Prevention program requirements are similar to those in the OSHA PSM Standard. The facility operator is required to produce a safety report for the purposes of demonstrating that:

- A written major-accident prevention policy has been established that includes the operator's overall aims and principles of action with respect to the control of major-accident hazards.
- A safety management system for implementing the prevention policy has been put into effect. The policy should include the organizational structure, responsibilities, practices, procedures, processes, and resources for determining and implementing the policy.
- Major-accident hazards have been identified.
- The necessary measures have been taken to prevent major accidents and to limit their consequences for people and the environment.
- Adequate safety and reliability have been incorporated into the design, construction, operation, and maintenance of any installation, storage facility, equipment, and infrastructure connected with its operation which are linked to major-accident hazards inside the establishment.
- Internal emergency plans have been drawn up.
- Information is supplied to enable an external plan to be drawn up in order to take the necessary measures in the event of a major accident (i.e., communication with external responders has taken place to provide for effective response in the event of a major accident).

In addition, sufficient information must be provided to the competent authorities to enable decisions to be made in terms of the siting of new activities or developments around existing establishments.

Building and fire codes address quantity storage of reactive chemicals. DOT/UN transportation regulations cover the shipping of reactive chemicals in bulk.

The information in this publication is applicable to many industrial facilities not covered by process safety regulations such as the OSHA PSM Standard and the Seveso II Directive. Many reactive chemicals are not listed as regulated materials, and chemical reactivity hazards include uncontrolled chemical reactions between materials not considered as highly hazardous, or under conditions not typically encountered in storage and shipping.

1.3. Unintentional/Intentional Chemistry Incidents

Three general situations involving chemical reactivity hazards are described in this section. Examples of significant incidents are given for each situation. Additional case histories are summarized in Appendix A-1, including more detailed accounts of the incidents summarized in this section.

The first two general situations are summarized by the headings ***storage, handling, and repackaging*** and ***mixing and physical processing.*** These include facilities where chemical reactions are not intended or expected to occur; i.e., are part of what would be considered abnormal operation. Hence, if a chemical reaction does take place, it would be considered "unintentional chemistry." The third general situation, summarized by the heading ***intentional chemistry,*** is where chemical reaction is desired and expected, and normal operation includes the reaction being controlled within safe operating limits.

Storage, Handling, and Repackaging

Reactive chemicals and other substances such as waste materials and off-specification product can be safely managed when properly characterized and stored and handled in appropriately designed tanks or containers, as long as the containment remains intact, the surroundings are maintained within established limits, and storage time and shelf life limitations are observed. No chemical reactions are expected in storage, with the possible exception of gradual reaction such as degradation or polymerization over time. Likewise, the combination of chemicals with other materials is not part of a storage or repackaging operation.

Nevertheless, as long as reactive chemicals are present, a chemical reactivity hazard exists that must be managed, since various abnormal situations can develop in storage such as loss of refrigeration or temperature control, fire or other external heating, contamination, and container failure. The following incident (EPA 1990) shows what can happen if storage of reactive chemicals is not properly managed.

Storage Incident:
Springfield, Massachusetts, June 17, 1988

Rainwater leaked into a room where hundreds of large cardboard drums of solid swimming pool chemicals were stored. The resulting explosion and fire set off a sprinkler system, soaking the remaining drums and spreading the fire. Explosions, fire, and chlorine releases lasted three days. Over 25,000 people were evacuated and 275 people went to the hospital with skin burns and respiratory problems.

Mixing and Physical Processing

Interactions between two or more materials can have unexpected consequences, even when they are intentionally combined or mixed. More opportunities for unintentional chemistry are present when mixing different substances than when just storing and handling individual materials. For example:

- The substances being mixed are no longer in the protection of storage containers (i.e., lid removed; exposed to the environment)
- One or more of the substances may be different than expected
- Contaminants can more easily be introduced
- Exposure to air or water may be more likely
- Operational errors or unmanaged changes may have more significant consequences
- Substances may be combined in situations where knowledge of the potential for a chemical reaction is inadequate.

The following incident (EPA 1997) illustrates what can be encountered when unintentional chemistry occurs during a mixing operation.

Mixing Incident:
Lodi, New Jersey, April 21, 1995

An explosion and fire at the Napp Technologies facility resulted in five deaths as well as injuries, public evacuations and serious damage both on and off site. According to a joint EPA/OSHA investigation report, water apparently leaked into a blender where sodium hydrosulfite, aluminum powder, potassium carbonate and benzaldehyde were being mixed. Operators noticed production of heat and the release of a foul-smelling gas, indicating an unexpected reaction taking place in the blender. The water caused the sodium hydrosulfite in the blender to decompose, generating heat, sulfur dioxide, and additional water. The decomposition process, once started, was self-sustaining. The reaction generated sufficient heat to cause the aluminum powder to react rapidly with the other ingredients and generate more heat. During an emergency operation to remove the contents of the blender, the material ignited, resulting in the severe consequences.

Many physical processes are employed where no chemical reaction is intended. Many of the operations in oil refineries involve only physical processes such as distillation. Other physical processes include unit operations such as crushing, screening, drying, absorption, heating, blending, crystallization and filtration. The following incident, resulting in the building damage shown in Figure 1.2, involved the physical processing of a solution containing a reactive material (CSB 2002a).

Figure 1.2. **Physical processing incident effects.** (Tom Volk/The Morning Call Inc., copyright 1999.)

Physical Processing Incident:
Hanover Township, Pennsylvania, February 19, 1999

A process vessel containing several hundred pounds of hydroxylamine exploded at the Concept Sciences, Inc., production facility near Allentown, Pennsylvania. Employees were distilling an aqueous solution of hydroxylamine and potassium sulfate, the first commercial batch to be processed at the company's new facility. After the distillation process was shut down, the hydroxylamine in the process tank and associated piping explosively self-reacted, most likely due to high concentration and temperature. Four Concept Sciences employees and a manager of an adjacent business were killed. Two employees and four people in nearby buildings were injured. Six firefighters and two security guards suffered minor injuries during emergency response efforts. The explosion caused extensive damage to the production facility, significant damage to other buildings in the Lehigh Valley Industrial Park, and shattered windows in several nearby homes.

Intentional Chemistry

Many millions of tons of useful products and substances are safely made by chemical reactions each year. Nevertheless, intended reactions can lead to major loss events if inadequately controlled. The following is an example of a chemical reactivity incident in a process with intentional chemistry (EPA 1999a).

Intentional Chemistry Incident:
Columbus, Ohio, September 10, 1997

An explosion at a Georgia-Pacific Resins, Inc. resins production unit killed one worker and injured four others. The vessel rupture explosion was caused by a runaway reaction. As detailed in an EPA Chemical Safety Case Study, the runaway was triggered when, contrary to standard operating procedures, all the raw materials and catalyst were charged to the reactor at once, followed by the addition of heat. Under the runaway conditions, the heat generated exceeded the cooling capacity of the system and the pressure generated could not be vented through the emergency relief system, causing the reactor to explode.

Physical processing is also employed at most facilities where intentional chemistry is practiced, such as for the purification of reaction products or removal of solvent. The following incident (Lees 1996) highlights the importance of thoroughly reviewing nonstandard operations before they are performed, including the testing of materials such as residues and by-products before heating them.

Physical Processing Incident:
Castleford, UK, September 21, 1992

At Hickson and Welch's Meissner plant, a jet flame erupted from a manway on the side of a batch still. The flame cut through the plant control/office building, killing four workers and severely burning one other. The flame also impinged on a much larger four-story office block, shattering windows and setting rooms on fire. The 63 people in this block managed to escape, except for one who was rescued but later died from smoke inhalation.

The flame came from a process vessel used for the batch separation of thermally sensitive nitrotoluene isomers. The vessel was being raked out for the first time, to remove sludge that had begun to accumulate following a process change. Prior to being raked out, heat had been applied to the residue for three hours through an internal steam coil. The investigation concluded that the steam heating had started self-heating of the residue, and that the resulting runaway reaction led to ignition of evolved vapors and to the jet flame.

1.4. How to Use This Publication

Each of the chapters in this Concept Book is aimed at a specific purpose. It is not necessary to go sequentially through all the material in this publication. Each chapter will be more or less applicable depending on the point at which a particular facility or company is starting in its efforts to identify, reduce, and manage chemical reactivity hazards. Figure 1.3 shows the interrelation between the chapters of this publication.

Chapter 2 introduces the management of chemical reactivity hazards throughout the life cycle of a facility, and shows how the essential practices

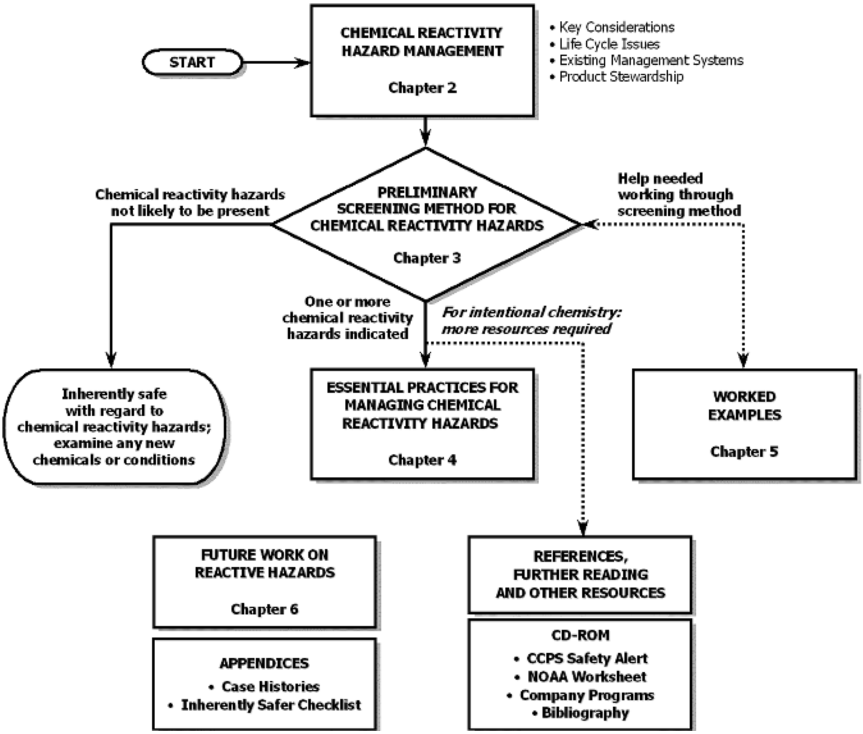


Figure 1.3. **Interrelation between book chapters.**

described in this Concept Book can be incorporated into existing management systems.

Chapter 3 is a Preliminary Screening Method designed to help identify whether chemical reactivity hazards are present at a facility. It can be used to determine whether the information in this publication is sufficient, or whether additional resources are going to be required, for managing identified chemical reactivity hazards.

Chapter 4 presents the practices that are considered essential to managing chemical reactivity hazards throughout the life of a facility.

Chapter 5 works through some examples of how the Preliminary Screening Method might be used in various situations.

Chapter 6 discusses what direction future work may take on managing chemical reactivity hazards.

A **Glossary** defines terms related to chemical reactivity hazards.

References for all chapters are compiled in one section. Resources are also listed that may be useful in understanding the concepts in this publication and in locating additional help.

Appendices contain case histories of chemical reactivity incidents, a sample inherently safer process checklist, and the Executive Summary of the CSB hazard investigation report on "Improving Reactive Hazard Management (CSB 2002b).

The **CD-ROM** included with this publication contains several additional resources that may be helpful:

- CCPS Safety Alert, "Reactive Material Hazards: What You Need To Know" (CCPS 2001a). Steps through how to identify if you have reactive chemicals or can have reactive interactions, what data and safeguards are needed to control reactivity hazards, and where to get additional information. Can be downloaded from the AIChE website at http://www.aiche.org/ccps/pdf/reactmat.pdf.
- U.S. National Oceanic and Atmospheric Administration (NOAA) Chemical Reactivity Worksheet, Version 1.5. As described elsewhere in this publication, the Worksheet can be used to identify chemical reactivity hazards and the general consequences of combining incompatible materials. Can be downloaded from the NOAA website at http://response.restoration.noaa.gov/chemaids/react.html.
- Documentation of example chemical reactivity hazard management programs from CCPS sponsor companies that practice intentional chemistry.
- Table 3.1, Example Form to Document Screening of Chemical Reactivity Hazards, with the accompanying flowchart of Figure 3.1, for use with the preliminary screening method of Chapter 3.
- Table 4.1, Gap Analysis: Chemical Reactivity Hazard Management System, and Table 4.2, Basic Chemical Reactivity Data to Collect.
- Bibliography of articles and publications related to chemical reactivity and intentional chemistry processes.
- English translation of "Guide for the Identification and Control of Exothermic Chemical Reactions" (TAA-GS-05 1994), described in Section 1.5.
- Full text of the U.S. Chemical Safety and Hazard Investigation Board report, "Improving Reactive Hazard Management" (CSB 2002b).

1.5. Related Resources

This publication focuses on *essential management practices* related to chemical reactivity hazards. The following are a few other sources of information on closely related topics that may be useful to the reader. A more complete list of references and resources can be found at the end of this publication, in addition to the bibliography included on the CD-ROM.

- *Guidelines for Safe Warehousing of Chemicals* (CCPS 1998a). Presents practical means of addressing personnel, property and environmental risks in initial or existing designs for warehousing facilities on a manufacturing site, for freestanding offsite buildings, and for strictly chemical or mixed-use storage.
- *Guidelines for Safe Storage and Handling of Reactive Materials* (CCPS 1995b). Explains the difference between various chemical reactivity hazards, steps through how to identify reactivity hazards and estimate the severity of chemical reactivity incidents, and summarizes industry practices for storing and handling reactive materials.
- *Guidelines for Chemical Reactivity Evaluation and Application to Process Design* (CCPS 1995a). Explains test methods for evaluating reactivity hazards and shows how this information is used in the design of chemical reaction processes.
- *Designing and Operating Safe Chemical Reaction Processes* (HSE 2000). Published by the U.K. Health and Safety Executive and directed to small to medium-sized chemical manufacturing companies using batch and semi-batch processes. It addresses chemical reaction hazards and inherently safer processes, hazards assessment, preventive and protective measures, and management practices.
- *Chemical Reaction Hazards: A Guide to Safety, 2nd Edition* (Barton and Rogers 1997). Produced by an IChemE Working Party, provides a basis for good practice in assessing chemical reaction hazards for batch and semi-batch processes. In addition to focusing on test methods for determining important reactivity parameters, it addresses the selection and specification of a basis for safety. One hundred brief case histories of chemical reactivity incidents are given in an appendix.
- *Safety of Reactive Chemicals and Pyrotechnics* (Yoshida et al. 1995). Addresses both the hazardous properties of reactive chemicals and appropriate handling methods. Describes several test methods and the evaluation of fire and explosion hazards of reactive substances, including the impact of initiating events such as earthquakes.
- *Rapid Guide to Chemical Incompatibilities* (Pohanish and Green 1997). Describes chemical combinations believed to be dangerously reactive. Listings are organized by chemical and by reactive group. It includes common synonyms and foreign language entries.
- *Thermal Hazards of Chemical Reactions* (Grewer 1994). Addresses the characterization of thermal hazards involved in reactions of liquid and solid substances and mixtures, particularly those having low to medium reaction energies. The publication aims to present methods for distinguishing hazardous from nonhazardous reactions.

- www.harsnet.de. Website of the European HarsNet project (Hazard Assessment of Highly Reactive Systems Thematic Network). The project is devoted to the characterization of thermal hazards and runaway reactions with the aim of incident prevention. Technical information on equipment, test strategies and engineering principles is available.
- “Guide for the Identification and Control of Exothermic Chemical Reactions” (TAA-GS-05 1994). A document in German by the Technischer Ausschuss für Anlagensicherheit (Technical Committee for Plant Safety) of the Federal Ministry of the Environment, Nature Conservation and Reactor Safety. Addresses safety assessment of reactions during both normal operations and excursions, as well as selection and extent of measures to be adopted. An English translation of this document is provided on the CD-ROM included with this publication.

Chemical Reactivity Hazard Management

2

Managing chemical reactivity hazards is not a one-time project, review, or audit. It is also not a written program document to put on the shelf and ignore. Managing chemical reactivity hazards is an ongoing effort to protect employees, contractors, customers, the public, environment, and property against the potential consequences of chemical reactivity incidents.

As with all effective safety management, chemical reactivity safety begins with an explicit *management commitment* to employees, the community, and other stakeholders to manage chemical reactivity hazards throughout the life of the facility. This includes a determination by line management to have clearly defined responsibilities, be held accountable to fulfill each responsibility, allocate needed resources, develop and maintain needed knowledge, be visibly involved, audit facilities and operations, investigate incidents and abnormal events, and resolve issues identified in these audits and investigations.

After emphasizing some key considerations for managing chemical reactivity hazards, this chapter points out how management commitment must be continually expressed in an environment of constant change, over the entire life cycle of a facility. It also shows how managing chemical reactivity hazards does not mean having to start from scratch. Many of the essential elements of chemical reactivity hazard management are likely to already be in place in existing facilities.

2.1. Key Considerations for Managing Chemical Reactivity Hazards

The remainder of this publication, and the many references cited at the end of this publication, will go into great depth on the detail necessary to formulate and execute a chemical reactivity hazard management system.

However, all of the practices rest on four simple principles: *Inform, Implement, Communicate,* and *Verify* (or, “Know, Do, Tell and Check”).

Inform

To adequately manage chemical reactivity hazards, you must:

- Know if you have the potential for uncontrolled reaction(s) to take place within your facility.
- Know how such reactions might be initiated (e.g., heat, contamination, inadvertent mixing, impact, friction, electrical short, lightning).
- Know how to recognize when an uncontrolled reaction is taking place.
- Know what the consequences would be if such a reaction took place (e.g., toxic gas release, fire, explosion).
- Know what safeguards are (or need to be) in place to prevent uncontrolled reactions from taking place, including how to avoid them altogether (inherently safer design/operations) and how to control them within safe limits (automatic controls, procedures, etc.).
- Know how to respond properly if an uncontrolled reaction takes place (including operator actions, emergency response plans, community alerting plans, etc.).

Implement

To ensure the management system is properly applied, you must:

- Do all of the required action items uncovered in reactive chemistry testing, hazard analyses and lessons learned from previous incident investigations.
- Do apply all basic process management practices, such as management of change (MOC), to accurately assess any chemical reactivity hazards that might be introduced into the process.
- Do investigate all reactivity-related incidents and near misses.

Communicate

To ensure the management system is properly applied, you must also:

- Tell all affected personnel of the potential hazards involved with the operation (including normal operating instructions, emergency procedures, etc.).
- Tell all affected personnel what to do (e.g., training, drills) to avoid chemical reactivity hazards, recognize when an uncontrolled chemi-

cal reaction is taking place, and respond properly if an uncontrolled reaction occurs.

- Tell customers, suppliers, trade and technical associations of any relevant information regarding the chemical reactivity hazards posed by raw materials, intermediates and products.
- Tell emergency responders and other potentially affected persons, including industrial and residential neighbors, what to expect and how to respond to a chemical reactivity incident if one occurs at your facility.

Verify

To ensure the management system is properly functioning, on a regular and routine basis you must:

- Check that all new information concerning chemical reactivity hazards is incorporated into current operational practices.
- Check that all items from hazard analyses, incident investigations and other discovery processes have been properly implemented and documented.
- Check that all communications protocols are being used as intended.
- Check that all key personnel, including the facility manager, have a complete understanding of the chemical reactivity hazards, including scenarios, lines of defense and emergency actions to mitigate the consequences of an uncontrolled reaction.

2.2. Life Cycle Issues

Processes and facilities go through various stages of development. Progression through these stages has come to be called the *life cycle* (Bollinger et al. 1996). Typical life cycle stages are:

- Initial concept/laboratory research
- Process development; small-scale or pilot plant operations
- Full-scale engineering design and facility construction
- Full-scale startup and operation, including shutdown and maintenance activities
- Modifications and expansions
- Mothballing/decommissioning and demolition.

Not all of these stages will be realized by every facility or for every process. For example, in contract manufacturing the technology may already be developed, and facility construction and start-up stages may only involve modifying existing facilities and re-training current staff. Other issues specific to outsourced manufacturing operations are addressed by CCPS (2000).

The following paragraphs highlight some of the most significant implications of managing chemical reactivity hazards at major life cycle stages, with some overlap between stages. This discussion reveals that different elements of chemical reactivity hazard management will be more important or prevalent at different points in the life cycle of a facility. More detailed explanations and examples of specific management practices are presented in Chapter 4.

Concept and Development Stages: Identify, Document and Reduce Hazards

The concept and early development stages of a process facility's life cycle, or the equivalent early-decision stages for other types of operations such as warehouses, will in large part determine the nature and magnitude of the chemical reactivity hazards that will need to be contained and controlled from startup to decommissioning. For example, a decision may be made to use a highly reactive raw material in a process design, based on success in the research laboratory with the formulation steps using this material. This will have the effect of requiring reliable safeguards to always be in place, over an entire 30-year or so facility lifetime, for the safe unloading, storage, and use of the highly reactive material.

For this reason, much attention has been focused in recent years on *inherently safer* technologies (e.g., Bollinger et al. 1996). Instead of choosing to receive and store a highly reactive raw material, it may be possible to use a less hazardous material that is one step farther along in the formulation or synthesis chain. Alternatively, a decision may be made to generate the highly reactive material on demand and eliminate essentially all storage and handling of the material. These are just two examples of inherently safer approaches.

The essence of the inherently safer approach to plant design is the avoidance of hazards rather than their control by added-on protective equipment (Kletz 1998). It particularly emphasizes eliminating large inventories of hazardous materials where feasible.

In addition to normally reducing the overall risk, this approach can have numerous safety, economic, and good-neighbor benefits, such as

- less potential for major incidents and injuries
- less-stringent siting requirements
- less-onerous regulatory requirements
- lower equipment costs
- less need for engineered and administrative controls

- lower inspection, testing and maintenance costs
- less manpower required for safety, health and environmental management efforts
- less potential for difficulties with neighboring populations
- less-stringent protective and response equipment requirements
- less difficulty with hazardous wastes and spill cleanups
- lower insurance premiums.

These kinds of benefits can be realized over the entire lifetime of a facility. Selecting and implementing an inherently safer option is generally much less costly and more feasible at the concept and development stages of a new process, as compared to implementing fundamental changes to an existing facility.

However, many benefits of inherently safer options tend to be difficult to quantify, as well as being more long-term in nature. They must be weighed against possible economic penalties or uncertainties. In addition, some risk reduction approaches can actually increase the overall risk by disproportionally increasing the probability to reduce the severity, or by transferring the operation to another facility that has a substandard risk management program.

Before efforts are made to reduce chemical reactivity hazards, the hazards must be recognized. As soon as decisions are made as to what materials may be handled, or what specific alternatives are being considered, it is time to begin collecting material safety data (Section 4.2) and identifying chemical reactivity hazards (Section 4.3). Screening tests (Section 4.4) may also need to be performed early in the development process to identify and possibly quantify potential hazards. You can begin to collect and assemble this information into a chemical reactivity hazard *documentation package*

Inherently Safer Process Example: MIC Generated on Demand

One company previously received and stored reactive and highly toxic methyl isocyanate (MIC) in bulk liquefied form, as an ingredient for agricultural chemical products. A process modification was made so that the MIC was generated as needed in vapor form, and piped directly to the process that consumed it. The average inventory of MIC was reduced from thousands of pounds to about two pounds of vapor in the transfer line between generation and consumption. The possibility of interrupting production (if a problem occurred in the process that generated MIC) was considered to be more than offset by the reduced safety risks.

that will, before the facility is operational, thoroughly characterize possible unintended chemical reactions (as well as intended reactions, for intentional chemistry situations). This documentation package, which is more fully described in Chapter 4, will then form part of the information base upon which safeguards can be developed to control chemical reactivity hazards.

During the development of a new facility or process, or when introducing a new process into an existing facility for the first time, an *inherent safety review* can be conducted to understand the chemical reactivity hazards and explore hazard reduction alternatives. The review need not be limited to chemical reactivity hazards. It can be used to address all other types of process hazards at the same time, including flammability/ combustibility; dust or mist explosibility; elevated or reduced pressures or temperatures; phase differences; and health hazards such as toxicity, corrosivity, and asphyxiation.

The following is a typical agenda for an inherent safety review at the concept or development stage of a new facility:

1. Review what is known of the chemical reactivity hazards (as well as other hazards) that will need to be contained and controlled in the proposed process. This existing level of knowledge might come from past experience, suppliers, literature reviews, incident reports, etc.
2. Based on the level of knowledge of chemical reactivity hazards, determine if additional screening of reactivity hazards is necessary. Having reactive functional groups might indicate the need to perform literature searches, access databases or run differential scanning calorimetry.
3. Discuss possible process alternatives and their relative hazards, including discussions on such topics as alternative solvents and possible incompatibilities to avoid.
4. Brainstorm and discuss possible ways to reduce the hazards (a checklist such as the one in Appendix A-2 can be used as an aid to the brainstorming process).
5. Obtain consensus on significant unknowns that will need to be addressed.
6. Document the review, including attendees, scope, approach, and decisions.
7. Assign follow-up items, with responsibilities, goal completion dates, and a closure mechanism such as reconvening in *x* weeks.

An inherent safety review should be conducted by a multidisciplinary team. For new facilities, the inherent safety review is an excellent opportunity to begin to involve those persons likely to have line responsibility for the facility that will need to deal with the chemical reactivity hazards

(Section 4.1). For existing facilities, operating and maintenance personnel should also participate in the inherent safety review. A smaller team may be appropriate for facilities such as warehouses. In any case, the review team must include one or more individuals with the background and experience to recognize and understand the chemical reactivity hazards and how they may lead to uncontrolled chemical reactions. In this regard, outside experts may need to be consulted.

Scale-Up and Engineering Design: Assess Risks and Build in Safeguards

As decisions are finalized on the materials and conditions to be encountered in the new facility, quantitative hazard data can be developed, by testing if necessary (Section 4.4), that will be needed to assess risks and identify process controls and risk management options (Sections 4.5 and 4.6). At this point, some chemical reactivity testing may have already been performed in the process of identifying and reducing hazards. New data, as they are discovered or developed, are added to the documentation package begun at the concept and development stages.

The search for previously unrecognized chemical reactivity hazards and places where inadequate safeguards exist is an activity that continues throughout the product/plant life cycle. Chemical reactivity hazards and risk management decisions need to be fully documented (Section 4.7). This documentation is the basis for hazard communication and training (Section 4.8), which should be fully completed before the chemical reactivity hazards are introduced into the facility.

Key Scale-Up Issue

*Heat generation in a reactive system is proportional to **volume**, whereas heat removal is proportional to **area** at best. Increasing the size of a reactor without adequately considering heat transfer, agitation and emergency relief can have disastrous effects.*

Startup/Full-Scale Operation: Maintain Controls and Learn From Experience

For some facilities, “full-scale operation” may mean only the warehousing or usage of chemicals or the batch mixing of solid or liquid materials. Regardless of the scale or complexity of an operation, hazards management requires continuing effort and vigilance to identify previously unrecognized hazards and to control all chemical reactivity hazards at all times, during the entire operational life of the facility.

Hazards management should also include being sensitive to abnormal situations and maintenance requirements, and learning everything possible from incidents and near misses. These may point to a previously unknown hazard, an incipient failure condition, or a breakdown in the management system. Even greater benefit can be gained by participating in an effective network within your company or industry that shares lessons learned from incidents and near misses. Section 4.9 summarizes what is involved in investigating chemical reactivity incidents.

Modifications and Expansions: Manage Change

Change is inevitable in any ongoing operation. Changes might be made to equipment, facilities, chemicals involved or procedures for numerous reasons. Personnel and organizations will change over time. Raw materials and product specifications may change slightly with different suppliers, customers or new quality requirements. Gradual changes such as wear and deterioration will lead to maintenance and change-out of equipment. If the basis for safe operation was the original process design and means of operating and maintenance, then changes might introduce new chemical reactivity hazards or amplify existing hazards. Even minor changes can significantly impact the chemical reactivity hazards of a process. Management of change must preserve and keep the design basis record current and protect against compromise of inherently safer features (Bollinger et al. 1996; see Section 4.7 for related documentation issues) or the introduction of new hazards. Reviews and audits need to be conducted to ensure the integrity of the system is maintained, the established management practices are continually observed, and continual improvement is sought (Section 4.10).

When modifications and expansions are first considered by an organization, many of the same opportunities are present as at the concept and development stages to make the facility inherently safer. New knowledge or technology may now be available that will make it possible to operate the facility with fewer hazards, lower inventories, or less severe operating conditions (e.g., lower temperatures or pressures). An appropriate level of inherent safety review can be built into the facility's management of change system, to prompt those responsible for proposing or reviewing changes to consider inherently safer alternatives. An Inherently Safer Process Checklist, such as the one in Appendix A-2, may be helpful in this regard.

Assessing the safety significance of proposed changes is generally more difficult when dealing with chemical reactivity hazards. New test data may need to be obtained, and experts may need to be consulted. Changes in process quantities, rates or conditions—especially temperature—or the introduction of new or modified materials must be carefully reviewed.

Mothballing and Decommissioning: Remember Shelf Life

Shutting down a process, either for an indefinite period of time or permanently, can introduce chemical reactivity hazard management considerations. For example, one facility wanted to dismantle some equipment for a process for which an ether was a feedstock. A review of facility records did not conclusively reveal whether the equipment had been thoroughly decontaminated after the process was shut down years before. This left open the possibility that the equipment might contain explosive peroxides that could have formed over time by peroxidation of the ether. In another example, an unstable byproduct exploded when piping removed from a process unit was being cut into smaller pieces for disposal.

Planning for the decommissioning of a process unit should include consideration of chemical reactivity hazard management issues, such as determining whether unstable residues may have accumulated in the equipment during its operating lifetime. Thorough decontamination of the equipment is necessary. Heels of material should not be left in vessels or in piping low spots. Complete documentation of the equipment status at the time it was mothballed must be maintained for the future use of those who eventually may restart or dismantle the facility. Chemical reactivity risks should be assessed (Section 4.5) when a temporary shutdown is to become a permanent shutdown.

Many of these same considerations apply when planning a maintenance turnaround. The incident at Hickson & Welch's facility, detailed in Appendix A-1, is a vivid reminder of the necessity to know what reactivity hazards are present and to plan and act accordingly.

2.3. Existing Management Systems

Good news! At many facilities where chemical reactivity hazards exist, chemical reactivity hazard management is already practiced to some extent. Many of the activities comprising chemical reactivity hazard management may be known by different names or be part of other site programs. For example, all raw materials might be sampled and tested for quality assurance/quality control purposes; this could also serve as a safeguard against unloading a contaminated or incompatible substance to a raw material storage tank. These current practices can provide a good foundation on which to build, if you are relating the information in this publication to an existing facility or management system.

Listed in Table 2.1 are the essential elements of managing chemical reactivity hazards, as described in Sections 4.1 through 4.10 of this publication. They are mapped to comparable elements in three other, broader process safety and risk management systems:

TABLE 2.1
Hazard Management Elements Map (Numbers refer to sections in this book)

Chemical Reactivity Hazard Management	**CCPS Elements**	**OSHA PSM Standard and EPA RMP Rule**	**Seveso II**
2.2 Life Cycle Issues	Management of Change	Management of Change	Management of Change
2.4 Product Stewardship	Enhancement of Process Safety Knowledge	—	—
4.1 Develop System to Manage Chemical Reactivity Hazards	Management Systems	Management System	Safety Management System
4.2 Collect Chemical Reactivity Data	Process Knowledge and Documentation	Process Safety Information	Identification of Major Hazards
4.3 Identify Chemical Reactivity Hazards	Process Risk Management	Process Hazard Analysis	Identification of Major Hazards
4.4 Test for Chemical Reactivity	Process Knowledge and Documentation	Process Safety Information	Identification of Major Hazards
4.5 Assess Chemical Reactivity Risks	Process Risk Management	Process Hazard Analysis	Evaluation of Major Hazards
4.6 Identify Process Controls and Risk Management Options	Process Risk Management	Process Hazard Analysis	Operational Control
4.7 Document Chemical Reactivity Risks and Management Decisions	Process Knowledge and Documentation Process Risk Management	Process Safety Information Process Hazard Analysis Operating Procedures	Operational Control
4.8 Communicate and Train on Chemical Reactivity Hazards	Training and Performance Process Risk Management	Training Contractors	Organization and Personnel
4.9 Investigate Chemical Reactivity Incidents	Incident Investigation	Incident Investigation	Monitoring Performance
4.10 Review, Audit, Manage Change, and Improve Hazard Management Practices/Program	Audits and Corrective Action Management of Change Enhancement of Process Safety Knowledge	Compliance Audits Management of Change	Audit and Review Management of Change

- The elements described by the Center for Chemical Process Safety (CCPS 1989)
- The Prevention Program elements that are common to two U.S. regulatory requirements, the OSHA Process Safety Management Standard (29 CFR 1910.119) and the Program 3 Prevention Program requirements of the EPA Risk Management Program Rule (40 CFR Part 68)
- The issues to be addressed by a safety management system as listed in Annex III of the Seveso II Directive [96/082/EEC].

Documentation of the chemical reactivity hazard management system will need to include how it relates to other regulatory elements.

It takes only a brief glance at Table 2.1 to notice that the essential practices for managing chemical reactivity hazards lean heavily toward *identifying and assessing chemical reactivity hazards*. This is due to the less-obvious nature of many chemical reactivity hazards, as compared to other more easily recognized process hazards such as toxicity and flammability. A chemical reactivity hazard investigation completed by the U.S. Chemical Safety and Hazard Investigation Board (CSB) supports this emphasis. The CSB found that, where causal information was available, more than 60 percent of the chemical reactivity incidents they studied involved inadequate practices for identifying hazards or conducting process hazard evaluations (CSB 2002b).

A comprehensive system to manage process hazards should also have other elements, in addition to those listed in Table 2.1. As such, Table 2.2 lists elements included in CCPS, OSHA/EPA, and Seveso II programs that are not explicitly addressed in this publication. This is not intended to imply that these other elements are unimportant. For example, all facilities handling hazardous materials and energies should engage in emergency

TABLE 2.2
Other Management Elements Not Explicitly Addressed

Chemical Reactivity Hazard Management Elements Not Explicitly Addressed:		
CCPS Elements	**OSHA PSM Standard and EPA RMP Rule**	**Seveso II**
Process Safety Review Procedures for Capital Projects Process and Equipment Integrity Human Factors Company Standards, Codes, and Regulation	Employee Participation Pre-Startup Safety Review Mechanical Integrity Hot Work Permit Emergency Planning and Response Trade Secrets	Planning for Emergencies

planning, and, when containment and control systems are needed, establishing and maintaining the integrity of process and equipment is essential to preventing incidents.

New Management System

If you do not have a management system in place, one will obviously need to be developed. The “gap analysis” of Table 4.1 could be used as an aid to communicate common expectations within the organization as it develops, as well as a checklist of management essentials.

The new management system must be in place and functional *before* introducing chemical reactivity hazards to the facility. Leaving the development of the management system to be done on an ad hoc basis after startup is equivalent to communicating right up front that production has priority over the management of chemical reactivity hazards.

Existing Management System

It is not necessary or desirable to create a separate system for managing chemical reactivity hazards if an appropriate management system is already in place. *All* management system essentials (see Table 4.1 in Chapter 4) apply to the management of other process hazards as well, such as the handling of toxic or flammable materials. Most apply to other essential practices as well, such as environmental management, occupational safety, and industrial hygiene.

Management systems may also be in place for initiatives not related to environment, safety and health, such as ISO certification and customer acceptance. Again, the management of chemical reactivity hazards should not be separated from these other management systems. Advantage can be taken of what approaches, such as information technologies and means of communication, have proven to work well within the specific organization.

Many issues in one management area are bound to affect performance in other areas. For example, an inherent safety review may propose a change in the process chemistry that will allow a definite reduction in chemical reactivity hazards, perhaps by eliminating a reactive intermediate. Such changes will have to fit with product quality requirements, and the customer may need to be included in the process of changing to the inherently safer alternative. Effective communication among all parts of the management team will avoid many problems and help identify what works best.

As mentioned earlier, most facilities need not start from scratch when seeking to effectively manage chemical reactivity hazards. Elements of a hazards management system, such as an emergency response plan or a

TABLE 2.3
Strategy for Getting Started

1. Determine what you already have in place to manage chemical reactivity hazards.
2. Compare what you have with the essential practices in Chapter 4.
3. Find any gaps.
4. Develop and implement a plan of action to fill the gaps.
5. Follow up and improve any areas not working smoothly.

training program, may already be in place. It may only need to be verified that these elements address chemical reactivity hazards. They can then be built upon to include all other essential aspects of managing chemical reactivity hazards, as described in Chapter 4.

Table 2.3 gives one way for an existing facility to get started toward successfully managing chemical reactivity hazards. This assumes you already have an idea as to what chemical reactivity hazards must be addressed by the management system, such as by answering the questions in the Preliminary Screening Method of Chapter 3.

New initiatives, programs, and emphases are rarely started in isolation. An existing management structure in some form will most likely be in place. Resources are available to help implement and integrate a hazards management system (CCPS 1994, 1997).

2.4. Product Stewardship

If your product can pose a chemical reactivity hazard by itself or in combination with other materials, good product stewardship includes providing safety-related information to customers and users. Other aspects of product stewardship, some of which are also applicable to chemical reactivity hazard management, are outlined in the American Chemistry Council's Product Stewardship Responsible Care Code (ACC 2001).

The objective to keep in mind is to get the safety information to the people that need to know it. Mechanisms that can be used to convey this information include:

- container labeling
- material safety data sheets
- sales literature
- application sheets
- technical literature
- recommendations related to handling and storage; e.g., materials of construction

- training
- technical services
- company websites or intranets.

Also, if you obtain new information or test data about products or hazards, make sure you convey this information to your customers by way of updated material safety data sheets (MSDSs) and product information.

Information related to broader industry issues, newly recognized hazards, and lessons learned from near misses and actual incidents can also be shared with customers and users as part of product stewardship. Trade, professional, and other cooperative organizations such as universities and local emergency planning committees (LEPCs) can be effective vehicles for information sharing, in addition to individual company initiatives.

Preliminary Screening Method for Chemical Reactivity Hazards

3

The information in this chapter is presented as a series of questions. They are intended to help you quickly decide whether chemical reactivity hazards are present at your facility. If chemical reactivity hazards are indicated, it points you to the essential practices in Chapter 4 for managing the hazards. It is also intended to indicate whether the essential practices presented in this Concept Book are sufficient to manage your chemical reactivity hazards, or whether additional resources will be required.

A form such as Table 3.1 can be used to document answers to the screening questions and the conclusions that are drawn. The flowchart in Figure 3.1 is an overview of how these questions are connected to determine whether a chemical reactivity hazard can be expected at your facility.

You may find the worked examples in Chapter 5 helpful for seeing how the Preliminary Screening Method is used and how the results are documented for a few typical situations. Each of the twelve questions in the screening method is explained in turn in the remainder of this chapter, with examples and other considerations.

The twelve questions are structured consistent with Figure 3.1, as if the screening method was being used to determine if *any* chemical reactivity hazards are present at your facility. However, the questions and a form such as in Table 3.1 can also be used to document *all* of the general kinds of chemical reactivity hazards indicated by this Preliminary Screening Method, if more than one is present. More detailed guidance on identifying all chemical reactivity hazards is given in Chapter 4, as this is one of the essential practices for managing chemical reactivity hazards.

This screening method may be used by either a single person or a group of persons. A team approach, involving several persons with different knowledge and functional perspectives, has the possibility of better identifying and assessing the potential for chemical reactivity hazards.

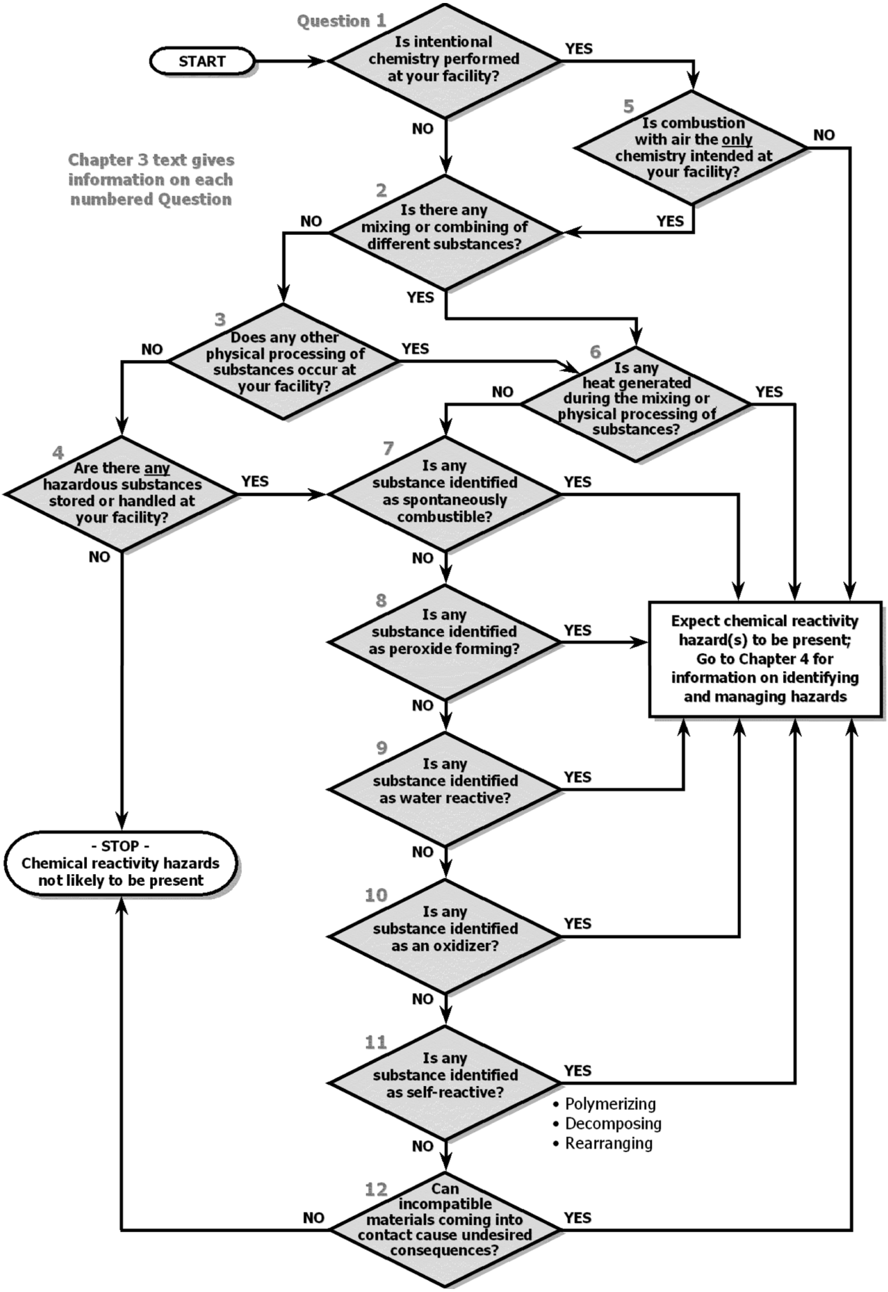


Figure 3.1. **Preliminary screening for chemical reactivity hazards: summary flowchart.**

TABLE 3.1

Example Form to Document Screening of Chemical Reactivity Hazards

FACILITY:	COMPLETION DATE:
COMPLETED BY:	APPROVED BY:

Do the answers to the following questions indicate chemical reactivity hazard(s) are present? [1] ___________

AT THIS FACILITY:	**YES, NO, or NA**	**BASIS FOR ANSWER; COMMENTS**
1. Is intentional chemistry performed?		
2. Is there any mixing or combining of different substances?		
3. Does any other physical processing of substances occur?		
4. Are there any hazardous substances stored or handled?		
5. Is combustion with air the only chemistry intended?		
6. Is any heat generated during the mixing or physical processing of substances?		
7. Is any substance identified as spontaneously combustible?		
8. Is any substance identified as peroxide forming?		
9. Is any substance identified as water reactive?		
10. Is any substance identified as an oxidizer?		
11. Is any substance identified as self-reactive?		
12. Can incompatible materials coming into contact cause undesired consequences, based on the following analysis?		

SCENARIO	**CONDITIONS NORMAL?[2]**	**R, NR, or ?[3]**	**INFORMATION SOURCES; COMMENTS**
1			
2			
3			

---

[1] Use Figure 3.1 with answers to Questions 1–12 to determine if answer is YES or NO

[2] Does the contact/mixing occur at ambient temperature, atmospheric pressure, 21% oxygen atmosphere, and unconfined? (IF NOT, DO NOT ASSUME THAT PUBLISHED DATA FOR AMBIENT CONDITIONS APPLY)

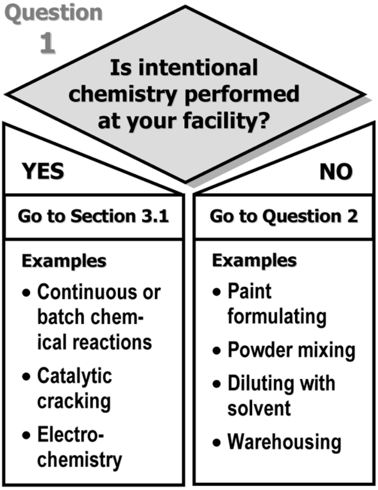
[3] R = Reactive (incompatible) under the stated scenario and conditions

NR = Nonreactive (compatible) under the stated scenario and conditions

? = Unknown; assume incompatible until further information is obtained

Regardless of how many persons are involved, make sure you get outside input and use outside resources if necessary to understand and answer each pertinent question. It will become evident that a person with knowledge of chemistry is particularly needed in this regard.

Question 1: Intentional Chemistry



The first question to be addressed is whether intentional chemistry is performed at your facility. *Intentional chemistry* means processing of substances, such that a chemical reaction is intended to take place. If so, then products are of a different chemical composition than the starting materials.

If your answer to Question 1 is clearly YES, then start at Section 3.1 of this chapter. If your answer is a definite NO, then proceed to Question 2. If you are uncertain whether chemical reactions are intended to take place, you need to determine a definite answer to this question before you go any further. A chemist or other expert should be consulted if you need assistance in determining whether intentional chemistry is being performed at your facility. The following information may also be helpful.

The following are some indications that intentional chemistry is being performed:

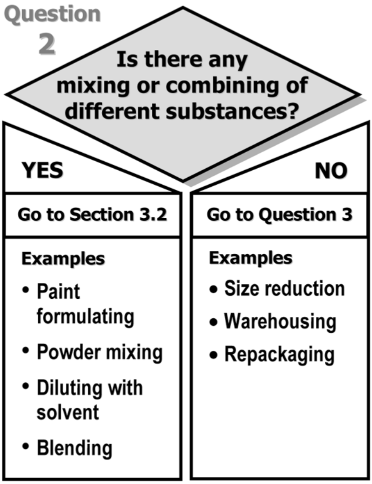
- The products have different chemical formulas or structures or chemical abstract numbers (CAS#'s) than the starting materials.
- A gaseous product is given off or a solid residue is formed that is different from any of the constituents or solvents in a starting mixture.
- A catalyst or initiator is added to the starting mixture.
- Heat is generated by the process, or heat must be added to the process.

Note that heat effects do not necessarily indicate that a chemical reaction is taking place. Some physical processes such as mixing or dilution can generate or absorb heat. However, heat effects are very often the result of a chemical process.

Various processes such as mixing, dissolving, distilling, or extracting may involve intentional chemistry or may be purely physical processes. A chemist or other expert should be consulted if you are still uncertain whether your facility does or will involve intentional chemistry.

One borderline circumstance, which should be considered as intentional chemistry for purposes of managing chemical reactivity hazards, is *hydration*. For example, anhydrous copper sulfate is a white solid with the formula $CuSO_4$. When it is crystallized from water, a blue crystalline solid with the formula $CuSO_4 \cdot 5H_2O$ results, and the water molecules are an integral part of the crystal (Parker 1997).

Question 2: Mixing/Combining

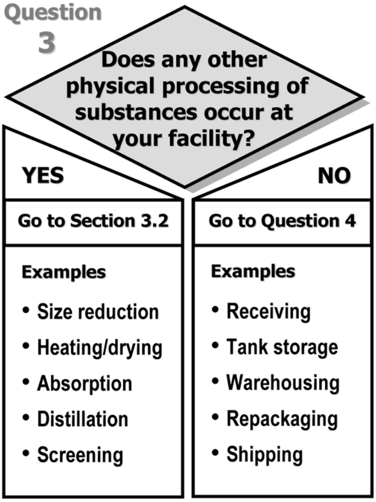


The next question to be addressed is whether any mixing or combining of different substances occurs at your facility. This could range from a large-scale formulation process to an individual procedure for dissolving a substance in water.

If your answer to Question 2 is clearly YES, then start at Section 3.2 of this chapter. If your answer is a definite NO, then proceed to Question 3. If you are uncertain whether mixing or combining of different substances takes place or will take place at your facility, you need to determine a definite answer to this question before you go further. This may involve systematically reviewing your facility's operations and procedures, talking with operations and maintenance personnel, and discussing with management what future activities can be anticipated.

One situation likely to be encountered is where mixing or combining of substances is not *intended*, but may occur from time to time, perhaps as an unauthorized or unsupervised activity. Such situations may include combining drain cleaners, cleaning solutions, or agricultural products because one product does not appear to work or the making of a more potent agent is attempted. They may also include cases where process steps that were originally conducted separately were combined for reasons of efficiency or productivity. Judgment may be required in these situations, to assess what might reasonably be *expected* to occur some time during the life of the facility, based on what substances are accessible to workers or what has happened in the past. One factor to be considered when making this judgment is the operating discipline at your facility. If rules against unauthorized combining of materials and solutions are always strictly enforced, what may need to be considered here will be different than if no rules exist or oversight is more lax. Adherence to rigorous management of change procedures should help avoid these issues.

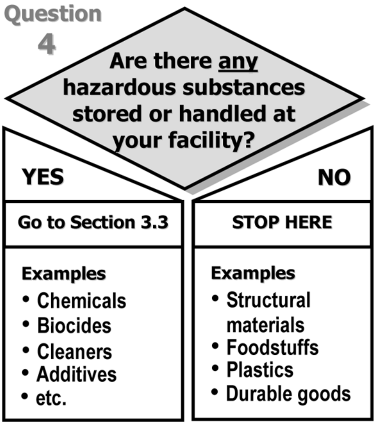
Question 3: Other Physical Processing



The third question to be addressed is whether any other type of physical processing takes place at your facility. *Physical processing* is any modifying of substances such that the resulting product or products are physically but not chemically different from the starting material. Some examples are shown at right. Transfer, handling, storage, and repackaging of materials are not considered physical processing.

If your answer to Question 3 is clearly YES, then start at Section 3.2 of this chapter. If your answer is a definite NO, then proceed to Question 4. If you are uncertain whether physical processing takes place or will take place at your facility, you need to determine the definite answer to this question before you go further. As before, this may involve systematically reviewing your facility's operations and procedures, talking with operations and maintenance personnel, and discussing with management what future activities are anticipated.

Question 4: Hazardous Substances



The fourth question to be addressed is whether any hazardous materials or dangerous goods are stored or handled at your facility. This would include materials for which material safety data sheets (MSDSs) are required. In the U.S., MSDSs are required for each chemical posing either a health hazard or a "physical hazard."

"Physical hazard" is defined by the OSHA Hazard Communication Standard (OSHA 1994) as an element, chemical compound or mixture of elements and/or compounds for which there is scientifically valid evidence that it is a combustible liquid, a compressed gas, explosive, flammable, an organic peroxide, an oxidizer, pyrophoric, unstable (reactive) or water reactive. Definitions for most of these terms are given in the Glossary.

It should be noted that MSDSs are not required for all chemical intermediates and byproducts. These should be considered in addition to raw materials and products. Also, be aware that storage, handling or processing at higher temperatures or pressures may initiate an uncontrolled reaction in a material or mixture that is apparently unreactive closer to ambient conditions.

"Dangerous goods" is defined in the context of recommended international hazardous material transportation regulations. The UN "Orange Book" should be consulted for further information on the definition of dangerous goods for transportation purposes (UN 2002).

If your answer to Question 4 is clearly YES, or if you are unsure of the answer to this question, then start at Section 3.3 of this chapter. (The answer to Question 4 will be YES for most manufacturing facilities and many industrial storage and warehousing facilities.) If your answer is a definite NO, then you are not likely to have any chemical reactivity hazards at your facility, and a system to manage chemical reactivity hazards is not warranted. The information in Section 3.3 can be reviewed as a further check to verify this conclusion.

3.1. Intentional Chemistry

The information in this section is only pertinent if intentional chemistry is performed at your facility. As stated earlier, *intentional chemistry* means processing of substances such that a chemical reaction is intended to take place, and products are of a different chemical composition than the starting materials.

Exothermic reactions are those chemical reactions that liberate heat as products are formed. The occurrence of an exothermic reaction in normal operations is usually an indicator that some intentional chemistry is taking place.

Endothermic reactions may not have obvious chemical reactivity hazards, but should nevertheless be expected to be associated with chemical reactivity hazards. *Endothermic* means a reaction that absorbs heat; i.e., heat must be added for the reaction to continue. Since energy is being put into the endothermic reaction system, the final products will have a greater internal energy content than the starting materials, so the products themselves may pose a chemical reactivity hazard. In addition, the endothermic reaction may be reversible under certain conditions and thus may result in a potentially dangerous exothermic reaction.

Note: It is not the intention of this Concept Book to cover all the complexities of the myriad of intentional chemical reactions being practiced in industry. Although the essential practices in Chapter 4 are appropriate considerations for facilities involving intentional chemistry, additional resources are likely to be required to identify and control the chemical reactivity hazards at such facilities. Some important references that should be consulted when intentional chemistry is practiced or being considered are Barton and Rogers (1997), CCPS (1995a, 1998b, 1999a), and HSE (2000). Example procedures from companies practicing intentional chemistry have been provided on the CD-ROM included with this publication.

What Can Go Wrong?

Many different loss event scenarios are possible with intentional chemistry. All of them relate to losing containment or control of the intended reaction, starting another reaction, side reaction or series of reactions that are not intended or expected. A process hazard analysis, using a hazard and operability (HAZOP) study or other appropriate method, should be used to systematically identify and evaluate a full set of loss event scenarios. General causes of uncontrolled reactions include, but are not confined to, the following list:

- Wrong material of construction used
- Inadequate cleaning or purging before introducing material into vessel or reactor
- Wrong material used or added
- Too much material added
- Too little or no material added
- Materials added in wrong sequence
- Material added too rapidly
- Material added too slowly
- Contaminated feed material
- Excess catalyst or promoter added
- Insufficient or no catalyst added
- Wrong catalyst added
- Catalyst addition delayed
- Heat-up delayed
- Cooling/refrigeration lost
- Heat added
- Heating lost
- Incoming material too cold
- Incoming material too hot

- Air leak under vacuum
- Heat transfer fluid leak
- Insufficient or no agitation
- Start of agitation delayed
- Excess agitation
- Level control lost
- Vessel overfilled
- pH control lost
- Inadequate inhibitor added
- Excess inhibitor added
- Inhibited material frozen
- Transfer pump blocked in
- Off-gas vent blocked or not opened
- Off-gas vent pressurized
- Contamination in off-gas header
- Containment vessel pressurized
- Material transferred out of reactor too soon
- Material transferred to wrong location
- Abnormal energy input such as by electrical discharge, friction or impact.

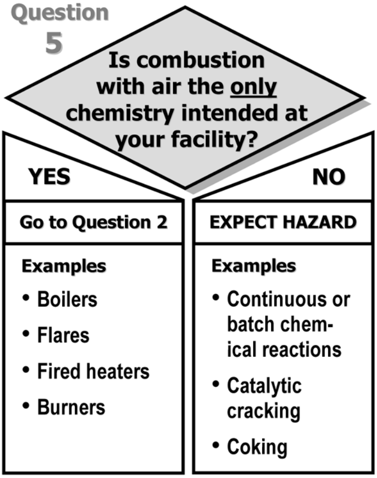
Key Factors

Some of the key factors to consider when designing, operating and maintaining intentional chemistry processes are listed below. These factors can have a major effect on either the likelihood of a chemical reactivity incident or the severity of the incident consequences.

- Energy content of reaction system
- Rates and activation energies of desired and undesired reactions
- Margin of safety between actual operating temperature and temperature at which uncontrolled reaction is initiated
- Diluent boiling point relative to temperature at which uncontrolled reaction is initiated
- Fail-safe design of valves and instrumentation, including entire cooling or heating loop
- Frequency of product changeovers
- Quality control of all incoming materials
- Viscosity of reaction mixture
- Potential for freezing
- Operating procedures
- Thermal stability of reactants, solvents, diluents, intermediates, products

- Reactivity with ubiquitous contaminants (oil, rust, air, water, etc.)
- Training and experience of operational personnel
- Reliability of metering, agitation and heat transfer systems
- Integrity of basic process control system
- Reliability of safety instrumented systems
- Effectiveness of last-resort safety systems (dump, quench, stop uncontrolled reaction)
- Selection and sizing of emergency relief systems
- Protection against external fires and other heat sources
- Blast walls, barricades, blow-out panels
- Toxicity, corrosivity or flammability of raw materials and normal/abnormal reaction products
- Siting of equipment relative to personnel, public and other facilities
- Company and industry experience with specific process and equipment involved.

Question 5: Combustion with Air



If intentional chemistry is performed, chemical reactivity hazards can be expected to exist at your facility. An exception is intentional, essentially complete combustion with air, such as the burning of propane in a gas-fired heater. The burning of ordinary flammable and combustible materials has been excluded from our definition of chemical reactivity hazards and is adequately treated elsewhere. If the answer to Question 5 is YES, then the rest of this section on intentional chemistry need not be considered further, and you should proceed to Question 2 at the beginning of this chapter.

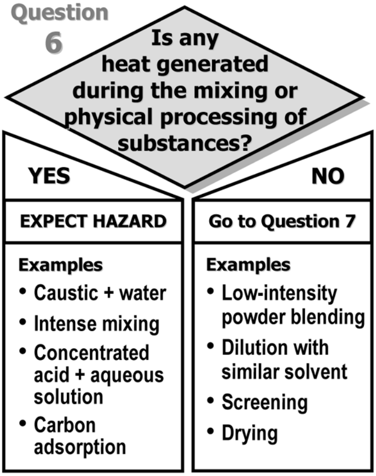
Note that processes involving *partial oxidation,* such as conversion of ethylene to ethylene oxide, can pose significantly different hazards than the combustion systems described above. As such, processes involving partial oxidation should answer NO to Question 5.

If intentional chemistry is practiced at your facility and the answer to Question 5 is NO, then chemical reactivity hazards can be expected. As was noted earlier, it is not the intention of this Concept Book to cover all the complexities of the intentional chemical reactions being practiced in industry. The essential practices in Chapter 4 are appropriate considerations for facilities involving intentional chemistry. However, additional resources are likely to be required to identify and control the chemical reactivity hazards at such facilities. Opportunities to make intentional chemistry facilities inherently safer (Section 2.2) are often possible, and should be pursued if feasible.

3.2. Mixing and Physical Processing

This section pertains to facilities where different substances are intentionally mixed, blended or combined together. It also pertains to facilities where physical processing (heating, filtration, absorption, crushing, screening, drying, distillation, etc.) is intentionally performed, but no chemical reaction is ever intended or expected to occur as part of the operation. The end product of the operation may be one or more substances, solutions or mixtures that may have different physical characteristics (appearance, phase, viscosity, etc.) from the starting materials, but the same chemical substances are present.

Question 6: Heat Generation



An important question to consider is whether the mixing or physical processing of substances *generates* heat (e.g., a mixture gets warm or hot upon combining the ingredients, or would get warm or hot if cooling was lost). Heat can be generated by heat of solution, heat of adsorption, mechanical energy, or other physical heat effects. Note that this is different from adding heat during a mixing or physical processing operation (such as by external steam heating); such a case is addressed by Question 3 above. However, recognize that a change in physical condition may result in a change in reactivity, such that materials or mixtures that were not apparently reactive at one temperature can become dangerously reactive at another temperature.

Abnormal situations can occur such that too much heat is generated (or too little cooling occurs) and a substance or mixture gets hotter than intended. Consequently, an unintended chemical reaction may be initiated at the higher temperature that may generate even more heat, evolve toxic or flammable gases, or be explosive. The heat for getting to the secondary unintended reactions might be added by nonchemical means. The Morton International case study in Appendix A-1 gives an example of this type of situation. The additional heating could also cause a vessel or container to be overpressurized due to liquid boil-off or heating of the gases inside an enclosure.

What Can Go Wrong?

Possible causes of uncontrolled reactions associated with heat-generating mixing or physical processing operations include abnormal events such as the following:

- Inadequate clean-out or purge
- Too much material added
- Too little or no diluent added
- Materials added in wrong sequence
- Material added too rapidly
- Contaminant or wrong material added
- Cooling lost
- Incoming material too hot
- Ability to transfer heat away from mixture reduced or lost
- Mixing or agitation lost
- Excess or prolonged mixing or agitation
- Off-gas vent blocked or not opened
- Off-gas vent pressurized
- Containment vessel pressurized.

If the answer to Question 6 is YES, then you should make use of the information in Chapter 4, because a chemical reactivity hazard may be present. The information in Chapter 4 should be sufficient to identify chemical reactivity hazards that must be managed. In addition, if hazards are identified, the essential practices presented in Chapter 4 should be sufficient to manage these types of chemical reactivity hazards.

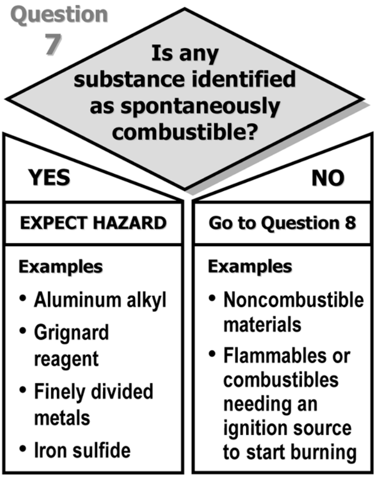
If you are certain that NO heat is generated, then the same considerations are present as for storage, handling and repackaging operations, so proceed to the next question (Question 7). If you are uncertain as to whether heat is generated, it may be possible to find out by heat balances or careful temperature measurements. A more definitive answer can be determined by conducting calorimetric tests that are representative of the full range of material compositions that will be encountered in the facility. Several screening tests are discussed in Section 4.4.

3.3. Storage, Handling, and Repackaging

The questions in this section pertain to all facilities that store, handle or repackage any hazardous materials, as well as facilities that produce and use hazardous materials. The questions also pertain to operations involving mixing or physical processing where heat is not generated during the mixing or physical processing, as discussed in the preceding section.

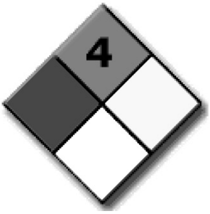
The first four questions address substances that are *reactive with air, water, or ordinary combustibles*—materials that are almost certain to be in close proximity to the reactive substances. The next question addresses *self-reactive* materials. This is followed by a final question combined with a series of steps for addressing *chemical incompatibility*.

Question 7: Pyrophorics and Other Spontaneously Combustible Substances



The next question pertains to substances that will readily react with the oxygen in the atmosphere, igniting and burning even without an ignition source. Ignition may be immediate, or may result from a self-heating process that may take minutes or hours; thus, some spontaneously combustible substances are known as *self-heating*.

Pyrophoric materials ignite spontaneously on short exposure to air under ordinary ambient conditions. (Some materials that are considered pyrophoric require a minimum relative humidity in the atmosphere for spontaneous ignition to occur.) The potential of pyrophoric materials to exhibit this behavior is usually well known due to the extreme care required for their safe handling.



Pyrophoric and other spontaneously combustible substances will generally be identified as such on their product literature, MSDSs or International Chemical Safety Cards (described in Section 4.2). These substances should be identified as DOT/UN Hazard Class 4.2 materials for shipping purposes and labeled as SPONTANEOUSLY COMBUSTIBLE. For pyrophoric substances, if the NFPA diamond (NFPA 704

2001) were used for container or vessel labeling, the red (top) quadrant would have a rating of 4, indicating the highest severity of flammability hazard.

What Can Go Wrong?

Since exposure of a spontaneously combustible material to air has obvious consequences, loss of containment or other means of air exposure is usually the most important issue regarding what can go wrong. It should be noted that pyrophoric materials often exhibit one or more other reactivity hazards as well, such as water reactivity. Possible causes of uncontrolled reactions associated with pyrophoric and other spontaneously combustible materials include abnormal events such as the following:

- Inadequate cleanout of equipment containing spontaneously combustible substances, prior to opening to the air for maintenance
- Inadequate purging of air prior to introducing spontaneously combustible material into piping, tubing or container
- Equipment or container purged with air instead of inert gas
- Air drawn into system under vacuum
- Containment overpressurized and vented to atmosphere
- Containment overpressurized and ruptured
- Piping/vessel/container punctured
- Piping/vessel/container corroded
- Leakage at seal or connection
- Mechanical failure of piping or tubing
- Evaporation of diluent solvent
- Cutting/grinding/milling
- Mechanical attrition; e.g., of metal packing.

An example of a scenario that has resulted in many fires and explosions in refineries relates to iron sulfide. An impure, pyrophoric sulfide is formed when streams containing hydrogen sulfide or other volatile sulfur compounds are processed in ferrous equipment. Oxidation of moist iron sulfide is highly exothermic (heat generating). Opening of sulfide-containing equipment without adequate purging can result in rapid self-heating and ignition of the iron sulfide, which can then ignite other residual flammable gases or liquids in the equipment.

Many scenarios involving spontaneous combustion involve a combination of materials exposed to sufficient air, often in an insulating situation that prevents heat from a slow oxidation reaction to dissipate and thus results in a self-heating situation. Examples include activated carbon exposed to a high concentration of organic vapors and cotton or cellulose materials contaminated with oil. These combination scenarios can be examined and documented with incompatible material scenarios (Question 12 below).

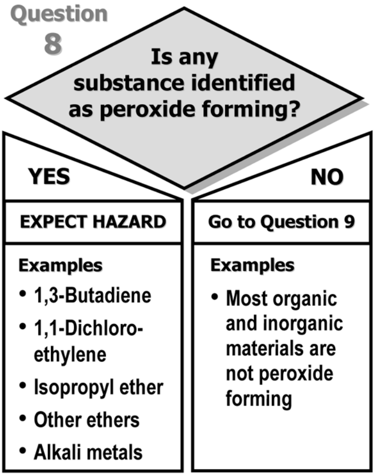
If the answer to Question 7 is YES, then you should make use of the information in Chapter 4, because a chemical reactivity hazard is present. The essential practices in Chapter 4 should be sufficient to manage this type of chemical reactivity hazards.

If you are certain that NO pyrophoric or other spontaneously combustible materials are present, then proceed to Question 8. Table 3.2 gives categories and examples of pyrophoric materials. More extensive lists that include less common chemicals, including metals, can be found in Urben (1999, 2:341–346). Other spontaneously combustible substances are tabulated by their proper shipping names and UN/NA numbers in the U.S. Department of Transportation regulation 49 CFR 172.101.

TABLE 3.2
Some Pyrophoric Materials (CCPS 1995b)

Category	Examples
Finely divided metals (without oxide film)	Aluminum, calcium, cobalt, iron, magnesium, manganese, palladium, platinum, titanium, tin, zinc, zirconium
Many hydrogenation catalysts containing adsorbed hydrogen (before and after use)	Raney nickel catalyst with adsorbed hydrogen
Alkali metals	Potassium, sodium
Metal hydrides	Germane, lithium aluminum hydride, potassium hydride, sodium hydride
Partially or fully alkylated metal hydrides	Butyllithium, diethylaluminum hydride, triethylbismuth, trimethylaluminum
Arylmetals	Phenylsodium
Alkylmetal derivatives	Diethylethoxyaluminum, dimethylbismuth chloride
Analogous derivatives of nonmetals	Diborane, dimethylphosphine, phosphine, triethylarsine
Carbonylmetals	Pentacarbonyliron, octacarbonyldicobalt
Grignard reagents (RMgX)	Ethylmagnesium chloride, methylmagnesium bromide
Metal sulfides	Iron sulfide
Miscellaneous	Phosphorus (white); titanium dichloride

Question 8: Peroxide Formers



This question pertains to substances that will react with the oxygen in the atmosphere to form unstable peroxides, which in turn might explosively decompose if concentrated. *Peroxide formation,* or *peroxidation,* usually happens slowly over time, when a peroxide-forming liquid is stored with limited access to air. Substances that are peroxide formers will often have an inhibitor or stabilizer added to prevent peroxidation. They are often not easily identifiable as peroxide formers using MSDSs or International Chemical Safety Cards. They are often identified by another characteristic, such as flammability, for storage and shipping purposes.

What Can Go Wrong?

Since exposure of a peroxide-forming material to air does not generally have obvious and immediate consequences, the scenarios for what can go wrong are usually more subtle than for other hazards. One general sequence of events is the formation and concentration of unstable peroxides over time, followed by an event such as the opening or agitation of a container that initiates explosive decomposition of the peroxide. Another general sequence is the formation of a peroxide, which in turn acts as an initiator of an uncontrolled polymerization reaction. Possible causes of uncontrolled reactions associated with peroxide forming materials include, but are not limited to, the following:

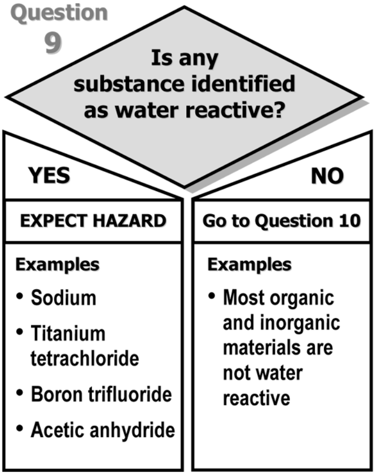
- Material stored beyond shelf life
- No or insufficient stabilizer/inhibitor added
- Wrong substance added as stabilizer or inhibitor
- Inhibitor depleted/consumed over time, or removed during a reaction
- Insufficient air in vapor space of container to allow inhibitor to be activated
- Leak or spill of substance
- Overheating or contamination of material, disabling stabilizer/inhibitor

- Exposure to light with air present
- Opening of container, allowing in air
- Concentration of peroxides by evaporation or distillation
- Precipitation of insoluble peroxides concentrating in process
- Material allowed to remain in, or inadequately cleaned out of, mothballed or decommissioned equipment.

If the answer to Question 8 is YES, then you should make use of the information in Chapter 4, because a chemical reactivity hazard is present. The essential practices in Chapter 4 should be sufficient to manage this type of chemical reactivity hazards.

If you are certain that NO peroxide forming substances are present, then proceed to Question 9. If you are uncertain as to whether a material is peroxide forming, a chemist or other expert should be consulted. Table 3.3 shows some chemical structures susceptible to peroxide formation.

Question 9: Water-Reactive Materials

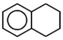


This question pertains to substances that will chemically react with water, particularly at normal ambient conditions. Some concentrated acids and bases can generate considerable heat of solution or heat of dilution when mixed with water. However, this can be considered a physical effect rather than a chemical reaction.

Water reactivity can be hazardous by one or more of several mechanisms. The heat of reaction can cause thermal burns, ignite combustible materials, or initiate other chemical reactions. Flammable, corrosive or toxic gases are often formed as reaction products. The violence of some reactions may disperse hazardous materials. Even slow reactions can generate sufficient heat and off-gases to overpressurize and rupture a closed container.

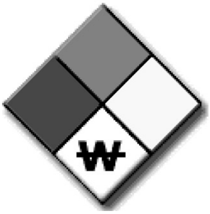
The potential hazards of most water-reactive materials are generally well known because of the precautions required for their safe handling. Substances that are water reactive will nearly always be identified as such on their MSDSs or International Chemical Safety Cards. They may be identified as DOT/UN Hazard Class 4.3 materials for shipping purposes and labeled as "dangerous when wet." However, some water-reactive materials

TABLE 3.3
Some Chemical Structures Susceptible to Peroxide Formation

STRUCTURE (not all bonds are shown)	EXPLANATION
Organic Substances	
$CH_2{-}O{-}R$	Ethers with alpha hydrogen atoms, especially cyclic ethers and those containing primary and secondary alcohol groups, form dangerously explosive peroxides on exposure to air and light
$CH({-}O{-}R)_2$	Acetals with alpha hydrogen atoms
$C{=}C{-}CH$	Allyl compounds (olefins with allylic hydrogen atoms), including most alkenes
$C{=}C{-}X$	Halo-olefins (e.g., chloroolefins, fluoroolefins)
$C{=}CH$	Vinyl and vinylidene esters, ethers, styrenes
$C{=}C{-}C{=}C$	1,3-Dienes
$CH{-}C{\equiv}CH$	Alkylacetylenes with alpha hydrogen atoms
$C{=}CH{-}C{\equiv}CH$	Vinylacetylenes with alpha hydrogen atoms
	Tetrahydronaphthalenes
$(R)_2CH{-}Ar$	Alkylarenes with tertiary hydrogen atoms (e.g., cumene)
$(R)_3CH$	Alkanes and cycloalkanes with tertiary hydrogen atoms (e.g., *t*-butane, isopropyl compounds, decahydronaphthalenes)
$C{=}CH{-}CO_2R$	Acrylates, methacrylates
$(R)_2CH{-}OH$	Secondary alcohols
$O{=}C(R){-}CH$	Ketones with alpha hydrogen atoms
$O{=}CH$	Aldehydes
$O{=}C{-}NH{-}CH$	Substituted ureas, amides, and lactams that have a hydrogen atom on a carbon atom attached to nitrogen
$CH{-}M$	Organometallic compounds with a metal atom bonded to carbon
Inorganic Substances	
Alkali metals, especially potassium, rubidium, and cesium	
Metal amides (e.g., $NaNH_2$)	
Metal alkoxides (e.g., sodium *t*-butoxide)	

are classified otherwise. Titanium tetrachloride, for example, is DOT/UN Hazard Class 8 (corrosive material) for shipping purposes, and its shipping label is likely to reflect both CORROSIVE and POISON hazards. Acetic anhydride is likewise designated Class 8 and may also be identified as a combustible liquid.

When the NFPA diamond is used for container or vessel labeling, and the white (bottom) quadrant contains the ~~W~~ symbol, the material will react violently or explosively with water, and a chemical reactivity hazard obviously exists. However, if the ~~W~~ symbol is not present, the material may still be water reactive, but at a slower rate, since the purpose of the NFPA symbol is to alert emergency responders to significant, immediate water reactivity hazards. Water reactivity is often very rapid, but can also be slow. The reaction may generate sufficient gas to rupture a closed container or vessel. The reaction of an organic material with water may be delayed due to reaction only occurring at the interface.



What Can Go Wrong?

Inadvertent contact of a water-reactive material with water is obviously the most important issue regarding what can go wrong. Due to the prevalence of water in living tissues, water-reactive materials are often toxic or corrosive as well, so loss of containment is often an additional concern. The following are some of the possible causes of uncontrolled reactions associated with water-reactive materials:

- Inadequate drying or purging of equipment before adding material
- Humidity in incoming air or gas
- Leakage of water from cooling coil into process
- Water line connected and valved in
- Aqueous instead of anhydrous raw material added
- Anhydrous instead of aqueous raw material received or selected
- Rainwater, sprinkler water, etc. onto cardboard container
- Cleanouts for maintenance
- Steam-out of equipment before use
- Piping/vessel/container punctured
- Piping/vessel/container corroded
- Spill into dike or trench containing water
- Mechanical failure of piping or tubing
- Uncontrolled mixing of reactive phases.

If the answer to Question 9 is YES, you should make use of the information in Chapter 4 because a chemical reactivity hazard is present. The essential practices presented in Chapter 4 should be sufficient to manage this type of chemical reactivity hazard.

If you are certain that NO water-reactive substances are present, then go to Question 10. If you are uncertain as to whether a material is water reactive, a chemist or other expert should be consulted or a simple test can be performed. For fire protection purposes, a material is considered water reactive if a gas or at least 30 cal/g of heat is generated when it is mixed with water (NFPA 704 2001), using a two-drop mixing calorimeter (Hofelich et al. 1994). Table 3.4 indicates some chemical categories susceptible to water reactivity. Table 3.5 lists some materials that react with water. These are not exhaustive lists.

TABLE 3.4
Some Chemical Categories Susceptible to Water Reactivity (CCPS 1995b, NOAA 2002)

Category	**Examples**
Alkali and alkaline-earth metals	Calcium, potassium, sodium, lithium
Anhydrous metal halides	Aluminum tribromide, germanium tetrachloride, titanium tetrachloride
Anhydrous metal oxides	Calcium oxide
Chlorosilanes	Methyldichlorosilane, trichlorosilane, trimethylchlorosilane
Epoxides (e.g., with acid present)	Butylene oxide, ethylene oxide, diepoxy butane, epibromohydrin
Finely divided metals, no oxide film	Aluminum, cobalt, iron, magnesium, titanium, tin, zinc, zirconium
Grignard reagents; organometallics	Ethylmagnesium chloride, methylmagnesium bromide
Inorganic acid halides	Phosphoryl chloride, sulfuryl chloride, chlorosulfuric acid
Inorganic cyanides	Barium cyanide, calcium cyanide, cyanogen chloride, silver cyanide
Isocyanates	*n*-Butyl isocyanate, methyl isocyanate, toluene diisocyanate
Metal alkyls	Aluminum alkyls, lithium alkyls
Metal amides	Lead amide, potassium amide, silver amide, sodium amide
Metal hydrides	Calcium hydride, lithium aluminum hydride, sodium borohydride
Nonmetal hydrides	Boron trifluoride, phosphorus trichloride, silicon tetrachloride
Nonmetal oxides	Phosphorus pentoxide, sulfur trioxide
Organic acid halides/anhydrides	Acetic anhydride, acetyl chloride
Nitrides, phosphides, carbides	Aluminum phosphide, calcium carbide, gallium phosphide

TABLE 3.5
Some Water-Reactive Chemicals (CCPS 1995b, NFPA 2002)

Rapidity of reaction with water varies among these chemicals from slow to explosively violent. Reaction with water may generate toxic, corrosive or flammable gaseous reaction products or generate sufficient heat or off-gas to rupture unrelieved containment.

This is not an exhaustive list of water-reactive chemicals. See Table 3.4 for additional categories.

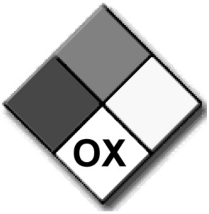
Acetic anhydride
Acetyl chloride
Alkylaluminums
Allyl trichlorosilane
Aluminum chloride, anhydrous
Aluminum phosphide
Amyl trichlorosilane
Benzoyl chloride
Boron tribromide
Boron trifluoride
Boron trifluoride etherate
Bromine pentafluoride
Bromine trifluoride
n-Butyl isocyanate
Butyllithium
Butyric anhydride
Calcium
Calcium carbide
Chlorine trifluoride
Chlorosilanes
Chlorosulfonic acid
Chromium oxychloride
Cyanamide
Decaborane
Diborane
Dichloroacetyl chloride
Dichlorosilane
Diethyl carbamyl chloride
Diethyl telluride
Diethylaluminum chloride
Diethylaluminum hydride
Diethylzinc
Diisobutylaluminum hydride
Dimethyldichlorosilane
Diphenyldichlorosilane
Dipropylaluminum hydride
Ethylaluminum dichloride
Ethylaluminum sesquichloride
Ethyldichlorosilane
Ethyltrichlorosilane
Fluorine
Gallium arsenide
Gallium phosphide
Germane
Isobutyric anhydride
Isophorone diisocyanate
Lithium
Lithium aluminum hydride
Lithium hydride
Methyl isocyanate
Methylaluminum sesquibromide
Methylaluminum sesquichloride
Methyldichlorosilane
Methylene diisocyanate
Methylpentaldehyde
Methyltrichlorosilane
Mono-(trichloro)-tetra-(mono-potassium dichloro)-penta-s-triazinetrione, dry
Monochloro-s-triazinetrione acid
Octadecyltrichlorosilane
Phenyl trichlorosilane
Phosphorus oxychloride
Phosphorus pentachloride
Phosphorus pentasulfide
Phosphorus tribromide
Phosphorus trichloride
Potassium
Potassium-sodium alloys
Propionyl chloride
Silicon tetrachloride
Silicon tetrafluoride
Sodium
Sodium dichloro-s-triazinetrione dihydrate
Sodium hydride
Sodium hydrosulfite
Sulfur chlorides
Sulfuric acid
Sulfuryl chloride
Tetraethyl lead
Tetramethyl lead
Thionyl chloride
Titanium tetrachloride
Toluene diisocyanate
Trichlorosilane
Triethylaluminum
Triethylborane
Triisobutylaluminum
Trimethylaluminum
Trimethylchlorosilane
Tripropyl aluminum
Vanadium tetrachloride
Vinyl trichlorosilane
Zirconium tetrachloride

Question 10: Oxidizers

Question 10 pertains to any material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials (NFPA 430 2000). Thus, most oxidizers can be thought of as being reactive with ordinary combustible liquids or solids, which are commonly used as process, packaging, general use, or structural materials. They can also react with many other substances.

Organic peroxides, included in the same general DOT/UN Hazard Class (Class 5) as oxidizers, are considered here to be self-reactive materials, so are addressed with Question 11 below.

Oxidizers will nearly always be identified as such on their MSDSs or International Chemical Safety Cards. They may be identified as DOT/UN Hazard Class 5.1 materials for shipping purposes and labeled as oxidizers. However, some oxidizers are classified otherwise. Chlorine, for example, is DOT/UN Class 2.3 (gases toxic by inhalation) and labeled as POISON GAS for shipping purposes; it may also be labeled as a corrosive material. Liquid oxygen is Class 2.2 (nonflammable nontoxic compressed gases) but should be labeled as NONFLAMMABLE GAS and OXIDIZER.



When the NFPA diamond is used for container or vessel labeling, and the white (bottom) quadrant contains **OX**, the material possesses oxidizing properties. It may be either an oxidizer or an organic peroxide. In either case, it should be considered to pose a chemical reactivity hazard.

What Can Go Wrong?

Inadvertent contact of oxidizers with reducing agents, including combustible materials, is the most important issue regarding what can go wrong when handling oxidizing substances. This contact will increase the burning rate of the combustible materials; it may also cause a fire to ignite without any additional ignition source. Some oxidizers can also undergo self-sustained decomposition, vigorously or explosively, when contaminated or exposed to heat or shock. Possible causes of uncontrolled reactions associated with oxidizers include abnormal events such as:

- Leak or spill of oxidizer from its containment
- Contamination of oxidizer with material that will promote or initiate its decomposition
- Water-soluble oxidizer dissolved in water, which contaminates packing material, pallets or drainage system
- Contact of oxidizer with heated surface
- Overheating of room or process containing oxidizer
- Involvement of both oxidizer and combustibles in building fire
- Improper disposal of off-specification or spilled oxidizer
- Re-use of containers without sufficient cleaning
- Inadvertent mixing of oxidizer with reducing agent/combustible material in process equipment
- Common dust collection system used for solid oxidizer and reducing agent/combustible material.

If the answer to Question 10 is YES, then you should make use of the information in Chapter 4, because a chemical reactivity hazard is present. The essential practices presented in Chapter 4 should be sufficient to manage this type of chemical reactivity hazard.

If you are certain that NO oxidizers are present, then proceed to Question 11. If you are uncertain as to whether a material is an oxidizer, a chemist or other expert should be consulted. Table 3.6, which was derived from NFPA 49 (2001) and Appendix B of NFPA 430 (2000), lists some typical oxidizers, but is by no means a complete list. Organic peroxides are not included individually in this list. NFPA 432 (1997) can be consulted for typical organic peroxide formulations. Volume 2 of *Bretherick's Handbook* (Urben 1999, 287–291) lists many structures and individual chemical compounds having oxidizing properties.

Question 11: Self-Reactive Materials

The next question pertains to substances that will self-react, often with accelerating or explosive rapidity. These substances have various chemical structures that make them susceptible to at least one of three forms of self-reaction:

- *Polymerizing* (individual molecules called *monomers* combining together to form very large, chain-like or crosslinked polymer molecules)
- *Decomposing* (larger molecules breaking apart into smaller, more stable molecules)

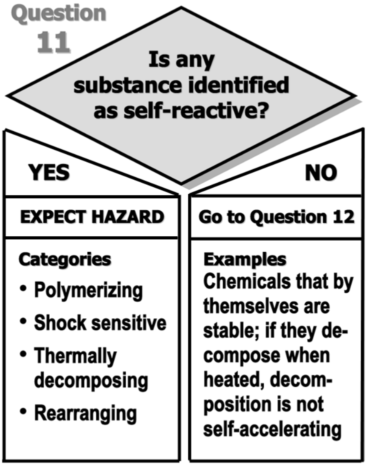


TABLE 3.6
Typical Oxidizers (NFPA 430 2000, NFPA 49 2001; see text)

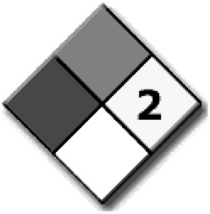
Organic peroxides are also typical oxidizers, but not listed individually.
See NFPA 432 (1997).

- Ammonium dichromate
- Ammonium nitrate
- Ammonium perchlorate
- Ammonium permanganate
- Ammonium persulfate
- Amyl nitrate
- Barium bromate
- Barium chlorate
- Barium hypochlorite
- Barium perchlorate
- Barium permanganate
- Barium peroxide
- Bromine pentafluoride
- Bromine trifluoride
- 1-Bromo-3-chloro-5,5-dimethylhydantoin (BCDMH)
- Calcium chlorate
- Calcium chlorite
- Calcium hypochlorite
- Calcium perchlorate
- Calcium permanganate
- Calcium peroxide
- Chloric acid (10 percent maximum concentration)
- Chlorine
- Chlorine trifluoride
- Chlorosulfonic acid
- Chromium trioxide (chromic acid)
- Copper chlorate
- Guanidine nitrate
- Halane (1,3-dichloro-5,5-dimethylhydantoin)
- Hydrogen peroxide solutions
- Lead dioxide
- Lead perchlorate
- Lithium chlorate
- Lithium hypochlorite
- Lithium perchlorate
- Lithium peroxide
- Magnesium bromate
- Magnesium chlorate
- Magnesium perchlorate
- Magnesium peroxide
- Manganese dioxide
- Mercurous chlorate
- Mono-(trichloro)-tetra-(mono-potassium dichloro)-penta-*s*-triazinetrione
- Monochloro-*s*-triazinetrione acid
- Nitric acid and fuming nitric acid
- Nitrites, inorganic
- Nitrogen oxides (NOx)
- Oxygen
- Peracetic acid
- Perchloric acid solutions
- Potassium bromate
- Potassium chlorate
- Potassium dichloro-*s*-triazinetrione (potassium dichloroisocyanurate)
- Potassium dichromate
- Potassium percarbonate
- Potassium perchlorate
- Potassium permanganate
- Potassium peroxide
- Potassium persulfate
- Potassium superoxide
- *n*-Propyl nitrate
- Silver peroxide
- Sodium bromate
- Sodium carbonate peroxide
- Sodium chlorate
- Sodium chlorite
- Sodium dichloro-s-triazinetrione (sodium dichloroisocyanurate)
- Sodium dichloro-s-triazinetrione dihydrate
- Sodium dichromate
- Sodium perborate (anhydrous)
- Sodium perborate monohydrate
- Sodium perborate tetrahydrate
- Sodium percarbonate
- Sodium perchlorate
- Sodium perchlorate monohydrate
- Sodium permanganate
- Sodium peroxide
- Sodium persulfate
- Strontium chlorate
- Strontium perchlorate
- Strontium peroxide
- Tetranitromethane
- Thallium chlorate
- Trichloro-*s*-triazinetrione (trichloroisocyanuric) (acid all forms)
- Urea hydrogen peroxide
- Zinc bromate
- Zinc chlorate
- Zinc permanganate
- Zinc peroxide

- *Rearranging* (the atoms in a molecule rearranging into a different molecular structure, such as a different isomer).

Some substances such as ethylene oxide can self-react in more than one way.

Self-reactive materials are generally identified as "polymerizing," "decomposing," or "unstable" on their MSDSs or International Chemical Safety Cards. Substances that are DOT/UN Class 1 (Explosives) and Class 5.2 (Organic peroxides) are likely to be self-reactive. However, some organic peroxide formulations—Class V formulations according to NFPA 432 (1997)—burn with even less intensity than ordinary combustibles and present no chemical reactivity hazard. Many self-reactive materials are classified in other categories; for example, most self-polymerizing materials are labeled as flammable gases or flammable liquids, due to their flammability in addition to being reactive. Examples of some polymerizing materials are listed in Table 3.7.



When the NFPA diamond is used for labeling containers or vessels of self-reactive materials, the yellow (right) quadrant should have some rating between 1 (lowest) and 4 (highest), inclusive. By the definitions in NFPA 704, this indicates the material poses an *instability* hazard (NFPA 2002). Having a nonzero NFPA instability rating is a straightforward means of identifying self-reactive materials. NFPA 49 and NFPA 325 give instability ratings for many different industrial chemicals (NFPA 2002).

TABLE 3.7
Some Polymerizing Compounds (Extracted from NFPA 49 2001)

Acrolein
Acrylamide
Acrylic acid
Acrylonitrile
1,2-Butylene oxide
Butylacrylate
1,3-Butadiene
Butyraldehyde
Crotonaldehyde
Dichloroethylene
Diketene
Divinylbenzene
Epichlorohydrin
Ethyl acrylate
Ethylene
Ethylene cyanohydrin
Ethylene oxide
Ethyleneimine
2-Ethylhexylacrylate
Hydrogen cyanide
Isoprene
Methacrylic acid
Methyl acrylate
Methyl isocyanate
Methyl methacrylate
Methyl vinyl ketone
Methylchloromethyl ether
Propargyl alcohol
Propionaldehyde
Propylene oxide
Styrene
Tetrafluoroethylene
Tetrahydrofuran
Toluene diisocyanate
Trimethoxysilane
Vinyl acetate
Vinyl acetylene
Vinyl chloride
Vinyl ether
Vinyl toluene
Vinylidene chloride

The common thread among self-reactive materials is that they have more internal energy than their polymerization, decomposition or rearrangement products, so that energy is released when a self-reaction occurs. If this released energy is not dissipated (such as by cooling) as fast as it is generated, it can go into preheating the unreacted material, and cause the reaction rate to accelerate out of control.

Some energy is required to start the self-reaction. On the molecular level, this is called the *activation energy.* It can be thought of as analogous to a train needing energy (the activation energy) to go up a slight incline before descending at an increasing speed down a hill. This effect is illustrated in Figure 3.2.

For some highly reactive materials such as shock-sensitive explosives and organic peroxides, mechanical shock, friction or spark may be sufficient to start a decomposition reaction. However, for most self-reactive materials, the energy input is in the form of thermal energy (heat). For storage situations, the critical temperature at which the thermal energy is sufficient to start an uncontrolled reaction in a particular storage configuration for a specified time is known as the *self-accelerating decomposition temperature* (SADT), as described in NFPA 49 (2001):

> Certain compounds, when held at moderate ambient temperatures for an extended period of time, may undergo an exothermic reaction that accelerates with increase in temperature. If the heat liberated by this reaction is not lost to the environment, the bulk material increases in temperature, which leads to an increase in the rate of decomposition. Unchecked, the temperature grows exponentially to a point at which the decomposition cannot be stopped or slowed. The minimum temperature at which this exponential growth occurs in a material packed in its largest standard shipping container is defined as the self-accelerating decomposition temperature. Self-accelerating decomposition temperature is a measure of the

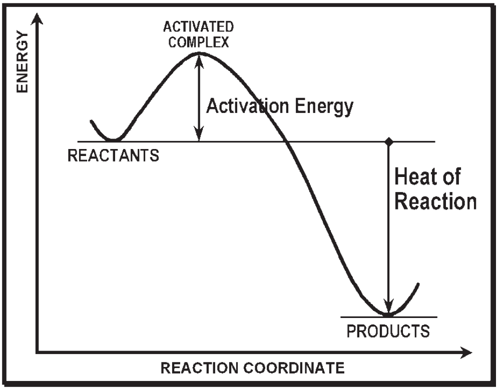


Figure 3.2. **Activation energy and reaction path.**

> ease in which decomposition occurs under normal storage conditions. It is not an indicator of the violence of any decomposition reaction under conditions of fire exposure or contact with incompatible materials.

Analogous thresholds can also be measured for mechanical-energy and electrical-energy initiation. For example, drop height tests are defined for initiating explosive decomposition of shock-sensitive materials by the impact of a weight being dropped on material samples. A similar test is conducted for studying friction initiation. Sensitivity to electrical spark initiation for vapor-phase decomposition is measured as the *minimum ignition energy* (MIE), similar to the MIE for initiating vapor or dust explosions.

What Can Go Wrong?

Five general categories of what can go wrong with self-reactive materials are:

- The occurrence of an abnormal energy input that is sufficient to initiate an uncontrolled self-reaction
- The presence of a catalytic substance that lowers the energy needed to initiate an uncontrolled self-reaction
- A reduction in the rate at which energy is dissipated to its surroundings, allowing initiation of an uncontrolled self-reaction
- The absence of sufficient activated inhibitor or stabilizer that is needed to prevent initiation of an uncontrolled self-reaction
- Concentration of self-reactive material, resulting in an uncontrolled increase in reaction rate.

(Abnormal reactions with other, incompatible materials that may also serve to initiate self-reactions that are more energetic are also possible. These can be addressed by the scenario approach that goes with Question 12.)

Initiation of uncontrolled self-reactions at a given facility can occur in storage or during handling, mixing, physical processing or chemical reactions. A few of the many possible causes of uncontrolled reactions associated with self-reactive materials include the following:

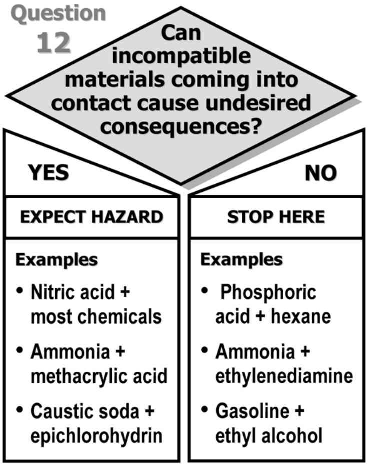
- External fire
- Building or process temperature control fails high
- Loss of building or process cooling
- Excess heating or drying
- Contact with hot surface/equipment
- Overheated seal or bearing
- Cavitation or dead-head pumping of liquid
- Adiabatic compression of self-reactive gas or vapor
- Hot work in area or on equipment containing self-reactive material

- Electric sparking or arcing
- Dropping of or impact with container
- Foreign object caught between agitator and tank wall
- Catalytic substance remains in container or equipment due to reuse, corrosion or inadequate clean-out
- Catalytic substance inadvertently added to process
- Improper material of construction or incorrect seal material, etc. in contact with substance
- Packaging material in too large of container
- Overstacking of containers or insufficient spacing between containers
- Loss of heat transfer due to fouling, added insulation, inadequate air movement, etc.
- Concentration of diluted formulation by evaporation or distillation
- Leak or spill of substance, especially where heat transfer is minimal (e.g., insulation)
- Accumulation of dust/powder in dust collection or vent system
- No or insufficient stabilizer/inhibitor added
- Wrong substance added as stabilizer or inhibitor
- Inhibitor consumed or reacted
- Air totally displaced in vapor space of container, not allowing inhibitor to be activated
- Overheating or contamination of material disables stabilizer/inhibitor
- Material stored for longer than its recommended shelf life; inhibitor or stabilizer consumed over time
- Segregation of inhibitor or stabilizer, resulting from freezing or precipitation
- Operation at too high pressure (e.g., acetylene, ethylene, ethylene oxide)
- Tool or other equipment dropped on shock-sensitive material
- Other abnormal energy input such as by electrical discharge or friction.

If the answer to Question 11 is YES, then you should make use of the information in Chapter 4, because a chemical reactivity hazard is present. The essential practices presented in Chapter 4 should be sufficient to manage this type of chemical reactivity hazard, excluding considerations for commercial explosives, which are also self-reactive materials.

If you are certain that NO self-reactive substances are present, then proceed to the next question (Question 12). If you are uncertain as to whether a material is self-reactive, a chemist or other expert should be consulted. Annex E to NFPA 704 (2001) gives a method for calculating an “instantaneous power density,” defined as the product of the enthalpy (heat) of the self-reaction and the initial rate of reaction, determined at 250°C (482°F). Two criteria that are considered to reflect an NFPA instability rating of zero and the absence of a self-reactivity hazard are an instantaneous power density value below 0.01 W/mL and no exotherm being exhibited by the material at temperatures less than or equal to 500°C (932°F) when tested by differential scanning calorimetry (NFPA 2002).

Question 12: Incompatible Materials



Up to this point, the chemical reactivity hazards of individual substances, either by themselves or in contact with common environmental materials, have been considered. This last question in the chemical reactivity hazards screening will address the potential for an unintended chemical reaction due to incompatible materials contacting each other. *Compatibility,* in this context, means the ability of materials to exist in contact without specified (usually hazardous) consequences under a defined scenario. A *scenario,* in this context, is a detailed physical description of the process whereby a potential inadvertent combination of materials may occur (ASTM E 2012-00).

This question especially pertains to mixing and formulation facilities, where materials are being intentionally combined together. However, it can also apply to facilities involving storage, handling, repackaging or physical processing facilities where incompatible materials are present and have the potential for contacting each other, or for the wrong material to be unloaded into a storage tank or facility.

Step One: Decide on Undesired Consequences of Concern

As the above definition of compatibility implies, the determination of whether materials are incompatible depends on what you consider undesired "consequences" in the context of your facility's operation. A suggested starting point may be to consider the undesired consequences as uncontrolled chemical reactions that can result in any of the following:

- Toxic gas generation
- Corrosive gas or liquid generation

- Flammable gas generation
- Formation of shock-sensitive or explosive material
- Explosion
- Ignition of combustible material
- Sufficient off-gas generation to rupture a container or enclosure
- Sufficient heating of substances to initiate chemical decomposition, thermal runaway reaction, or another, more energetic chemical reaction
- Reduction of thermal stability of material to point of initiating decomposition.

The facility owner (as discussed in Section 4.1) should decide upon or agree to the undesired consequences of concern before proceeding further.

Step Two: Identify Mixing Scenarios

The next step is to identify specific scenarios by which materials could be combined. Chemical compatibility depends heavily on the mixing scenario, which should consider at least the following (ASTM E 2012-00):

- Materials that could be combined, including their compositions or concentrations
- Specific quantities of materials
- Storage temperatures
- Confinement (closed or open system)
- Atmosphere (air, nitrogen inerted, oxygen enriched)
- Maximum time the materials may be in contact.

Depending on the nature of your facility, many different scenarios may be possible for the unintentional mixing or combining of different substances. A few example causes (starting points) for these scenarios include:

- Leaking liquid contacts adjacent material or container
- Raw material pumped into wrong storage tank
- Material pumped or transferred to wrong process vessel
- Cross-connecting line left open
- Wrong material or concentration received from supplier
- Material mislabeled or unlabeled
- Wrong material selected by operator to add to mixture or formulation
- Waste materials combined in same tank or container
- Waste materials combined in plant sewer system
- Inaccurate pH measurement
- Incoming material impure or contaminated
- Wrong material of construction used

- Material left in process equipment from previous batch or run
- Cleaning materials or other contaminants left in process equipment prior to startup
- External force (earthquake, crane, fire, explosion, etc.) causes simultaneous or domino failure of adjacent tanks or containers
- Product or waste is transferred into container with residual material present
- Unauthorized combination of materials occurs
- Full range of operating parameters not studied
- Calorimetric test stopped too soon.

Note that positive measures can be taken to eliminate the potential for inadvertent mixing such as by storage segregation, elimination of excess inventory, just-in-time delivery, or in-situ manufacturing. If so, then you may be able to significantly reduce the number of potential scenarios that need evaluation.

Step Three: Document Mixing Scenario Consequences

It is suggested that a table such as the bottom part of Table 3.1 be set up to capture and document scenarios that are identified and whether an incompatibility hazard exists for each scenario. This is illustrated in the examples shown in Table 3.8.

Describe in the first column of the table what specific materials and quantities could be combined, how they could be combined, and for how long. Use the second column to indicate whether or not ambient, unconfined conditions apply (ambient temperature, atmospheric pressure, noninerted and nonenriched atmosphere with 21% oxygen, and no enclosure or confinement). *Assume published compatibility data will be valid only if ambient, unconfined conditions apply*, unless the data indicate otherwise. Use the third column to indicate that, for this scenario under these conditions, a chemical reaction will occur that has the potential for any of your predetermined undesired consequences. Document any comments and the source of your information in the last column.

The best data to use for determining whether an incompatibility exists will obviously be from testing the actual scenarios and conditions that are identified. However, this is often not practical or possible. Small-scale tests can be performed in a laboratory that can give an indication whether a reaction is expected. However, be wary of concluding that since no reaction is seen on a small scale, no effects will be realized in an industrial facility. Heat transfer effects and scale-up issues are especially important to be careful of when extrapolating small-scale results. Differences in heat transfer, mixing and other scale-up effects can cause a significant and potentially

TABLE 3.8
Example Inadvertent Mixing Scenarios and Compatibility Findings

SCENARIO	CONDITIONS NORMAL?[1]	R, NR or ?[2]	INFORMATION SOURCES; COMMENTS
1 Mix one liter of household ammonia cleaner into one gallon of household chlorine bleach in an open bucket, with intention of immediate use	Yes	R	Based on sodium hypochlorite solution MSDS. Generates heat and toxic vapors; can form explosive nitrogen trichloride under certain conditions
2 Pour 2 gal of used motor oil into open 55 gal drum containing waste turpentine, then close bung and leave in outside drum storage area for up to 3 months	No	NR	No contaminants in waste turpentine identified that would be incompatible; NOAA Chemical Reactivity Worksheet used; confinement in drum for up to 3 months not expected to cause reaction, based on experience with actual mixture and lack of DSC exotherm below 500 °C
3 Inadvertently pump up to 400 gal of 100°F (37.8°C) cyclohexane at 5 gpm into closed, temperature-controlled storage tank of between 200 and 800 gal of acrylic acid with 200 ppm MEHQ inhibitor, maintained at 68°F (20°C)	No	?	Compatibility information only known for ambient conditions; no reaction with cyclohexane expected, but may be hot enough to increase dimer formation and possibly initiate polymerization

[1] Does the contact/mixing occur at ambient temperature, atmospheric pressure, 21% oxygen atmosphere, and unconfined? (IF NOT, DO NOT ASSUME THAT PUBLISHED DATA FOR AMBIENT CONDITIONS APPLY)

[2] R = Reactive (incompatible) under the stated scenario and conditions
NR = Nonreactive (compatible) under the stated scenario and conditions
? = Unknown; assume incompatible until further information is obtained

disastrous divergence between actual effects and those estimated from small-scale results.

Lacking actual test results, the next best option is to check chemical-specific safety data such as MSDSs or International Chemical Safety Cards (ICSCs) for the particular compounds and concentrations involved. Section 10 (Stability and Reactivity) of standard MSDSs should contain information on Incompatibilities with Other Materials. Similar information should be in the Chemical Dangers section of ICSCs. However, these are rarely more than lists of incompatible materials, and do not indicate what consequences can be expected. The listed incompatibilities should be considered as only applying to ambient conditions.

References on incompatibilities, such as *Bretherick's Handbook of Reactive Chemical Hazards* (Urben 1999), *Sax's Dangerous Properties of Industrial Materials* (Lewis and Irving 2000) and NFPA 491, *Hazardous Chemical Reactions* (NFPA 2002), summarize published literature and incidents on incompatibilities. They may give more detailed information on what to expect when specific materials are combined.

If chemical-specific information is not available, the consequences may be able to be predicted by methods using *compatibility groups,* or chemicals with similar chemical structures that are expected to have similar chemical reactivity characteristics. One computerized tool that uses this approach is the Chemical Reactivity Worksheet made available by the U.S. National Oceanic and Atmospheric Administration (NOAA 2002). This program has over 6000 chemicals, mixtures, and solutions included in its database. It also predicts chemical reaction consequences of combining two materials at a time (e.g., "Heat generation by chemical reaction, may cause pressurization"). Examples from the Chemical Reactivity Worksheet are shown in Section 4.2. It is critical that all chemicals be positively identified to have a complete evaluation of all potential incompatibilities.

If any incompatibilities are found (R or ? in the third column of Table 3.8), the answer to Question 12 is YES. However, some judgment will be needed as to the likelihood of each scenario occurring. For example, a scenario may be judged *not expected to occur any time during the life of the facility.* This could be noted in the Comments column along with information supporting this judgment, and you may decide to focus your management of chemical reactivity hazards on hazards that are more likely to result in loss events.

For facilities where many different materials are stored, processed or mixed, it may be desirable to use a matrix approach to investigating all possible combinations of materials, including contaminants, materials of construction, additives, catalysts, utilities and common substances such as air and water. The development of a compatibility matrix is discussed in Section 4.3.

For larger or more complex facilities, a systematic approach to identifying incompatibility scenarios and analyzing their severities and likelihoods may be warranted. A process hazard analysis (PHA) approach such as a hazard and operability (HAZOP) study can be an effective tool to facilitate such an effort, and may be required by regulation if the process falls within the scope of regulations. These methods are discussed in Section 4.5.

If the answer to Question 12 is YES, then you should make use of the information in Chapter 4, because one or more chemical reactivity hazards are present. The information in Chapter 4 should be sufficient to manage these types of chemical reactivity hazards.

If you are certain that NO incompatible materials have a reasonable likelihood of contacting each other and causing undesired consequences, then stop here. If the decision flow of Figure 3.1 has been followed, the Preliminary Screening Method indicates that no significant chemical reactivity hazards are expected at your facility.

This should not be considered a definitive answer for the entire life of the facility. Special care needs to be taken whenever introducing new chemicals or processes to a facility, and management controls need to be in place to prevent unauthorized materials from being brought on-site. You can go back through the screen for each new chemical discovered or being considered, and see whether its presence would introduce chemical reactivity hazards that must be managed and controlled on an ongoing basis.

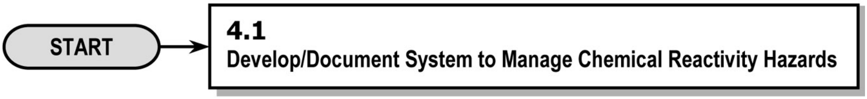
Essential Management Practices

4

Presented in this chapter are ten essential practices for managing chemical reactivity hazards. Management elements common to all safety management systems, such as emergency response, have not been included in this chapter. Figure 4.1 shows how these practices come together in a logical framework for developing and maintaining chemical reactivity hazard management throughout the life cycle of a facility. As discussed in Section 2.3, some of these practices are likely to be already in place in an existing facility, but may need to be extended and applied to managing chemical reactivity hazards.

This chapter assumes chemical reactivity hazards exist at your facility. If you are uncertain whether or not you have any chemical reactivity hazards, the Preliminary Screening Method in Chapter 3 can be used to help identify whether chemical reactivity hazards may be present.

4.1. Put into Place a System to Manage Chemical Reactivity Hazards



As the Figure 4.1 flowchart implies, managing chemical reactivity hazards starts with a *management system*. To prevent incidents, a facility must not only be well designed, but also properly operated and maintained. A commitment to safety from all levels of management is essential, to ensure that all safety aspects receive adequate priority. In practice, conflicts of interest may arise between safety and other goals such as production demands and

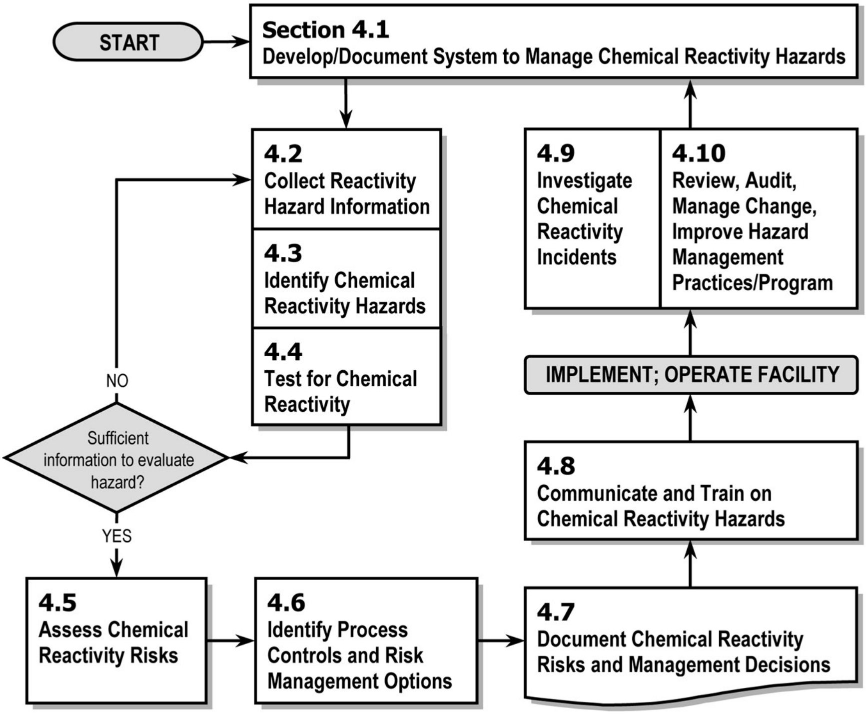


Figure 4.1. **Flowchart for implementing chemical reactivity hazard management.** (Numbers refer to sections in this book.)

budgets. In these cases, the management attitude will be decisive. In reality, such a conflict may only be an apparent one, because safety, efficiency, and product quality all depend on a reliable production facility with a low frequency of technical troubles and safety problems (CCPS 1995a).

Developing a management system is not a one-time project. It must be able to manage even subtle material, equipment or personnel changes that may have a significant effect on the safety of the operation. These may include a minor change in raw material purity, a modification to the shape of a vessel where heat transfer is important, or a change in how an operation is supervised.

Table 4.1 lists essential ingredients of a management system for successfully managing chemical reactivity hazards. An honest comparison of a company's current practice with the items in this list can be used to point out the gaps that need to be filled. If you are just getting started with chemical reactivity hazard management, this shows what is needed to develop a successful management system.

TABLE 4.1

Gap Analysis: Chemical Reactivity Hazard Management System

____ Top management commitment has been expressed in written form and personally communicated to site management and employees.

____ Business decisions and allocation of resources are consistent with this expressed top management commitment.

____ Ownership of the facility or process involving chemical reactivity hazards is clearly established.

____ Line management is committed to managing chemical reactivity hazards, from the chief executive officer to first-level supervisors.

____ An appropriate system to manage chemical reactivity hazards has been developed and formally documented.

____ This system includes clear, written statements of what needs to be done and documented, when, how, how often, and by whom.

____ Means and resources have been permanently allocated, and training to the appropriate level is conducted and verified, to equip every person throughout the organization with the knowledge and skills needed to carry out his/her responsibilities.

____ It is understood by every person that following all established procedures for managing chemical reactivity hazards is a condition of employment.

____ Technical resources are readily available to identify chemical reactivity hazards, acquire needed data, assess risks, and develop safeguards.

____ The design basis of the facility and its safety systems, including operating and maintenance procedures, are established and documented.

____ All process, equipment and personnel changes are managed such that the safety of the facility is not compromised by any change.

____ Line management participates in regularly scheduled audits to ensure the procedures and practices for managing chemical reactivity hazards are being consistently followed.

____ Line management participates in the investigation of all chemical reactivity incidents and near misses, and makes resources available to implement corrective actions.

____ An attitude and practice of continuous improvement is cultivated within the organization, including looking outside to keep abreast of new or updated information and striving to make the facility inherently safer.

It is fully recognized that having a management system in place that matches all of the items in Table 4.1 can be a major undertaking, and may require some significant changes in “corporate culture” that may not happen overnight. Nevertheless, these items are fundamental, and attempts to continue with the remaining essential elements in this chapter will not likely succeed over time if management commitment and involvement are not obvious or adequate resources are not made available.

Case histories of chemical reactivity incidents, such as those in Appendix A-1, are useful in getting needed attention and priority for a chemical reactivity hazard management system. Other companies’ programs, such as the ones shared on the CD-ROM accompanying this publication, can be helpful in building on what has worked in other organizations. However, it should be noted that the company programs on the CD-ROM are for facilities practicing intentional chemistry which, as noted in Section 3.1, require additional resources and involve a greater degree of complexity than facilities not involving intentional chemistry. The attributes of a management system listed in Table 4.1 apply to all facilities having chemical reactivity hazards, whether a warehouse, contract blender, paint manufacturer, research laboratory, or world-scale chemical plant.

The keystone of managing chemical reactivity hazards is *line responsibility*. The "line" referred to here is the chain of command and authority that extends from the operator to the chief executive officer of the company. When all the advice and consultation is gathered relative to an issue, such as from relevant area experts and safety personnel, it is the business' responsibility to provide leadership. It does so by communicating values, setting policy, making appropriate decisions, allocating the necessary resources, and following up to ensure implementation.

Implied in line responsibility is a clear understanding of facility ownership, including who "owns" the facility's chemical reactivity hazards. This generally falls to the plant superintendent or plant manager. One company implements this by defining and documenting ownership of the reactive chemistry during the initial concept and development stages of a new process. Ownership of the reactive chemistry is then formally passed to line management of the actual facility when built.

Safety Policy

The process of hazard management begins with management support, commitment, and action. It is essential that management establishes, clearly communicates and sustains a consistent policy regarding managing these hazards. This is most often expressed in a formal statement containing the following attributes:

- It reflects the values of the company—what is really important (Dowell 2002).
- It communicates management's commitment to identifying, reducing, and controlling chemical reactivity hazards throughout the entire facility life.
- It recognizes the importance of managing chemical reactivity hazards to avoid serious incidents.
- It endorses sustained commitment of resources for all necessary activities, including material testing, as well as the timely completion and documentation of review, audit, and investigation action item resolutions.

- It strongly supports reporting and investigating incidents and near misses, and emphasizes the value and necessity of communicating and sharing the lessons learned to all that could benefit.

Organizations may have an existing policy that can be modified to incorporate the above concepts. It may not be necessary to establish a new and separate policy.

Resource Allocation

A policy statement alone is worth very little. Management must provide a sustained commitment of resources for an ongoing program. The most important resources are the right people having the background, qualifications, experience and commitment needed to safely operate and maintain the facility. This includes the technical expertise to understand chemical reactivity hazards and their control and the means to maintain the needed knowledge over time.

Another major area where management commitment is expressed is allocating the manpower and resources for timely implementation of action items. New facility design, inherent safety reviews, process hazard analyses, incident investigations, audits, and other activities associated with hazard management will result in the formulation of many action items. If real improvement is to occur, these action items must be properly addressed and closed out. This will rarely happen, especially in a timely manner, unless a system is in place for documenting, assigning, and tracking them to resolution, and management regularly oversees their status and pushes for their completion.

Responsibilities and Accountability

A system to manage chemical reactivity hazards will obviously look different for a warehouse than for a facility where intentional chemistry is practiced. Nevertheless, common to both is the need to specifically define and document responsibilities for every aspect of managing chemical reactivity hazards, and then for line management to hold all persons in positions with designated responsibilities accountable to perform their duties. This obviously goes hand in hand with line management allocating sufficient resources to make fulfillment of the responsibilities possible, and equipping the responsible persons with the information and training needed to do their jobs safely. The latter is especially important when managing chemical reactivity hazards, since the nature of the hazards requires some degree of understanding of the chemical reactivity hazards and the possible consequences if an uncontrolled chemical reaction occurs.

The responsibilities are best laid out in a controlled document that includes clear statements of what needs to be done, when, how, how often, and by whom. Procedures and job descriptions may specify some of these responsibilities for an existing facility. Development of a management system will be most effective with broad input from the persons who will be given the designated responsibilities and be held accountable to fulfill them.

Reviews, Audits, and Investigations

Process hazard reviews should begin with a thorough understanding of all the factors and conditions associated with a process. Starting a process hazard analysis, much less a detailed reactivity testing program, before gaining this understanding will be inefficient.

Periodic reviews and reevaluations are necessary to ensure the chemical reactivity hazard management system continues to function as originally intended and continues to achieve the desired results. This periodic review recognizes the fact that organizations are dynamic entities with constantly evolving management staffing. One obvious benefit of periodic reviews is verification that audit findings and preventive action recommendations have been resolved to completion and documented. Another obvious benefit is early detection of disturbing trends, such as low reporting of near misses. (A *near miss* is defined as an unplanned sequence of events that could have caused harm or loss if conditions were different or had been allowed to progress.)

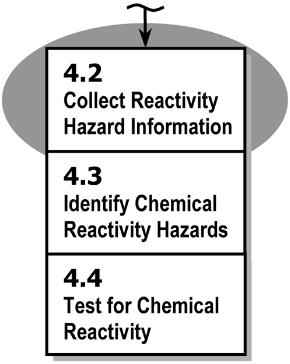
Management has the responsibility to create and maintain an atmosphere of trust and respect to encourage openness in reporting near misses and actual loss events. Failure to achieve this positive atmosphere will result in low or no reporting of near misses, which may ultimately lead to a catastrophic incident that could have been otherwise avoided.

System Development

The initial developer of a chemical reactivity hazard management system must first achieve the support of top management. The person, team, or ad hoc committee who is initially facilitating the setting up of the management system should begin preparations by gaining an understanding of the basic principles and priorities of chemical reactivity hazards. They must determine what methods best fit into the particular culture and perspective of their organization. They have a responsibility to educate management (in management's own terms) and to give management the opportunity to participate in the development activities. Members of top management may not intuitively understand the details of reactive chemistry. However, educating top management is critical. Management participation helps promote a sense of "ownership" and helps establish chemical reactivity hazard management as a normal part of line management responsibility. Promoting ownership by managers reduces the tendency to perceive chemical reactivity hazards as primarily the domain of a narrowly focused group of technical personnel. "Chemical reactivity hazards are the Safety Office's responsibility" should never be heard.

4.2. Collect Reactivity Hazard Information

An essential practice for managing chemical reactivity hazards is to gather chemical reactivity data on the chemicals likely to be present *at your facility*. This can be done based either on a current chemical inventory, or on a list of chemicals expected to be present. In either case, your management system must also include a means of detecting and checking any new or variant chemicals brought onsite for the first time.



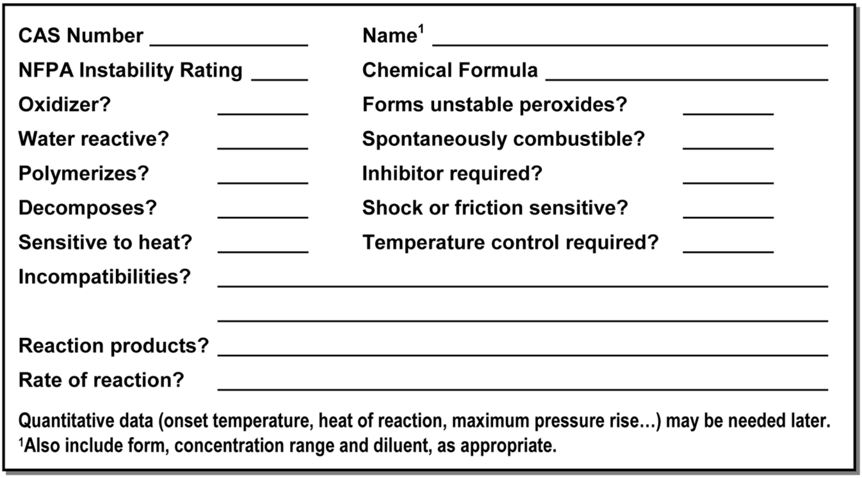
What To Look For

The list in Table 4.2 indicates the basic chemical reactivity hazard information that needs to be known for each substance. This is an extension of the information needed for the Preliminary Screening Method of Chapter 3. The Glossary at the end of of this publication gives definitions for most of the terms used in the table.

Temperature control is included in Table 4.2 since reactive chemicals as a whole are more sensitive to temperature than other parameters such as pressure. A chemical can require temperature control for various reasons. For example, many organic peroxides must be refrigerated to control the heat generated by slow decomposition of the peroxide in storage. Some materials, such as acrylic acid, must be maintained within a certain temperature range. If it gets too hot, the self-polymerization rate increases and the heat of reaction will not be dissipated fast enough to maintain control. If it is allowed to freeze, its added inhibitor will separate out and an uncontrolled reaction can be initiated during thawing of the material.

Suggestions for finding the data listed in Table 4.2 are given in the rest of this section. Other data sources and compilations, including MSDS services, are listed and described in *Guidelines for Safe Storage and Handling of Reactive Materials* (CCPS 1995b), Appendix A. Table 4.3 shows an example of what might be entered for ammonium nitrate.

TABLE 4.2
Basic Chemical Reactivity Data to Collect (See Glossary for Definitions)

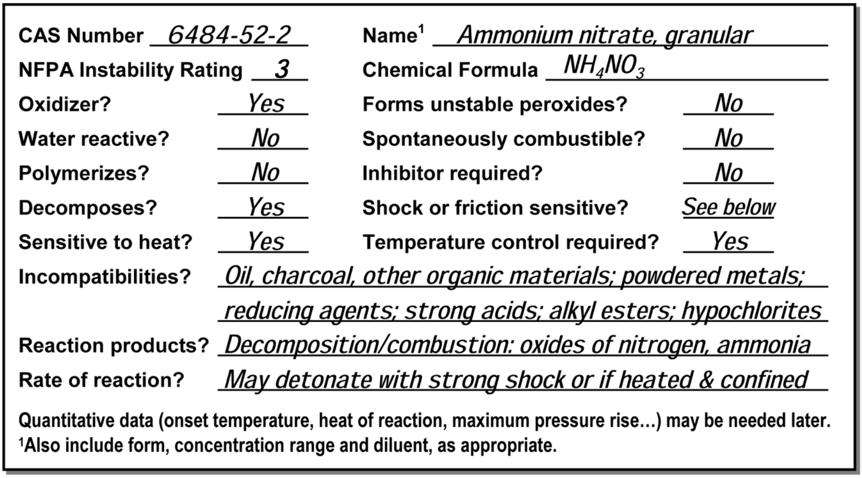


CAS Number		**Name[1]**	
NFPA Instability Rating		**Chemical Formula**	
Oxidizer?		**Forms unstable peroxides?**	
Water reactive?		**Spontaneously combustible?**	
Polymerizes?		**Inhibitor required?**	
Decomposes?		**Shock or friction sensitive?**	
Sensitive to heat?		**Temperature control required?**	
Incompatibilities?			
Reaction products?			
Rate of reaction?			

Quantitative data (onset temperature, heat of reaction, maximum pressure rise…) may be needed later.

[1] Also include form, concentration range and diluent, as appropriate.

TABLE 4.3
Example Chemical Reactivity Data for Ammonium Nitrate



CAS Number	*6484-52-2*	**Name[1]**	*Ammonium nitrate, granular*
NFPA Instability Rating	*3*	**Chemical Formula**	NH_4NO_3
Oxidizer?	*Yes*	**Forms unstable peroxides?**	*No*
Water reactive?	*No*	**Spontaneously combustible?**	*No*
Polymerizes?	*No*	**Inhibitor required?**	*No*
Decomposes?	*Yes*	**Shock or friction sensitive?**	*See below*
Sensitive to heat?	*Yes*	**Temperature control required?**	*Yes*
Incompatibilities?	*Oil, charcoal, other organic materials; powdered metals; reducing agents; strong acids; alkyl esters; hypochlorites*		
Reaction products?	*Decomposition/combustion: oxides of nitrogen, ammonia*		
Rate of reaction?	*May detonate with strong shock or if heated & confined*		

Quantitative data (onset temperature, heat of reaction, maximum pressure rise…) may be needed later.

[1] Also include form, concentration range and diluent, as appropriate.

Data from Manufacturers or Suppliers

Your first source for chemical reactivity data should be your material manufacturer or supplier/distributor. Some manufacturers and suppliers have developed pamphlets or other product literature giving more extensive information than what is on the Material Safety Data Sheet (MSDS). You

TABLE 4.4
Emergency Response and Advisory Services

Country	Service	Operated By	Telephone Number
Canada	CANUTEC (Canadian Transport Emergency Centre)	Transport Dangerous Goods Directorate of Transport Canada	613-992-4624 (non-emergency information line)
Mexico	SETIQ (Emergency Transportation System for the Chemical Industry)	National Association of Chemical Industries (ANIQ)	01-800-00-214-00 in the Mexican Republic; 5559-1588 for calls originating in Mexico City and the Metropolitan Area
United States	CHEMTREC®	American Chemistry Council	1-800-424-9300

should ask if such information is available, and request copies of the latest versions, including any additional information not on the MSDS that will help you manage the hazards. Other sources of chemical reactivity data are available and should be consulted, particularly when suppliers' information appears incomplete, questionable, or contradictory.

If you supply chemicals to others, whether you are a manufacturer or distributor, you obviously need to provide your customers with the data they need to safely handle any reactive materials. Do not use published data indiscriminately. If possible, track down and consider the original source. It may be necessary to have your own testing performed, if the available sources of data are questionable or your own experience indicates that testing may be warranted. Your customers may be looking to you as the first and best source of data and information on the reactive properties of your products.

Nationwide emergency response and advisory services can be called to obtain a manufacturing contact, when one is not known for a specific chemical. These include the services listed in Table 4.4. Other services are also available, such as those listed in the *2000 Emergency Response Guidebook* (DOT 2000).

Material Safety Data Sheets

Each hazardous chemical brought on-site is required by OSHA (in the U.S.) to have a Material Safety Data Sheet (MSDS), which lists the hazardous ingredients and includes a section on Reactivity Hazards. However, there are some significant limitations on using MSDSs to identify chemical reactivity hazards:

- MSDSs generally contain the most apparent chemical reactivity hazards. However, they cannot be relied upon to give complete information, particularly with regard to chemical incompatibilities and chemical reactivity at actual process conditions.
- MSDSs only provide chemical reactivity information for individual materials. Combining materials, intentionally or inadvertently, may create a reactive mixture with properties not described on any individual MSDS.
- MSDS data are likely to pertain only to ambient and fire-exposure conditions. If the material is handled under different or unusual conditions, such as at high pressure or in an oxygen-enriched atmosphere, the data may be useless or misleading.
- The presence of catalysts or impurities can significantly affect the chemical reactivity properties of many materials, especially chemicals subject to decomposition or polymerization.
- MSDS chemical hazard information can vary substantially between suppliers. An EPA Safety Alert showed a striking variability between MSDS data from four different suppliers for azinphos methyl, a pesticide involved in a violent explosion at an agricultural packaging facility that killed three responding firefighters and seriously injured a fourth (EPA 1999b). Ask for data from each trusted supplier, and make sure the MSDS you are using is the most current version.
- If you are in the business of mixing, formulating, or reacting materials, and you sell your products to others, supplier MSDSs for raw materials will not generally pertain to your products. You are then responsible to provide your employees and customers with material safety data. In this case, you may need to have your own chemical reactivity testing performed (Section 4.4 below) to ensure you are communicating complete and accurate information about your products, as well as having this information for your own safe storage and handling of the products. Your raw material supplier may be able to supply helpful information. The 1995 explosion and fire at Napp Technologies (EPA 1997), included as a brief Case History in Appendix A-1, is an example where a mixture of materials did not have the same hazard properties as indicated on the individual MSDSs.

MSDSs should be available from material suppliers. An Internet search will generally turn up MSDSs for most commercially available hazardous substances, but the above list of limitations, as well as technical and legal liabilities, must be kept in mind. Some companies subscribe to a service that provide MSDSs in a standard format.

Trade associations are also an excellent source of detailed and up-to-date material safety information, such as for ethylene oxide and acrylic monomers. For example, a European Chemical Industry Council guidance document for distribution of ethylene oxide can be accessed via the Internet at www.cefic.be/sector/eodsg/guide9701/eo.htm. An ethylene oxide industry safety web page can be found at www.ethyleneoxide.com.

International Chemical Safety Cards and NIOSH Pocket Guide

The International Programme on Chemical Safety (IPCS), in the context of cooperation with the Commission of the European Communities, is developing brief "shop floor" summaries of safety data, known as "International Chemical Safety Cards" (ICSCs), including general chemical reactivity hazards information. The cards are available in several languages, with two English versions ("International" and "U.S. National"). They can be accessed from the U.S. Centers for Disease Control and Prevention (CDC) website at www.cdc.gov/niosh/ipcs/icstart.html. Similar information is also available in the *NIOSH Pocket Guide to Chemical Hazards* (NIOSH 2001). An online version of the *NIOSH Pocket Guide* can be downloaded from the CDC website at www.cdc.gov/niosh/npg/npg.html.

NFPA Literature

Four National Fire Protection Association (NFPA) documents contain helpful chemical reactivity data. All four of these documents are included in the *Fire Protection Guide to Hazardous Materials, 13th Edition* (NFPA 2002):

- NFPA 49, *Hazardous Chemical Data,* gives a brief summary of instability and reactivity hazard data for commercially significant chemicals with NFPA Health Hazard Ratings of 2 or higher or having an Instability Rating of 1 or higher (except explosives, blasting agents and organic peroxide formulations). The data are given for guidance on storage and fire fighting techniques.
- NFPA 325, *Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids,* gives NFPA Instability Ratings and indications of water reactivity for flammable liquids, flammable gases, and volatile flammable solids.
- NFPA 432, *Storage of Organic Peroxide Formulations,* presents data with a classification system and storage requirements for organic peroxide formulations.
- NFPA 491, *Hazardous Chemical Reactions,* includes over 3500 documented hazardous or potentially hazardous chemical reactions.

Bretherick's Handbook

The voluminous *Bretherick's Handbook of Reactive Chemical Hazards* (Urben 1999) gives brief summaries of published accounts of numerous incidents involving reactive chemicals and interactions. *Bretherick's Handbook* includes reactivity information on over 5000 materials, plus a like number of secondary entries involving interactions between two or more materials. *Bretherick's Handbook* is also available in an electronic format.

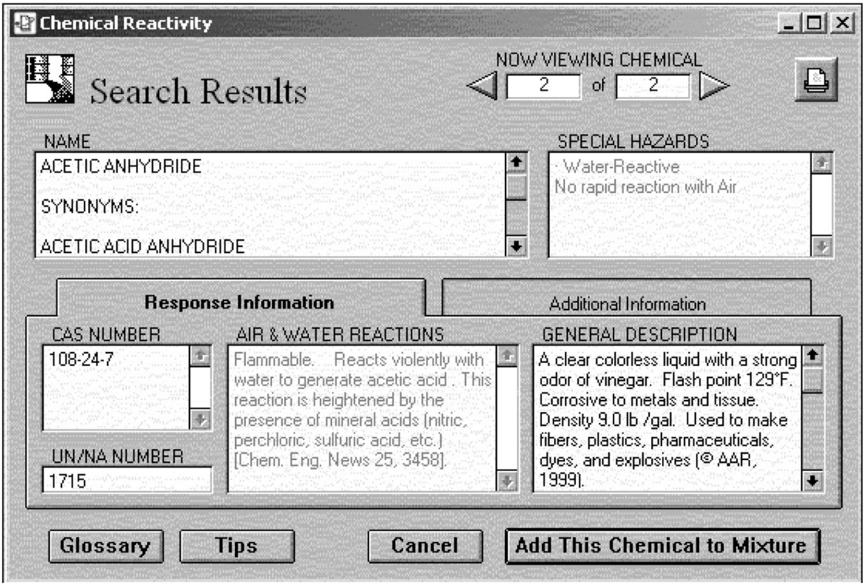
CHRIS Database

The U.S. Coast Guard's online Chemical Hazards Response Information System (CHRIS) Manual (USCG n.d.) contains a chemicals database with a specific section on Chemical Reactivity for each material in the database. Items listed in this section are Reactivity with Water, Reactivity with Common Materials, Stability During Transport, Neutralizing Agents for Acids and Caustics, Polymerization, and Inhibitor of Polymerization. Other sections include information on Coast Guard Compatibility Group, Formula, Behavior in Fire, Storage Temperature, NFPA Hazard Classification, Heat of Decomposition, and Heat of Polymerization. A separate Compatibility Chart indicates incompatibilities expected between general groups of chemicals (organic acids, nitro-compounds, etc.), with a limited number of exceptions listed in a separate table. It should be kept in mind that this database was designed to provide information needed for decision making by responsible Coast Guard personnel during emergencies that occur during the water transport of hazardous chemicals.

NOAA Chemical Reactivity Worksheet

The U.S. National Oceanic and Atmospheric Administration provides a Chemical Reactivity Worksheet program free of charge (NOAA 2002). This program has over 6000 chemicals in its database, including many common mixtures and solutions. For each substance, a general description and chemical profile are given, along with special hazards such as air and water reactivity. The chemical information for acetic anhydride, for example, is shown in Figure 4.2.

The program predicts the results of binary mixtures by reactive group combinations. The Worksheet not only indicates possible hazardous interactions, it also sets up a compatibility chart and indicates potential consequences of the interactions (e.g., "Heat generation by chemical reaction, may cause pressurization"). The Worksheet does not predict reaction products, though it may suggest flammable or toxic gas generation. Figure 4.3 shows a compatibility chart for the mixing of acetic anhydride and sodium hydroxide (caustic).



NAME

ACETIC ANHYDRIDE

SYNONYMS:

ACETIC ACID ANHYDRIDE

SPECIAL HAZARDS

· Water-Reactive
No rapid reaction with Air

CAS NUMBER

108-24-7

UN/NA NUMBER

1715

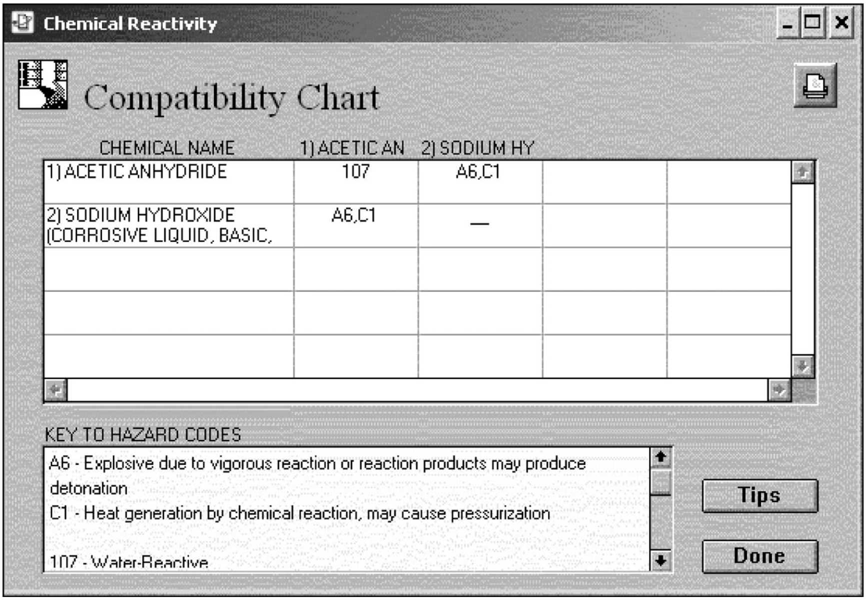
AIR & WATER REACTIONS

Flammable. Reacts violently with water to generate acetic acid . This reaction is heightened by the presence of mineral acids (nitric, perchloric, sulfuric acid, etc.) [Chem. Eng. News 25, 3458].

GENERAL DESCRIPTION

A clear colorless liquid with a strong odor of vinegar. Flash point 129°F. Corrosive to metals and tissue. Density 9.0 lb /gal. Used to make fibers, plastics, pharmaceuticals, dyes, and explosives (© AAR, 1999).

Figure 4.2. **NOAA Worksheet chemical information display.**



CHEMICAL NAME	1) ACETIC AN	2) SODIUM HY		
1) ACETIC ANHYDRIDE	107	A6,C1		
2) SODIUM HYDROXIDE (CORROSIVE LIQUID, BASIC,	A6,C1	—		

KEY TO HAZARD CODES

A6 - Explosive due to vigorous reaction or reaction products may produce detonation
C1 - Heat generation by chemical reaction, may cause pressurization

107 - Water-Reactive

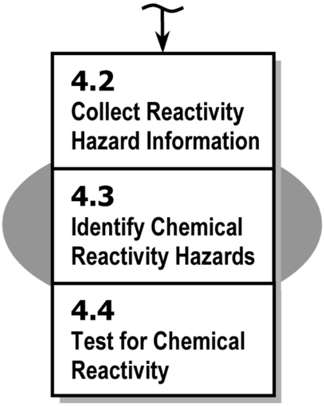
Figure 4.3. **NOAA Worksheet compatibility chart display.**

Sax

The three-volume reference *Sax's Dangerous Properties of Industrial Materials* (Lewis and Irving 2000) includes hazard information on substances likely to be encountered in the workplace. It has over 20,000 entries; however, the reactivity and incompatibility information tends to be relatively brief. Sax is also available in electronic format (Lewis 1999).

4.3. Identify Chemical Reactivity Hazards

Use of the Preliminary Screening Method of Chapter 3, along with the chemical reactivity data collected so far (Section 4.2), should begin to give at least a qualitative idea of the chemical reactivity hazards that may be present in an actual or proposed facility. However, the absence of particular information does not imply that no hazards exist. For this reason, a systematic search to attempt to identify *all* chemical reactivity hazards, in the context of *how materials will be used in the actual process*, is the next step in effectively managing chemical reactivity hazards. If a particular hazard is not recognized, it is not likely to be adequately controlled.



Literature Surveys

The systematic search for all chemical reactivity hazards, beyond the information gained from the sources listed in Section 4.2, should begin with a literature survey of the chemicals to be used and the type of processing, if any, that will be employed. The literature survey might turn up quantitative hazard data or previous incidents. Other information that will be useful later, such as standard practices or model prevention programs, may also be uncovered.

The Chemical Incidents Report Center (CIRC) is an incident database initiated by the U.S. Chemical Safety and Hazard Investigation Board. An online search of this database (www.chemsafety.gov/circ), as well as a more general web search, may be a good starting point for a literature survey.

Heat of Reaction

The next part of a systematic search for chemical reactivity hazards is gaining an understanding of the inherent chemical energy present and conditions under which it can be released.

A useful indication of a chemical reactivity hazard is the *heat (energy) of reaction*. For some reaction types, the heat of reaction may be known by another name, such as heat of decomposition, heat of combustion or heat of polymerization.

If not available in published references, the heat of reaction can be calculated from the difference in heats of formation of the reactants and products, as described in any college chemistry text. The accuracy of the calculation obviously depends on knowledge of the reaction products, reaction path and the accuracy of the heat of formation data. Any changes of state (heats of solution, vaporization, etc.) must also be taken into account. Not taking account of these changes of state can have a marked effect on the calculation and may lead to a false sense of security (HSE 2000) or an overestimation of the hazard.

Approximate heats of formation can be estimated by other methods, such as calculations that sum average bond energies. Computer programs such as the ASTM CHETAH program (Balaraju et al. 2002) use these types of calculations. Such programs may require expertise to understand and interpret.

A greater heat of reaction indicates the potential for a more energetic uncontrolled reaction. The heat of reaction can be used to predict the *maximum temperature rise* expected in a reactive mixture. A typical assumption is that all the energy from the heat of reaction increases the temperature of the mixture. Adding this maximum temperature rise to the highest expected starting temperature could also give an idea whether other consequences are possible, such as a decomposition reaction or overpressurization from increased vaporization or liquid thermal expansion. It should be noted, however, that the temperature at which decomposition or a runaway reaction can occur varies with the conditions under which the materials are held. The adiabatic temperature rise may also be underestimated, particularly if any changes of state or side reactions are not taken into account (HSE 2000).

What Heat of Reaction Does Not Reveal

A chemical reactivity incident does not have to be a violent fire or explosion. In reality, uncontrolled reactions can be slow or start slowly and still result in injury, loss or environmental damage. As useful as they may be for identifying chemical reactivity hazards, heats of reaction (thermodynamic calculations) do not yield information on:

- Which reactions actually occur
- Reaction kinetics (how fast a chemical reaction will proceed, and the rate of heat production and off-gas evolution)
- Whether reactions will proceed to completion
- Additional undesired side reactions, including decompositions
- The thermal inertia of the environment surrounding the reaction.

No general rules or easy answers exist for understanding the potential consequences of uncontrolled chemical reactions, due to the diversity of chemicals and reaction pathways. Table 4.5 shows the potential consequences of oxidizers as one specific category of reactive chemicals. Table 4.6, taken from the NOAA Chemical Reactivity Worksheet, lists some general consequences that could occur if incompatible materials are combined.

Reactive Chemical Structures and Bonds

Certain kinds of molecular groupings are more likely to show chemical reactivity than other kinds. For example, *Bretherick's Handbook* (Urben 1999 2:129–131) lists many bond groupings and functional groups that tend to contribute explosive instability to substances or substance mixtures.

Trends show that groups of the same atom (except carbon) or carbon atoms with double or triple bonds may be hazardous (Leggett 2002). The more bond strain that is present, and the larger the potential energy release, the more likely it is for a chemical reactivity hazard to be present. "Endothermic" compounds that have a significantly positive heat of formation (i.e., produced by an endothermic reaction) are often self-reactive and capable of an uncontrolled release of the stored chemical energy. The activation energy is also important in determining the rate at which such materials will react at a given temperature.

Be Suspicious of:

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

TABLE 4.5
How Stored Oxidizer Hazards Can Be Manifested

Stored Oxidizers:

- **Increase the burning rate of combustible materials**
- **Can cause spontaneous ignition of combustible materials**
- **Can decompose rapidly**
- **Can liberate hazardous gases**
- **Can undergo self-sustained decomposition, which can result in an explosion**
- **Can react explosively if mixed with incompatibles or in fire conditions**

TABLE 4.6
Chemical Reactivity Consequences in Reactivity Worksheet (NOAA 2002)

A1 – Explosive when dry
A2 – Risk of explosion by shock, friction, fire or other sources of ignition
A3 – Forms very unstable explosive metallic compounds
A4 – External heating may cause an explosion
A5 – May form explosive peroxides
A6 – Explosive due to vigorous reaction or reaction products may produce detonation
A7 – Explosive when mixed with oxidizing substances
A8 – Explosive when mixed with combustible material
A9 – Heat generated from chemical reaction may initiate explosion
B1 – May cause fire
B2 – Contact with combustible material may cause fire
B3 – Spontaneously flammable in air
B4 – Fire from exothermic reaction–ignition of products or reactants
B5 – Flammable gas generation
B6 – Flammable, toxic gas generation; causes pressurization
C1 – Heat generation by chemical reaction, may cause pressurization
C2 – Dangerous heat generation due to heat of solution
D1 – May cause violent polymerization, possibly with heat/toxic or flammable gas generation or with explosive reaction; causes pressurization
D2 – Can become highly flammable in use; causes pressurization
D3 – Contact with substance liberates toxic gas; causes pressurization
D4 – Innocuous and nonflammable gas generation; causes pressurization
D5 – Contact with acids produces combustion enhancer (e.g., O_2)
E – Generates water soluble toxic products
F – May be hazardous but unknown
G – Reaction may be intense or violent
H – Possible exposure to radiation

Other methods such as oxygen balance are available that point to chemicals likely to show self-reactivity. These methods are described in CCPS (1995b) and elsewhere. The ASTM CHETAH program (Balaraju et al. 2002) is useful for this purpose, if both the program and the expertise to use it are available to you.

Interaction Matrix (Compatibility Chart)

The accurate assessment of binary chemical compatibility is an important part of the safe handling, transport and processing of industrial chemicals. The most common and convenient way to represent binary chemical incompatibility is by a simple two-dimensional chart or matrix. Binary compatibility charts are an extremely useful teaching tool for new and even veteran employees.

Ideally, all components of interest (including such entities as common cleaning materials, air, water, heat, materials of construction, additives, catalysts, other utility services, etc.) are listed on both the x and y axes of the grid. The intersections of the cells in the matrix represent the consequences of each mixed pair. Presentation of the data in chart form allows for quick use, especially during a process upset (i.e., emergency) situation.

A spreadsheet program can be used to capture and display the chart information. The chart can then be made accessible via a network server to all those involved in a common operation. Use of the Chemical Reactivity Worksheet provided by NOAA (2002) automatically generates a compatibility chart, as shown in the example of Figure 4.3.

Some general guidance for preparing a compatibility chart is given in Table 4.7. Hofelich et al. (1994), CCPS (1995b), and Frurip et al. (1997) provide more detailed information. Mosley et al. (2000) work through an example chemical reaction system.

ASTM (E 2012-00) has developed a “Standard Guide for the Preparation of a Binary Chemical Compatibility Chart.” The hypothetical example given in ASTM E 2012-00 is reproduced in Figure 4.4; specific mixing scenarios associated with this example are not described.

The method shown in Table 3.8 in this publication can be an effective way to capture and document the specific mixing scenarios and conditions evaluated in a chemical compatibility chart. It should be noted that a binary chart only considers pairs of materials and therefore does not cover all possible combinations. The presence of a catalytic substance, for example, may cause a reaction between otherwise compatible materials to proceed fast enough to result in a consequence of concern. This is one reason why broad thinking should be encouraged when developing mixing scenarios to be evaluated.

TABLE 4.7
Guidance for Preparing a Compatibility Chart

State the Scenario. By *scenario* is meant a detailed physical description of the sequence of events whereby a potential inadvertent combination of materials may occur. Details such as specific amounts of materials, temperature, confinement (closed or open system) and how long the materials will be in contact contribute to the definition of compatibility.

Decide on a Hazard Rating Scheme. For example, a numerical score of 1, 2 and 3 might be appropriate with "1" indicative of a compatible mixture, a "2" might indicate a moderate hazard (e.g., a temperature increase) and a "3" might indicate a severe hazard. A "?" can indicate an unknown, indicating where more information must be obtained.

Consider the Hazards for All Binary Combinations. The potential hazard for each binary mixture needs to be carefully considered. Avoid using blanks (empty cells) in compatibility charts since blanks may indicate that there is no hazard, or simply that the hazard is unknown.

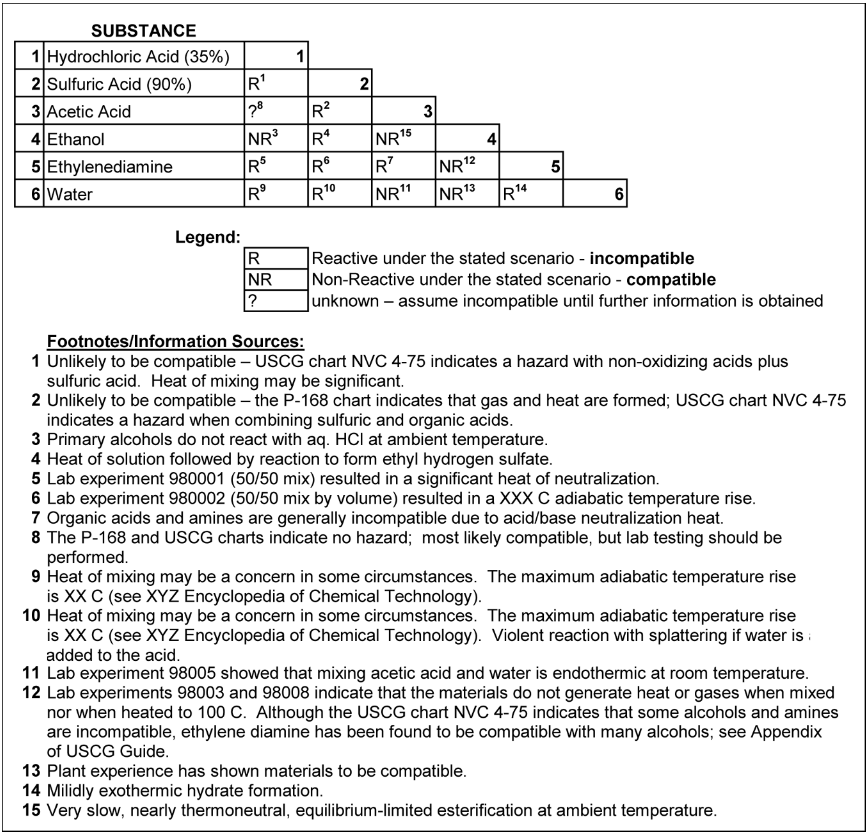
Define the Categories. The definition of categories for the chart is an important part of construction. For small plants and operations, each specific chemical may be included and the chart may still be of manageable size. For more "general" compatibility charts, the best manner to construct a chart is to group chemicals into natural groupings based on their chemical structure. Examples of these groupings are mineral acids, aliphatic amines, monomers, water-based formulations, halogenated hydrocarbons, etc.

Document How the Decisions Are Made. Backup and supporting data should be easily accessible, both for chart users and to allow easy chart updates. If testing was performed to make a decision about a particular binary combination in a chart, then reference this test in the chart.

Evaluation of Extrinsic Factors

Whether or not chemical reactivity hazards are present is a function not only of each chemical's reactivity (by itself and in combination), but also of various extrinsic factors; i.e., factors that are not intrinsic properties of the chemicals being handled. As the design for a facility progresses, decisions will be made regarding these factors that will affect the magnitude of the chemical reactivity hazards and the potential consequences if their control is lost. A partial list of extrinsic factors includes:

- Quantities of materials stored or handled
- Form of material (e.g., particle size)
- Process conditions such as temperature and pressure
- Degree of mixing
- Presence of diluents, contaminants or catalysts
- Degree of confinement
- Containment (pressure rating, gas-phase volume, normal and emergency venting)
- Layout of the facility and proximity to sensitive populations and environments
- Segregation of incompatible materials, including the use of dedicated equipment and connections.



	SUBSTANCE						
1	Hydrochloric Acid (35%)	1					
2	Sulfuric Acid (90%)	R[1]	2				
3	Acetic Acid	?[8]	R[2]	3			
4	Ethanol	NR[3]	R[4]	NR[15]	4		
5	Ethylenediamine	R[5]	R[6]	R[7]	NR[12]	5	
6	Water	R[9]	R[10]	NR[11]	NR[13]	R[14]	6

Legend:

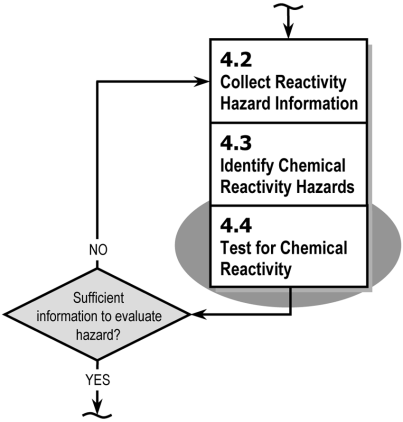
R	Reactive under the stated scenario - **incompatible**
NR	Non-Reactive under the stated scenario - **compatible**
?	unknown – assume incompatible until further information is obtained

Footnotes/Information Sources:

1 Unlikely to be compatible – USCG chart NVC 4-75 indicates a hazard with non-oxidizing acids plus sulfuric acid. Heat of mixing may be significant.
2 Unlikely to be compatible – the P-168 chart indicates that gas and heat are formed; USCG chart NVC 4-75 indicates a hazard when combining sulfuric and organic acids.
3 Primary alcohols do not react with aq. HCl at ambient temperature.
4 Heat of solution followed by reaction to form ethyl hydrogen sulfate.
5 Lab experiment 980001 (50/50 mix) resulted in a significant heat of neutralization.
6 Lab experiment 980002 (50/50 mix by volume) resulted in a XXX C adiabatic temperature rise.
7 Organic acids and amines are generally incompatible due to acid/base neutralization heat.
8 The P-168 and USCG charts indicate no hazard; most likely compatible, but lab testing should be performed.
9 Heat of mixing may be a concern in some circumstances. The maximum adiabatic temperature rise is XX C (see XYZ Encyclopedia of Chemical Technology).
10 Heat of mixing may be a concern in some circumstances. The maximum adiabatic temperature rise is XX C (see XYZ Encyclopedia of Chemical Technology). Violent reaction with splattering if water is added to the acid.
11 Lab experiment 98005 showed that mixing acetic acid and water is endothermic at room temperature.
12 Lab experiments 98003 and 98008 indicate that the materials do not generate heat or gases when mixed nor when heated to 100 C. Although the USCG chart NVC 4-75 indicates that some alcohols and amines are incompatible, ethylene diamine has been found to be compatible with many alcohols; see Appendix of USCG Guide.
13 Plant experience has shown materials to be compatible.
14 Milidly exothermic hydrate formation.
15 Very slow, nearly thermoneutral, equilibrium-limited esterification at ambient temperature.

Figure 4.4. **Hypothetical compatibility chart.** (Copyright ASTM International. Reprinted with permission.)

4.4. Test for Chemical Reactivity



An understanding of how chemicals are used in your facility needs to occur before any detailed testing is performed. Quantitative reactivity testing need only be performed when data, such as heat of reaction and safe operating temperatures, are not available from other sources. For example, in a warehouse where no chemical or physical processing is being done, material suppliers may be able to provide sufficient data on the thermal stability of stored materials to determine parameters such as the maximum allowable storage temperature.

When you get into a situation where reactivity testing is necessary, it is essential to work with someone who understands what the tests are, when you should do what tests, what their limitations are, and how to interpret and use the results. CCPS (1995a) provides a thorough discussion of test methods. Other references such as CCPS (1995b) and Leggett (2002) present approaches for conducting reactivity screening tests.

Interpreting Screening Data

The selection and use of testing equipment and procedures, and particularly the interpretation of the results, requires competent people. Some major companies have their own testing facilities, but there are a number of testing houses and consultancies available that you could use.

The results of reactivity screening tests will give a preliminary indication of:

- The possibility of thermal decomposition
- The quantity and rate of heat release
- Gas evolution
- Induction time effects (autocatalysis); e.g., the development of thermal instability after prolonged storage
- High-rate decompositions (showing that a substance could deflagrate)
- Special hazards such as water reactivity, friction sensitivity and shock sensitivity.

Table 4.8 provides one summary of reactivity test methods and results. In the paragraphs that follow, brief descriptions of some chemical reactivity test methods are given, after HSE (2000).

Deflagration Screening Tests

A simple test, which an experienced chemist could do in a protected laboratory hood with proper safeguards, can indicate the possibility of deflagration. This is to drop a small quantity, no more than a few milligrams of the substance, onto a hot plate or to heat it on a spatula to a temperature that might be expected in the process or facility. Rapid decomposition or burning suggests that the substance is capable of deflagration. More standardized UN deflagration tests have been defined for the classification of organic peroxides and fertilizers.

More complicated explosibility tests need expert advice and specialized facilities. If your calculations or testing demonstrate potentially explo-

TABLE 4.8
Summary of Reaction Hazard Testing Methods (Leggett 2002)

Hazards Test Stage	Method	Typical Information	Comments
Hazard Screening	Desk Calculation	Reaction enthalpy, ΔH_{RXN}	Need formation energy data or derive it Must know precise stoichiometry Known reactions only, no rate information
	Mixing Calorimetry	Instantaneous heat of mixing, ΔH_{MIXING} Gas generation rates	Isothermal, from ambient to 150°C Cannot test multi-phase systems
	DSC/DTA	Reaction enthalpy, ΔH Reaction 'onset' temp, T_{ONSET}	Very quick (~2 hours), needs little sample No mixing, no pressure data, no multiphase, although some systems mix the sample by rotating the sample container Difficult to get representative mixture
	Adiabatic Screening	$\Delta H_{UNDESIRED}$, T_{ONSET}, ΔT_{ADIAB} $P, T, t, dP/dt, dT/dt$ Simple kinetics E_A, A	Sample ~ a few grams Reasonably quick to test (~½ day) Poor/moderate sample agitation Not reliable for scale-up (high ϕ-factor)
Develop Desired Reaction	Reaction Calorimetry	$\Delta H_{DESIRED}$ Power output, Q_{RXN} Heat transfer rate Accumulation, X_{AC}	Normally 0.1 to 2 liter scale Mimics normal operation Essential information for safe scale-up Very useful for process development
Detailed Hazard Assessment	Low Thermal Inertia (ϕ-factor) Adiabatic Calorimeter	$\Delta H_{UNDESIRED}$, ΔT_{ONSET} ΔT_{ADIAB} dT/dt; dP/dt; T_{SADT}, T_{NR}, t_{MR} estimates Vent sizing data	Sample size ~ 100 ml to 1 liter Safe for general laboratory work Good mimic of large-scale runaway Ideal for 'what-if' scenario study
Special Studies	High Sensitivity Calorimetry	$\Delta H_{DESIRED}$, $\Delta H_{UNDESIRED}$ dT/dt; ΔT_{ADIAB} Kinetics, E_A, A	Sample size 1– 50 ml, μW/g sensitivity Shelf life studies by accelerated aging Combine with low adiabatic to confirm solids low self-heating rate studies

sive properties, then you should not use the material further until you have done a detailed evaluation of its properties.

Small-Scale Screening Tests

A number of small-scale test methods (0.01 to 10 g sample size) are available that can be used to give an indication of

- The rates and quantities of heat and gas evolution,
- Whether a runaway reaction may occur, and
- What the consequences are of a runaway in terms of the heat and gas evolution rates.

These tests include differential scanning calorimetry (DSC) and various forms of differential thermal analysis (DTA): the insulated exotherm test (IET), decomposition pressure test (DPT), and the Carius (or ICI) sealed tube test. Commercial variants of these tests are available.

Differential Scanning Calorimetry

DSC can be used to indicate the thermal stability of a reactant, reaction mixture or product, and the heat of reaction or decomposition. The temperature trace of the sample indicates whether heat is being absorbed or generated by means of peaks, troughs or discontinuities. The trace gives the total amount of energy released (i.e., measuring the area under the trace determines the heat of reaction or heat of decomposition, etc.) and an estimate of the rate of the release (by measuring the slope of the peaks, etc.). Both the total energy and the maximum rate of energy release are indicators of the degree of the hazard.

If DSC data have been obtained for a pure material or a reaction mixture, several thermal stability indicators (ASTM E 1231-96) may be estimated from the data. These are adiabatic temperature rise, explosion potential, instantaneous power density, time to maximum rate, and NFPA instability index (Leggett 2002).

Insulated Exotherm Test

This test can be used to give early detection of the initial exothermicity. It is possible to estimate thermokinetic parameters (e.g., the activation energy and the adiabatic self-heat rate) and to estimate how the initial temperature for self-sustaining reactions will vary with the quantity of material present.

Decomposition Pressure Test

The DPT can be used to determine the pressure characteristics and gas generation rates where they occur during a decomposition reaction. The output from the test is a pressure-time plot that you can use to determine the volume of gas generated in the decomposition reaction.

Carius (or ICI) Sealed Tube Test

A number of variations of this test exist. An oven temperature is increased linearly. Continuous monitoring of the temperature and pressure outputs from a sample tube in the oven provides qualitative information about the thermal characteristics of the sample. In many cases, the pressure data can also yield valuable information. Any discontinuity in a plot of $\ln P$ against $1/T$ indicates noncondensable gas generation. (The plot is often an essentially straight line if the pressure increase is due solely to the vapor pressure.)

Reaction Calorimetry

It is possible to directly measure the instantaneous heat output of a nonexplosively reacting system due to chemical or physical processes as a function of the process time. This quantity shows directly whether and how quickly chemical conversions occur in the process phase under consideration. Such an approach can be useful, not only from a safety perspective but also for process design and optimization.

From the measured heat production rate, the quantities important for safe process control can be derived such as the required heat removal rates and the expected temperature and pressure changes in the case of a malfunction. The effects on the reaction kinetics and rates of heat generation and gas evolution need to be investigated. Factors such as stirring speed, agitator configuration, materials of construction, variations in addition rate, reactant concentrations and hold times can affect these rates. The effects of any foreseeable process maloperations also need to be established. Safety considerations are important when designing and carrying out experiments at this scale.

Experimental calorimetry methods have been developed which:

- Simulate the full-scale reactant addition rates, batch temperature and time profiles and processing conditions (e.g., stirring, distillation, boiling under reflux, etc.);
- Include any other source of heat gain or heat loss (e.g., energy input from a stirrer, heat loss from a condenser, etc.); and
- Measure the effects of changes in physical properties (viscosity, specific heat, precipitation, etc.) during the reaction.

Therefore, the data that can be obtained from these tests, which will help in specifying the safe operating envelope on the full-scale plant, include:

- Heat of reaction
- Heat capacity
- Rate of heat production
- Heat transfer properties of the reaction mixture
- Dependence of reaction kinetics on reactant concentrations
- Factors that affect accumulation or rate of heat production (temperature, catalysts, pH, etc.)
- Amount and rate of gas evolution.

The two basic types of reaction calorimeters commonly used for safety assessments are isothermal (including both heat flow and power compensation calorimeters) and adiabatic.

Isothermal Calorimeters

Heat flow calorimeters simulate closely the operation of plant reactors. Removing the heat of reaction at the same rate as it is generated results in a constant reaction temperature. The temperature difference between the reactor and vessel jacket is a measure of the rate of heat production.

In power compensation calorimeters, the jacket temperature is set slightly below the desired reaction temperature. A heater in the reaction mass maintains the set temperature. A change in electrical power to the heater compensates for any change in reaction temperature. This provides a direct measure of the heat produced by the chemical reaction.

Usually, isothermal calorimeters are used to measure heat flow in batch and semi-batch reactions. They can also measure the total heat generated by the reaction. With careful design, the calorimeter can simulate process variables such as addition rate, agitation, distillation and reflux. They are particularly useful for measuring the accumulation of unreacted materials in semi-batch reactions. Reaction conditions can be selected to minimize such accumulations.

Adiabatic Calorimeters

There are a number of different types of adiabatic calorimeters. Dewar calorimetry is one of the simplest calorimetric techniques. Although simple, it produces accurate data on the rate and quantity of heat evolved in an essentially adiabatic process. Dewar calorimeters use a vacuum-jacketed vessel. The apparatus is readily adaptable to simulate plant configurations. They are useful for investigating isothermal semi-batch and batch reactions, and they can be used to study:

- The effects of mischarging
- The temperature range in which an undesired reaction occurs
- The kinetics (including autocatalysis) of the undesired reaction.

By replacing the glass dewar with a stainless steel vessel, reactions can be studied that generate pressure. Such equipment needs to be placed in a blast cell where it can be operated remotely. Placing the dewar in an oven whose temperature is controlled to follow that in the reaction mass allows the study of the reaction under near adiabatic conditions.

In addition to the adiabatic dewar, several adiabatic calorimeters are commercially available that allow emergency pressure-relief system sizing. These include:

- The pseudo-adiabatic Reactive System Screening Tool (RSST, ARSST)
- The Vent Sizing Package (VSP, VSP2)
- The Phi-Tec adiabatic calorimeter
- The Automatic Pressure Tracking Adiabatic Calorimeter (APTAC).

The Accelerating Rate Calorimeter (ARC®) is another adiabatic test instrument that can be used to test small samples. The ARC with the clamshell containment design can handle explosive compounds. It is a sensitive instrument that can indicate the onset of exothermicity where the reaction mixture can be accurately simulated (HSE 2000). ARC testing results can be used in determining a time to maximum rate of decomposition, as well as in calculating a temperature of no return for a container or vessel with specific heat removal characteristics. Further information and references related to the ARC are given in CCPS (1995a) and Urben (1999).

Point of Decision

A decision will need to be made at this point, whether sufficient information has been generated to evaluate the chemical reactivity hazards that are or will be associated with a facility. If not, then some or all of the steps outlined in the preceding Sections 4.2 through 4.4 need to be repeated before proceeding to assessing risks and identifying controls.

4.5. Assess Chemical Reactivity Risks

To the degree that chemical hazards are identified and understood (Sections 4.2 to 4.4), and to the extent that the facility has been designed or is currently operational, facility-specific risks can be analyzed.

Risk, in this context, is a combination of the likelihood and the severity of losing control of chemical reactivity hazards, taking prevention and mitigation safeguards into account.

The goal of assessing risk is to build on the knowledge of chemical reactivity hazards, to understand how the hazard properties may lead to loss scenarios in the facility context, and to determine whether existing safeguards are adequate. Therefore, the assessment of risk can be performed at any stage of facility design, development, operation, or alteration. Of course, the more that is known about the facility and its equipment and operation, the more detailed the risk assessment can be. Methods used to determine chemical reaction risks are varied, as are their objectives and data requirements.

Consequence Assessment/Appropriate Design Basis Determination

Consequence assessment for the purposes of establishing design basis differs from consequence assessment in the context of a risk analysis study (see *Qualitative and Quantitative Methods*, below). A qualitative, or semiquantitative (order of magnitude) consequence severity estimate may suffice for the latter.

By contrast, the nature of certain accident scenarios could prove to be quite sensitive to some design parameters. It should not be ruled out during the risk assessment phase, especially during detailed design, that discoveries during consequence analysis could lead to the revision of the design basis of the facility or some equipment or components.

Detailed analyses that may need to be performed fall into two categories:

1. Modeling intrasystem events (e.g., internal reactions and material behavior). For example, it may be determined that a certain undesired, yet potential, reaction could lead to two-phase flow through the relief valve of a storage or mixing vessel. If such flows were not previously anticipated in the design of the system, then the relief valve design basis must be updated, and the valve re-specified accordingly.
2. Modeling extrasystem events (e.g., potential releases from the system). For example, maximum intended inventory might be intentionally limited by that below which there would be no off-site impacts. CCPS (1999b) gives a complete discussion of this type of analysis.

In the course of the analysis, it may be determined that more data are required in order to achieve the goals of the study. If so, then activities described in Sections 4.2 through 4.4 may need to be revisited.

Information Sources—Where to Get Input

Risk assessment studies can be performed using whatever process information is available (CCPS 1992a). Obviously, the more information and knowledge that is available, the more thorough and valuable the risk study can be. For facilities that must meet regulatory requirements for process hazard analyses, certain process safety information (PSI) is required to be compiled and up to date before starting the analysis.

Realistically, the information available to perform risk studies varies over the lifetime of a process. During the early stages of process development, analysis teams may only have access to basic chemical reactivity hazard data, such as may be obtained from suppliers and literature resources. By the time a facility reaches the detailed design phase, most of the basic design and operating information should be available and used in any study of the facility hazards and risks.

The experience base provided by the analysis team members is just as important as the written process documentation for identifying and assessing possible incident scenarios. Team members will need to make estimates of how often certain failures occur, and how effective responses will be to specific upset conditions.

Failure and incident databases are available that provide generic or industry-wide in-service failure rates and on-demand failure probabilities for various components. These can be used for assessing risks of new facilities with no operating experience, as well as for estimating the likelihood of rare events such as vessel mechanical failures at operating conditions and for fully quantitative risk studies.

Qualitative and Quantitative Methods

Many methods have been developed that are suitable for assessing risks associated with the operation of facilities involving chemical reactivity hazards. The more commonly used methods are summarized in Table 4.9. They differ in their applicability, level of effort, and how systematic they are in identifying accident scenarios. All of the methods except layer of protection analysis (LOPA) may be applied qualitatively, and all except checklist reviews may be performed in at least a semiquantitative manner. CCPS (1992a) is a basic source of information on each of these methods.

Fault tree analysis (FTA) and event tree analysis (ETA) are the methods most commonly applied quantitatively. Since they only address the likelihood of undesired events, these methods are often combined with consequence severity calculations in a quantitative risk analysis, as described by CCPS (1999b). Layer of protection analysis (LOPA) uses a semiquantitative, order-of-magnitude approach. It is documented with worked examples in CCPS (2001b).

TABLE 4.9

Process Hazard Analysis Methods

Method	Attributes	How is the analysis structured?	Best for analyzing what type of processes?	Comprehensiveness?	Relative level of effort?
Checklist Analysis	Experience-based	By checklist question	Very simple and/or fully standardized operations	Checklist-dependent	Lower
What-If Analysis; What-If/Checklist Review	Scenario-based; Inductive	By what-if question and/or checklist item	Relatively standard operations Good for both procedure-based and continuous operations Mostly appropriate for simpler processes, although capable of developing and analyzing multiple-safeguard scenarios	Only looks at causes prompted by checklist and what-if questioning	Moderate
Hazard and Operability (HAZOP) Study	Scenario-based; Inductive/deductive	By deviation from intended operation	Processing systems with parameters such as flow, pressure, and temperature Good for both procedure-based and continuous operations Can analyze complex processes with multiple safeguards	Only looks at causes that could lead to identified deviations	Higher
Failure Modes and Effects Analysis (FMEA)	Scenario-based; Inductive	By component	Mechanical/electrical systems Best for analyzing effects of single failures, although capable of developing and analyzing multiple-safeguard scenarios	Looks at all failure modes of all components	Higher
Layer of Protection Analysis (LOPA)	Scenario-based; Order-of-magnitude	By pre-identified scenario	Processes likely to require independent protection layers, such as safety instrumented systems, to meet predefined risk criteria	Dependent on comprehensiveness of scenario list identified by other method(s)	Higher
Event Tree Analysis (ETA)	Scenario-based; Inductive	By initiating event	Best for analyzing a limited set of initiating events protected by administrative and engineering controls	Looks at all safeguards protecting against initiating event	Higher
Fault Tree Analysis (FTA)	Scenario-based; Deductive	By undesired event	Can analyze complex processes with multiple safeguards and operator interactions	Only looks at events that precede the selected top event	Highest

Scenarios Involving Reactive Chemistry

Mosley et al. (2000) describe a "chemistry hazard analysis" approach, similar to a hazard and operability (HAZOP) study method applied at the early development stages of a new process. Deviations from an intended chemical reaction are identified using typical HAZOP guidewords. Examples of deviations and consequences developed using this approach are shown in Table 4.10. Analyzing the basic chemistry of a process, where chemical reactions are intended to occur, can help ensure the consequences of deviating from the intended reaction are understood.

Deviations are abnormal situations, outside the bounds of intended design and operation. (The example shown in Table 4.10 does not indicate the possible *causes* for each deviation.) Examples of other deviations that are typically encountered in reactive systems involving intentional chemistry include:

- Not charging any of a particular ingredient
- Not charging enough or charging too slowly
- Charging too much or too fast, including double charging
- Excessive or delayed catalyst addition
- Starting temperature too high or too low
- Loss of heating or cooling during reaction
- Excessive or prolonged heating or cooling during reaction
- Loss of vacuum if reaction performed under vacuum
- Inadequate venting of off-gases
- Loss of pH or level control

TABLE 4.10
Example Chemistry Hazard Analysis Scenarios (Mosley et al. 2000)

Guideword	Deviation	Consequences	Comments/Actions
No	No Catalyst C added	No reaction when Reactants A and B are mixed; if Catalyst C is added after the entire charge of Reactants A and B has been completed, a rapid and violent reaction can occur	Develop kinetic and thermodynamic data on this reaction
More	High temperature; greater than 70°C	Side reactions have been observed in similar systems above 70°C, and may also occur with this chemistry	Investigate the behavior of the reaction at elevated temperature
As well as	Rust, as well as normal materials	The effect of contamination with iron or rust is unknown	Determine the effect of iron/rust contamination

- Inadequate, delayed or excessive agitation
- Contamination (by material left from previous batch, leaking coolant, rust, etc.)
- Adding a material out of sequence
- Adding the wrong material
- Delayed discharge of material from vessel.

Many of these deviations also pertain to systems where only physical processing is intended.

Scale-up Issues—Equipment and Auxiliary System Sizing

When analyzing a chemical reaction process, especially in the scale-up and design stages, the review team must keep in mind some significant differences between the behavior of a chemical system in the laboratory or pilot operation and in a full-scale facility. Reaction rate and process temperature parameters, for example, do not generally scale up directly from the laboratory scale due to reasons such as:

- Proportion of the heat of reaction that heats the container (thermal inertia, phi factor)
- Heat transfer limitations
- Mixing/agitation limitations
- Temperature gradients
- Localized heating; e.g., at the point of contact of reactants
- Capability of off-gas venting and treatment.

Qualifications/Requirements of the Hazard Evaluation Team

Chemical reactivity risks are generally assessed using a team approach, rather than by a single analyst. The involvement of a team in risk analysis will help achieve a useful assessment in which a high level of confidence can be placed. This is accomplished by bringing diverse perspectives on the facility and its systems to the assessment, as well as by ensuring the proper and thorough application of the analysis method. Depending on the stage of the facility life cycle, the complexity of the process, and the objectives of the analysis, the team may include:

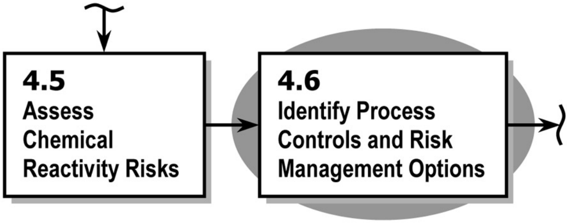
- A person familiar with each analysis method to be employed.
- A person familiar with the chemical and physical properties of materials handled in the facility, as well as their chemical behavior under both normal and upset conditions; this is especially important for facilities with chemical reactivity hazards.

- Persons familiar with the operation of the facility; if the facility has no operating history, then operators from similar facilities may be included on the team. Frontline personnel are preferable, as they usually have the most accurate knowledge of the process equipment and procedures used during day-to-day operation, and are highly motivated to identify and eliminate hazards.
- A person familiar with the maintenance of associated equipment.
- A person familiar with the design and design bases of the facility or equipment.
- As needed, people with special knowledge of process chemistry, inspection, instrumentation, environmental regulations, and corporate and industry safety standards.

Not all team members need participate in the entire review. Some may only attend part of the meetings. Others may simply be on call to help resolve specific issues.

The team must be able to systematically identify abnormal situations involving chemical reactivity, estimate the likelihood of each abnormal situation occurring, and assess the consequences of each situation if it continues uncontrolled. The team must also be able to come to a consensus on where existing safeguards are inadequate and where risk control actions are needed.

4.6. Identify Process Controls and Risk Management Options



Various measures can be used to reduce the risks assessed using the methods of Section 4.5. These measures can be classified into four types: Inherent, Passive, Active, and Procedural. Risk control strategies in the first two categories, inherent and passive, are considered more reliable because they depend on the physical and chemical properties of the system rather than the successful operation of instruments, devices, procedures, and people. Inherent and passive strategies differ, and are often confused. A truly inherently safer process will reduce or eliminate the hazard (Kletz 1998), rather than simply reducing its impact. These categories are not rigidly defined, and some strategies may include aspects of more than one category (Bollinger et al. 1996).

Inherently Safer Alternatives

Inherently safer approaches, such as reducing the hazard by using materials and process conditions that are less hazardous, should always be kept in mind when considering ways to reduce risk. The most effective time to consider inherently safer alternatives is in the early development stages of a product, process or facility. Nevertheless, approaches such as inventory reduction and seeking out less hazardous alternative materials are pertinent at any time. Inherent safety was addressed in Section 2.2, with the checklist in Appendix A-2 providing suggestions for inherently safer alternatives. Questions to ask that particularly pertain to reducing chemical reactivity hazards include (HSE 2000):

(a) Is it possible to eliminate hazardous raw materials, process intermediates or byproducts by using alternative chemistry?
(b) Is it possible to substitute less hazardous raw materials?
(c) Have all in-process inventories of hazardous materials in storage tanks been minimized?
(d) Has all processing equipment handling hazardous materials been designed to minimize inventory?
(e) Is process equipment located to minimize the length of hazardous material piping?
(f) Is it possible to generate hazardous reactants in situ from less hazardous raw materials, rather than store them on site?
(g) For equipment containing materials that become unstable at elevated temperatures or freeze at low temperatures, is it possible to use heating and cooling fluids that limit the maximum and minimum temperatures attainable?
(h) Can equipment be designed so that it is difficult or impossible to create a potentially hazardous situation due to operating error?
(i) Can process units be located to reduce or eliminate adverse impacts from other adjacent hazardous installations?

Hendershot (2002) gives additional inherently safer process considerations when dealing with intentional chemistry.

Passive Controls

Passive controls minimize the hazard by use of process and equipment design features. They reduce either the frequency or consequence of the hazard without the active functioning of any device. Examples include dikes, firewalls, orifice plates or narrow bore piping to control flow, and the use of equipment rated for higher pressure. Passive controls cannot be ignored, however; they may require routine inspection and maintenance to retain their protective properties, and their effectiveness can be defeated by changes such as erosion of an orifice plate over time.

Active Controls

Active controls use engineering controls, safety interlocks and emergency shutdown systems to detect process deviations and take appropriate corrective or remedial action. Their effectiveness depends on proper selection, installation, testing, and maintenance.

For reactive chemical storage and handling facilities such as warehouses, engineering controls are best implemented during design and layout and before equipment is specified. For example, some additional engineering controls to consider for a chemical warehouse are:

- Implementing automated product identification systems for inventory control. Bar code systems can code incoming products with information regarding composition, compatibility, storage location, and quantity.
- Installing detection alarms to alert staff to levels that approach the threshold limit value (TLV), permissible exposure level (PEL), or other predefined concentration of the material.
- Designing emergency ventilation systems to capture fugitive emissions of toxic, corrosive, or malodorous gases or vapors.

Systems such as sprinkler protection and security systems that are provided primarily for building, product, or environmental protection, may also reduce risks (CCPS 1998a).

Where loss of control could lead to severe consequences, the integrity of the basic process control system and the protective safeguards must be designed, operated and maintained to a high standard. Industry standards such as ANSI/ISA-S84.01 (1996) and IEC 61508 (2000) address the issues of how to design, operate and maintain safety instrumented systems such as high temperature interlocks to achieve the necessary level of functional safety. The scope of these standards includes hardware, software, human factors and management (HSE 2000).

Procedural Controls

Procedural controls (sometimes called administrative controls) use operating procedures, emergency response and other management approaches to prevent incidents or to minimize their effects. In other words, they involve human intervention to control hazards. Examples of such controls are sampling and analysis of materials and operator responses to upset conditions. Supervision, personnel selection, training and scheduling policies are all aspects of administrative controls. Some aspects of procedural controls when handling chemical reactivity hazards include:

- When procedures involve critical steps that must be performed correctly in order to prevent uncontrolled reactions, consider the use of checklists where critical steps or tasks are signed or initialed when completed.
- Review of and training on these procedures should be on a regular basis.

An example of a chemical reactivity hazard that might be addressed with procedural controls is taking procedural precautions (warnings, training) to ensure incompatible materials are not combined together. Some alternatives to relying on procedural controls might be to switch to a compatible chemical or replacing incompatible materials of construction.

Mitigation Techniques

Mitigation refers to any design feature, system or action intended to reduce the severity of consequence of a loss event, given that an uncontrolled release of material or energy (such as a container rupture, fire, or spill) has already occurred. Therefore, mitigation techniques are typically tailored to specific materials or classes of materials. Examples of mitigation techniques include emergency cooling of an out-of-control chemical reaction, secondary containment, fire protection systems, all aspects of emergency response, and spill response measures.

Emergency relief systems are last-resort safety systems. They vary from a simple vent or plug to very complex relief, header and effluent treatment/disposal systems designed to limit pressure build-up during an out-of-control chemical reaction while preventing discharge of the vapor or gas directly to the atmosphere. The Design Institute for Emergency Relief Systems (DIERS) and others have done considerable work in the area of relief sizing for various types of reacting systems, including consideration of multiphase flow (Fisher et al. 1992). Sources such as CCPS (1998b) should be consulted when designing emergency relief protection in physical and chemical processing systems involving chemical reactivity hazards.

Safe Operating Limits

Whatever risk reduction methods or technologies are applied, the net result will be a system that must be operated within certain limits. It is essential that safe operating limits be established, documented, and incorporated into facility or process documentation, operating procedures, and training materials.

For relatively common or simple storage and use facilities (e.g., for a facility storing pool water treatment chemicals), limits such as maximum storage temperatures may be available from suppliers. In other cases, the limits will need to be developed through combination of reactivity information (discussed in Sections 4.2 through 4.4) and hazard analyses (discussed in Section 4.5). The schematic in Figure 4.5 presents the relationships between safe operating limits, normal operating range, and equipment containment limits (Bollinger et al. 1996; see also Dowell 2001). It should be noted that safe operating temperatures and pressures for reactive systems might be well below the design temperatures and pressures of the equipment.

Physical or chemical processes involving chemical reactivity hazards require carefully determined, facility-specific operating limits, which may go well beyond temperature control. Limits may need to be specified for addition quantities, rates and sequences; agitation; pH; conductivity; concentration; pressure; and other variables that either keep an undesired chemical reaction from starting or control a desired chemical reaction. Determination of these limits is outside the scope of this publication; references such as Barton and Rogers (1997), CCPS (1995a) and HSE (2000) can be consulted for further information.

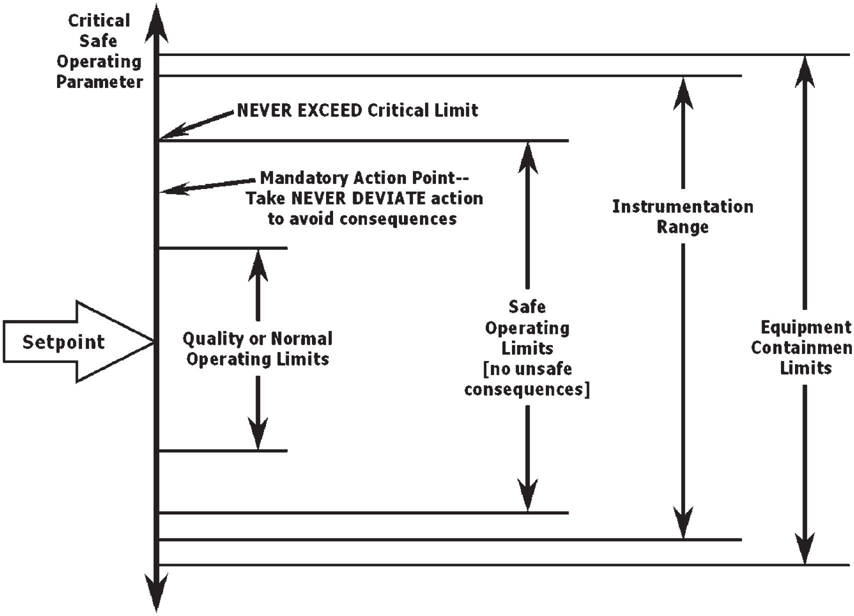
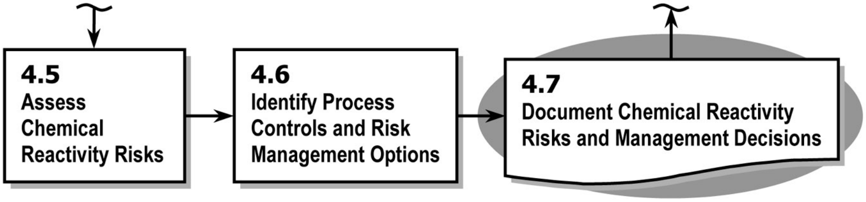


Figure 4.5. **Operating ranges and limits.**

4.7. Document Chemical Reactivity Risks and Management Decisions



Capturing process knowledge and safety information is fundamental to many aspects of managing chemical reactivity hazards. However, merely maintaining factual design information is not sufficient. Administrative procedures and control limits are not always documented with adequate explanation of their underlying basis. Consequently, when something needs to be changed, or operating personnel need to respond to an abnormal situation, false assumptions are often made as to why the controls and procedures are the way they are. Therefore, the technical basis needs to be documented, including the WHYs.

Both preserving and making available this process knowledge within a company are important (CCPS 1989), in order to:

- Preserve a record of design conditions and materials of construction for existing equipment, which helps ensure that operations and maintenance remain faithful to the original intent
- Allow recall of the rationale for key design decisions during major capital projects; this may also aid in future projects and modifications
- Provide a basis for understanding how the process should be operated and why it should be run in a given way
- Offer a baseline for use in evaluating process change
- Document systematic hazard reviews and the basis for risk-based decisions
- Record accident/incident causes and corrective actions and other operating experience for future guidance
- Protect the company against unjustified claims of irresponsibility and negligence
- Retain basic research and development information on process chemistry and hazards to guide future research efforts
- Have the safety information required to be available to employees and other stakeholders.

In addition, Process Safety Information (PSI) is an explicit element of PSM and RMP programs, requiring chemical hazard, technical, and process equipment information to be compiled and kept up to date. In some states, legislation now requires owners of chemical plants to maintain up-to-date documents and procedures on many aspects of plant design and operation.

This section provides guidance for creating the element of a chemical reactivity hazard management system that will ensure the capture and retention of safety-related process knowledge and documentation. The components of this element are:

- Chemical reactivity hazards information and reactivity data
- Process definition and design criteria
- Process/equipment design and operating procedures
- Protective systems
- Process risk management decisions
- Corporate memory.

Much of the process knowledge and documentation is developed through the earlier life cycle stages of a facility. Most of these components need to be retained or kept up to date during the entire facility lifetime.

Chemical Reactivity Hazards Information and Reactivity Data

While collecting reactivity data, identifying hazards, and testing for chemical reactivity, much important information will be generated. Your facility or company will need to document basic reactivity properties (e.g., heat of reaction), the hazard information, and test results. An organized approach will be needed for storing this information and making it accessible to users when needed.

This includes, for example, documenting how compatibility chart decisions are made. Backup and supporting data should be easily accessible for chart users and for easy chart updates. If testing was performed to make a decision about a particular binary combination in a chart, then this test can be referenced in the chart.

Another example of one larger company's method for data archiving includes the requirements shown in the box on page 103.

Process Definition and Design Criteria

The design basis, especially safety features that are built into the installation, must be documented. Management of change programs must preserve and keep the base record current and protect against degradation or elimination of safety features, including such measures as maximum intended inventories and passive protection systems.

Procedure

1. *All chemical safety test results obtained through the Chemical Safety Testing Lab Network will be archived in a central database. The database is available for use at local workstations for the retrieval of archived data. Test results and reports, including plots, graphs and charts, are scanned into the database. The optical character recognition capabilities of the database allow users of the database to view graphs and curves on their local personal computers and to print hardcopies on their local printers. Installation and training is available through the Central Safety Testing Lab.*
2. *Some test results associated with chemicals that have product numbers will be recorded on MSDSs, Survey Sheets, and/or Workplace Precaution Statements.*

Responsibility

1. *It is the responsibility of the Central Safety Testing Lab staff to scan test results into the database and to serve as database administrators.*
2. *It is the responsibility of the Product Safety and Product Regulatory Programs to develop MSDSs and Workplace Precaution Statements.*
3. *It is the responsibility of the project/process leader to ensure the Survey Sheets have been completed, and that MSDSs or workplace precaution statements have been requested.*

The documentation should include the basic process knowledge and design considerations that form the foundation for facility design and operation. Prior to design, it is essential that this documentation be as complete as possible, since the identification and control of chemical reactivity hazards will be developed from this information. As subsequent knowledge is obtained or developed as a result of process or technology modification, it should also be incorporated into the documentation and carefully reviewed.

This documentation starts with the process definition. The process definition should include the fundamental process chemistry and conceptual process flow configuration, including major steps or unit operations to the extent known.

The process definition should be documented in a single document or set of documents, bringing all process-related information together. The management system for this component must reflect many considerations.

Organizing issues related to process definition documentation begins with the assignment of responsibility for compiling and maintaining the process document. While it may be easy during the research stage to keep all relevant information coordinated, as a process moves further into its life cycle the information coordination process becomes more complex. Creating a group responsible for the development of each specific technology and conducting periodic technology audits are two techniques that have been used to facilitate the maintenance of good documentation.

Another issue related to organizing the process definition documentation management system involves assigning responsibility for reviewing and endorsing the process on behalf of the company. As the process documentation is being prepared, it should serve as a guide for the company in the design and development of the process. Someone, often the senior engineering and senior research and development officers, should indicate acceptance of the technology as it evolves during the design process.

Appropriate skills must be made available during the development of process documentation. For example, for a large facility, process engineers, chemists, and health and safety specialists should be involved. These staff members should have access to appropriate information sources, including:

- Internal personnel who have designed and operated the process in question (or related processes)
- Process licensors
- Engineering contractors
- Reference materials
- On-line databases that include hazard and engineering information.

The management system for process definition documentation should ensure that the contents of the process documentation package are accurate and complete. A suitable review and quality assurance program should be implemented for the process documentation. This may involve a hierarchical review process, and/or using external experts in a review capacity.

Two control issues involved in developing and maintaining process definition documentation are as follows. First, there should be a mechanism for keeping track of the dissemination of copies of the documentation (e.g., a system for numbering copies). This is important to ensure that changes and updates are distributed to all affected parties so that no one is working from obsolete information. Second, there should be a review process for changes to ensure that changes to process documentation receive the same degree of scrutiny that was applied to the original documentation package (CCPS 1989).

Process/Equipment Design and Operating Procedures

Much effort is expended to design and install a safe industrial process. A great deal of information has been developed and obtained about the process. This has been used to develop process-specific information such as safe upper and lower operating limits and operating procedures, and to reduce the risks to as low a level as is reasonably practicable.

After safety has been built into the process, it must be maintained throughout the remaining life cycle stages of the process, beginning with facility startup and operation.

The design assessments and basis of safety must be recorded and available for consultation, and the process must be operated as required. The operating phase involves two sets of process documentation—the detailed technical documentation, and safe operating instructions (HSE 2000) for every operational phase, including startup, shutdown, maintenance and emergency operations.

Protective Systems

In addition, where appropriate, the lines of defense should be tested and practiced on a regular basis to ensure the reliability of the systems. These tests should be documented as part of the facility records. Unreliability of protection systems must not be allowed to be a cause of an accident or allow an accident to result in more severe consequences.

Process Risk Management Decisions

During the course of facility design and operation, certain actions are taken to reduce the risk of chemical reactivity incidents. The decisions to take these actions are often prompted by the need to address findings from activities such as process hazard analyses, incident investigations and audits. Other decisions relate to the allocation of capital and labor resources. Although line management (as discussed in Section 4.1) has the responsibility to make risk management decisions, other knowledgeable personnel have input into the decision process. Information is generated that forms the basis for sound decisions and that documents how the decisions were implemented.

Technical evaluation of options and consequence and risk analyses may be prepared. The analyses might include calculation of consequence severities for possible incidents. Subsequently, the basis for a mitigation system may be generated. This might involve, for example, a secondary containment structure, explosion suppression system, or scrubber. The rationale and technical design basis for such decisions should be documented and retained as part of the process knowledge.

The management system for documenting risk management decisions must address the sensitive issue of legal liability. The law departments of some companies believe that documentation of risk analysis, wherein the company acknowledges the possibility of incidents, creates unacceptable liabilities. Many other attorneys see this as an important exercise in demonstrating the company's affirmative action in trying to understand and manage risks. The management system for risk management decision documentation should be carefully coordinated with the company's attorneys, who are likely to have concerns over such issues as intellectual property and confidentiality, use of incriminating and inflammatory language, documentation of mitigation measures, and record retention.

The management system for risk management decisions must be designed to capture information that describes not only what decision was made, but also why it was made. This can be important in explaining differences among plants within a single company. However, there are not always rigorous systems for capturing the "why" information. Accordingly, the management system for documenting process risk management decisions should enlist the cooperation of individuals throughout both the safety and the capital expenditure approval chains. This management system should be designed to receive every safety analysis as well as every capital project request. With these as triggers, the system should prompt the fulfillment of a complete "chain of thought" regarding risk. This might include what initiated the study (or request), what was recommended and why, was it accepted and, if not, why, and was it implemented (CCPS 1989).

Corporate Memory

Knowledge and information obtained from plant experience and mistakes frequently result in enhanced operations. In other words, plants often settle on a way of conducting an operation because of practical experience. However, if the reason for having adopted this practice is not documented, later generations of supervisors may develop or adopt ineffective alternatives, not knowing that they have already been tried.

The process and equipment documentation, as well as the operating and upset procedures, should create an archival history of the operation. In addition, while it is important to know the status of the operation, it is also important to be able to look back and learn from the operation's history to improve process safety continuously.

Retention of historical information must be done in accordance with the company's record retention policy, where one exists. However, in all cases, it is important to think in terms of when the information will be needed and not simply when it was created.

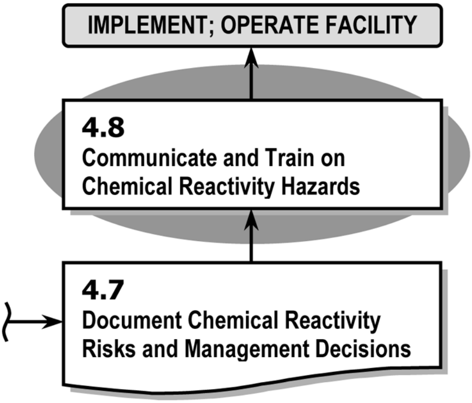
There should be specific responsibility assigned for the maintenance of historical records. Issues of importance, which should be addressed by the management system, include specifying who will keep the records, where and how they will be maintained, and how they can be retrieved and used at both the facility and company-wide levels. In addition, there should be adequate consideration for backing up critical records and protecting the records against loss.

An important aspect of the company memory is the knowledge and experience possessed by senior operators, supervisors, and engineers. Over the years, many things happen in a plant that are not written down, but the ability to relate new questions or problems to past experience is critical to effective problem solving.

This experience is usually passed on from older to younger workers over time. However, when downsizing or streamlining programs results in many of these experienced people leaving an organization at once (e.g., to take advantage of early retirement incentives), a gap in the company memory can be created.

Should such situations threaten to arise, the process knowledge management system should prompt the initiation of programs to capture as much experience-based information as possible. This might involve such activities as engaging early retirees temporarily as consultants, or undertaking organized "debriefing" sessions. The use of "knowledge engineering" techniques, now employed in developing expert systems, provides a structured way to capture this information (CCPS 1989).

4.8. Communicate and Train on Chemical Reactivity Hazards



Communication and training are vital to the management of hazards. However, it is quite easy to pass off some information as being "common sense" or as too obvious to require formal communication or training. Other information such as detailed process chemistry might be considered too involved. When this information relates to the control of chemical reactivity hazards, its communication and related training should not be overlooked. All operating personnel should have a good idea of what will happen, for example, if certain materials are mixed together or if a process is operated in the wrong range.

This applies to contract personnel as well as employees. How to communicate chemical reactivity hazards is not a trivial matter, especially when contractors are involved. Confidentiality agreements may need to be put into place, and issues may need to be addressed on a case by case basis. Communication with contract personnel and broader outsourced manufacturing issues are addressed by Early (1996) and CCPS (2000).

When previous chemical reactivity incidents have been examined, particularly where established instructions were not followed, it is often found that facility personnel did not know that violating the procedure could lead to an uncontrolled reaction. Knowledge of the chemical reaction hazards would make procedural violations less likely.

Training Vehicles/Methods

Several channels of training and communication should be opened to various recipients under the chemical reactivity hazard management system. Training and communication involve combinations of various media, including:

- Degree programs in chemistry or appropriate chemistry courses at local colleges
- Printed pamphlets and flyers (such as with basic facility information)
- Printed or electronic procedures (operating and emergency response)
- Videos
- Computer-based presentations
- Live presentations and demonstrations
- Drills or other on-the-job activities
- Product labels and MSDSs.

The information and training that should be provided along these channels is summarized in this section.

Intraplant Training

All affected personnel should be universally informed of the chemical reactivity hazards at the facility. Training and communication must address:

- Chemical reactivity hazards that are present
- Where to find hazard information, including any facility-specific compatibility charts
- Any responsibility for which the affected personnel are accountable, as part of the management system

- Any procedure they may need to follow to safely operate the facility; such training would naturally make use of the written operating procedures
- Any additional safe work practices
- The use of any tools and personal protective equipment required in the performance of their responsibilities
- Reporting procedures for abnormal situations, near misses, incidents, leaks and spills
- Any procedures they may need to follow to respond to or otherwise protect themselves in response to an emergency; such training should include the use of any personal protective equipment, special tools, or equipment required for these actions.

Training methods should be selected which build familiarity with facilities, equipment and operational tasks as well as an understanding of the chemical reactivity hazards involved. In particular, written operating procedures should be referred to whenever possible during training. If operating procedures are not presented clearly enough for use in training, or if they do not represent the way a task should be performed, then they should be revised. CCPS (1996) addresses content and format issues for effective written procedures.

Periodic retraining will normally be required. Also, for some training it is important, or a regulatory requirement, to verify that the training was understood. Such means may include:

- Evaluation of drills or on-the-job training activities
- Written or computer-based tests
- Verbal tests
- Demonstration of skills and knowledge.

Intracompany Training and Communication

Within a company (e.g., where similar facilities are in design or operation, where the chemical reactivity hazards will be present, or where knowledge is maintained at the corporate level), the following information or training should be provided.

- Lessons learned (e.g., from incident investigations)
- Operational refinements (e.g., those underlying management of change cases)
- Opportunities for experienced employees to be on analysis teams for similar facilities
- Operating procedures applicable to the handling of the chemical at other facilities.

Third-Party Training and Communication

Contractors, contract manufacturers, transporters, warehousers, and end users of reactive chemicals should be informed not only of chemical reactivity hazards, but provided information or training on how to control them. This should be done as part of product life-cycle management and Responsible Care/Product Stewardship. Specific issues needing to be addressed may include but probably are not limited to those that are highlighted during the hazard/risk analyses (Section 4.5), including:

- Engineering and administrative requirements for safe storage, including the full range of consequences should requirements not be met or procedures not followed
- Responses to process upsets, including releases
- Emergency response guidelines.

Audience Issues

The same information may need to be presented using very different styles, formats, and media, depending on the intended audience (operators, management, technical staff, etc.) and use of the information. For example, an explanation to a design engineer why a particular design basis was chosen will be a significantly different communication than emergency response training of operations personnel.

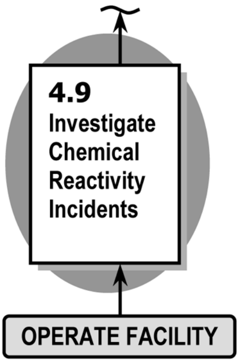
For all training and communications, keep in mind:

(a) The objective to be achieved, including retention and use of the information.

(b) The audience to be reached.

(c) The most effective, efficient and timely means of conveying the information to the audience to achieve the objective.

4.9. Investigate Chemical Reactivity Incidents



During facility operation, a chemical reactivity incident or near miss may occur despite all efforts to effectively manage chemical reactivity hazards. An essential element of managing chemical reactivity hazards is to appropriately report and investigate every incident or near miss involving chemical reactivity hazards. By investing the time and effort to determine the root causes and take corrective action, as well as to document and broadly communicate the lessons learned, previously unrecognized hazards can be identified, weaknesses in the facility safeguards and management system can be corrected, and future incidents can be avoided. This section focuses on a management system for investigating chemical reactivity incidents.

The objective of incident investigation is to prevent recurrence of similar events. This is accomplished by establishing a management system for investigation that ensures:

- All incidents are reported, including near misses
- Investigations identify root causes
- Investigations identify recommended measures that reduce or eliminate the underlying chemical reactivity hazard, reduce the likelihood of recurrence, or reduce the severity of potential consequences
- Effective follow-up actions are made to complete or resolve all recommendations.

These goals are listed in the order of importance to a company. Of greatest importance is to get near misses reported so that investigation can be used to learn from the incident. Note that incident investigation techniques are essentially the same whether applied to chemical reactivity hazards or to other hazards.

Near-Miss Incidents

Near misses deserve special attention in facilities handling chemical reactivity hazards. Unusual occurrences involving reactive chemicals and uncontrolled reactions can point to where knowledge is lacking or prevention safeguards are inadequate. For example, any occurrence of an unexpected temperature excursion, bulging container or generation of fumes should be taken as a strong warning sign that an unexpected or uncontrolled chemical reaction has taken place. The making of an off-specification product is often treated as a quality problem; however, it may also be an indicator of a chemical reactivity near miss.

The first step in the learning process is investigation, to determine the causes and underlying reasons why accidents and near misses occur. It is an axiom of chemical process safety that "process safety incidents are the result of management system failures" (CCPS 1989). A thorough investigation to root causes will identify the management system weaknesses. Learning which management system weaknesses are leading to near misses and actual loss events is one of the highest value activities in which a company can invest. Learning from near misses is much less costly than learning from loss events.

By way of definition, a *near miss* is an unplanned sequence of events that could have caused harm or loss if conditions were different or were allowed to progress, but actually did not. *Incidents* include both near misses and actual loss events.

It is often difficult to make a determination whether a specific event is a near miss or a "nonincident" (neither an actual loss event nor a near miss). If the users of the investigation system do not identify an event to be at least a near miss, then the event will not be investigated and valuable lessons may be lost. Depending on the definition of a near miss, roughly 50 to 100 near misses occur for every actual loss event and 50 to 100 precursors for every near miss. Figure 4.6 depicts the general relation between precursors, near misses and loss events.

Essential Practices

The essential practices for investigating chemical reactivity incidents can be grouped into three categories:

1. What to do before an incident occurs
2. What to do when an incident occurs
3. What to do after an incident investigation is completed.

Figure 4.6. **Relation of precursors to major incidents.**

General guidelines for conducting process incident investigations are given by CCPS (2003). Specific practices that relate to the nature of chemical reactivity hazards are discussed below.

When conducting an investigation that may have involved uncontrolled chemical reactions, careful and extensive sampling needs to be performed, including residues, unused raw materials, products, relief effluents, and dispersed reaction products. It is likewise important to collect and retain material and process information such as lot numbers, instrumentation readouts, temperature and pressure profiles, and log sheets—before written records are lost or computer records are erased or overwritten. Testing may need to be done on the raw materials to check for any unusual thermal behavior, and on residues to identify their chemical composition.

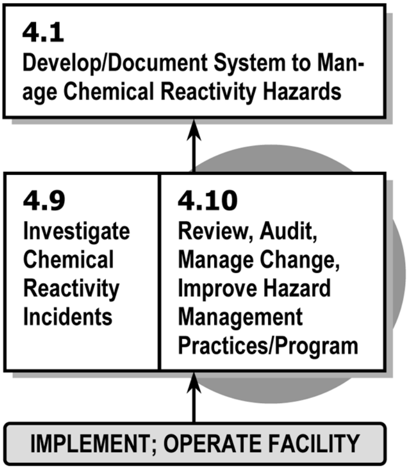
Identifying causes is one of the primary objectives of the entire investigation process. Initial selection of the root cause determination process will most likely require some special attention to the concepts of multiple causes (especially when dealing with reactive chemistry) and to underlying system-related causes.

Identifying and evaluating practical recommendations are obviously critical parts of any incident investigation. Ineffective recommendations can serve to merely transfer the risk or even to create a new hazard that was not present before the initial incident. Recommendations should be broad enough to address general causes, rather than serving only to prevent recurrence of the specific sequence of events leading to the incident. For facilities with chemical reactivity hazards, this requires a thorough understanding of possible chemical reaction scenarios with the actual equipment, controls and environment of the facility.

Implementing a recommendation must go beyond an equipment, process or procedural change. What was learned about an incident or near miss and its causes, as well as the changes made to prevent recurrence, needs to be effectively communicated to employees. As a result, they will have a greater understanding to better identify future near misses and the factors that could lead to a chemical reactivity incident at their facility. This will also encourage employees to report other near misses.

4.10. Review, Audit, Manage Change, and Improve Hazard Management Practices and Program

Managing chemical reactivity hazards so that uncontrolled chemical reactions are avoided is an ongoing endeavor, throughout the facility lifetime. Establishing a management system to ensure chemical reactivity hazards are identified and controlled is likewise not a one-time project. The management system itself, as well as the various control methods used, should be not only maintained in an operational condition but also continually improved. These improvements need not only happen after lessons are learned from an incident, as discussed in Section 4.9. Avenues for maintaining and proactively improving a hazard management program include:



- Active monitoring
- Employee input
- Periodic reviews of programs and procedures
- Audits of various types
- Management of change
- Keeping abreast of new technology.

Making use of all these elements is a visible sign of management commitment and an essential means of continually improving the management system.

Active Monitoring

Regular involvement, walk-around inspections, informal spot checks, and specific topical discussions by line management and staff can be used to ensure that chemical reactivity hazard management systems and procedures are actually being implemented and followed on a day to day basis. Questions should be raised if unexpected changes have been made or unusual circumstances are detected.

Auditing

Audits can be defined as methodical, independent, and typically periodic examinations—involving analyses, tests, and confirmation—of local procedures and practices (CCPS 1989). Audits provide management with a tool for measuring facility performance. The general goal of most process safety audit programs is to verify whether a facility's procedures and practices comply with legal requirements, internal policies, company standards and guidelines, and/or accepted practices. In addition, today the public, government, company managers, and operating personnel want to be assured that an organization is acting as a "good corporate citizen." Audits can help ensure that compliance is being achieved with a sound process safety program, and that risks are being appropriately managed.

Beyond playing a significant role as a measurement tool, audits provide the opportunity to share a set of fresh perspectives on areas where requirements have yet to be codified (e.g., process control procedures, management information systems, and maintenance programs). Audits also serve to indicate ongoing efforts to reexamine and reevaluate operations to further reduce operational risks and consequent liabilities (including property damage and business interruption).

Audits can be focused on physical systems (facilities and equipment) or on administrative systems (management programs, recordkeeping systems, etc.). Audits, either by company personnel or by third parties, complement monitoring activities by looking to see if the chemical reactivity hazard management policies, organization and systems are actually achieving the desired objectives.

Corrective actions, in a general sense, are the steps taken by a company in response to recognition of a process safety deficiency, either through audit findings or by other means. Some actions may be taken immediately upon notification of a problem, deficiency, or uncontrolled hazard, while other actions may be longer term and require action planning (CCPS 1989).

Audit protocols are tailored to their subject and to the answer desired of the audit. CCPS (1993a) provides more details on audit planning, audit protocols and teams, and other audit issues.

Managing Change

Management of change (often known as MOC) was addressed in Section 2.2 as a life cycle issue, since changes occur throughout the lifetime of a facility. The objective of managing change, in the context of chemical reactivity hazards, is to ensure that all changes made to a facility after startup that might

- introduce a new chemical reactivity hazard,
- increase the likelihood of an uncontrolled chemical reaction,
- make safeguards against uncontrolled chemical reactions less effective, or
- make the consequences of an uncontrolled chemical reaction more severe

are identified, evaluated, and addressed so that chemical reactivity incident risks are adequately controlled.

Identifying changes that may affect chemical reactivity risks is often difficult, since subtle differences in operating procedures or in material composition, concentration, operating temperature, etc. can have a great effect on the ability of a system to maintain control. The repackaging example in Section 5.3 illustrates the same point with respect to a change in a material of construction. Even changes made for safety or environmental improvements need to be evaluated for their possible effects on chemical reactivity. For example, insulation of a storage tank for fire protection purposes will reduce heat dissipation to the surroundings, and may allow self-heating to accelerate out of control.

For this reason, all personnel need to be trained to recognize changes and consistently be required to have all changes approved before proceeding, according to the facility's management of change policy and procedure. Persons with responsibility to review and approve changes must have a good understanding of the chemical reactivity hazards at their facility, as well as the factors that might affect the likelihood or severity of a chemical reactivity incident.

Time and resources need to be made available to assess the safety significance of proposed changes when dealing with chemical reactivity hazards. The effects of proposed changes need to be carefully reviewed, new test data may need to be obtained, and experts may need to be consulted. This issue is especially challenging in some types of facilities such as specialty chemical operations, where many different products and processes are introduced on a regular basis.

Keeping Abreast of Advancing Technology

Companies with strong chemical reactivity hazard management programs should strive to benefit from the latest advances in process safety technology, and keep abreast of technological advances through active participation in professional and trade associations.

Organizations with outstanding programs contribute to advancing the state of the art of chemical reactivity safety by sharing nonproprietary results of internal safety research and supporting the safety-oriented research and development programs of professional and trade associations and universities. Organizations should encourage technical staff participation in professional and trade association programs and provide for the development of chemical reactivity safety reference libraries. Financial grants and active volunteerism are also viable options open to most organizations, regardless of size or resources.

The enhancement of chemical reactivity safety knowledge also provides broader benefits. Improved process knowledge and understanding can produce a competitive advantage—for example, through improved yields, better quality, and increased productivity (CCPS 1989).

Many industry-oriented organizations provide avenues for sharing or learning about new technologies for chemical reactivity hazards assessment and management, through conferences, periodicals, and books, as well as codes and standards. These include AIChE, CCPS, the European Federation of Chemical Engineering, the European Process Safety Center, the Mary Kay O'Connor Process Safety Center, and the Design Institute for Emergency Relief Systems (DIERS). Larger corporations or industry groups may also have the resources to sponsor research into the understanding and controlling of chemical reactivity hazards.

Ensuring Information Handoff (Laboratory to Pilot Plant to Plant)

In order to maximize the benefit of any identified improvement, administrative procedures should be created and implemented which define distribution or lines of communication for information related to chemical reactivity hazard management improvements. Examples of such lines include those from laboratories to pilot plants to production facilities.

Dividing Responsibility for Oversight (Process versus Plant versus Corporate)

Multiple facilities in an organization may have similar chemical reactivity hazards; similar storage, handling or processing operations; or use similar technologies to control the associated hazards. If so, it may be more efficient for a corporate office or personnel to assume responsibility for some improvement activities such as auditing and research. This can also facilitate communication of incidents and best practices between facilities.

Implementing Corrective Actions

Corrective action, broadly defined, includes not only the process of addressing identified deficiencies, weaknesses, or vulnerabilities, but also the processes for corrective action planning and follow-up. The corrective action process can be summarized as follows.

(a) Prepare and distribute audit report
(b) Develop action plans
(c) Review action plans
(d) Implement action plans
(e) Verify completion.

To control the corrective action process, many companies make use of a tracking system. To assist in the tracking of corrective actions, a variety of reporting mechanisms can be used, such as:

- Periodic status reports (e.g., quarterly/monthly)
- Milestone reports (summarizing accomplishments)
- Exception reports (other major milestones).

Corrective action tracking provides management with the status of audit issues and agreed-upon corrective actions. It also provides an opportunity, in some cases, to review corrective action at a later date subsequent to completion (e.g., a year later). CCPS (1989) provides more detail on the corrective action process.

5

Worked Examples

Several worked examples of identifying chemical reactivity hazards are presented in this chapter. The objective of this chapter is to illustrate the use of the Preliminary Screening Method for Chemical Reactivity Hazards (Chapter 3) by way of a few, relatively simple examples that show different decision paths.

5.1. Intentional Chemistry Example

> *Charbroiled Chemicals has one facility adjacent to an industrial park on the outskirts of the city. The facility manufactures a range of products in 200 to 1000 gal batch reactors by chlorinating various organic feed materials. The reaction products go through several purification stages, with the chlorinated organic products sealed and labeled in 55 gal drums for delivery to customers. Byproducts that cannot be recycled are neutralized and stabilized in the waste treatment facility prior to disposal.*

The "Questions" in these worked examples refer to the twelve questions in Chapter 3. Question 1 ("Is intentional chemistry performed at your facility?") should be answered YES for this example, since raw materials are processed such that a chemical reaction is intended to take place. Products are of a different chemical composition than the starting materials. Intentional chemistry is also likely being practiced in the waste treatment facility.

Question 5 ("Is combustion with air the only chemistry intended at your facility?") should be answered NO, since the intentional chemistry involves chlorination reactions. The Note in Section 3.1 pertains to this process. It states that it is not the intention of this Concept Book to cover all the complexities of intentional chemistry. Although the essential practices in Chapter 4 are appropriate considerations for facilities such as this one, additional resources are likely to be required to identify and control the chemical reactivity hazards.

Table 5.1 shows what the documentation of the screening might look like for this example, if the user decided to proceed to answer the remaining questions. The Comments column is used to indicate where information was obtained for answering each question. The information in Table 5.1 gives an idea of what chemical reactivity hazards will need to be controlled to operate the facility safely.

Figure 5.1 indicates the path taken through the screening flowchart for this example.

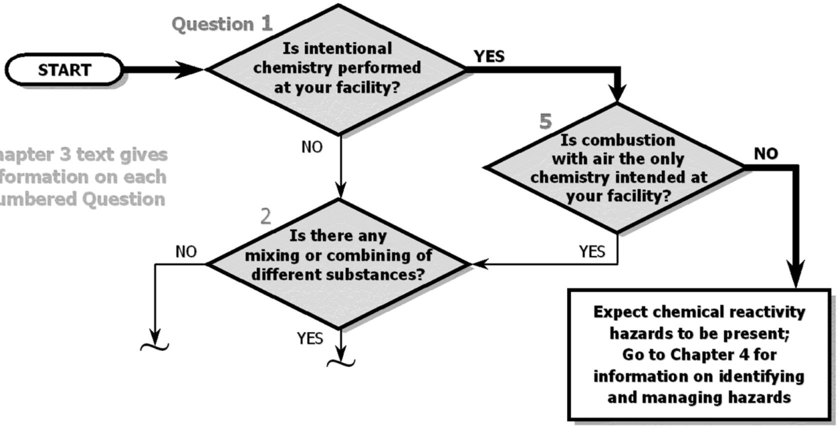


Figure 5.1. **Screening flowchart path for intentional chemistry example.**

5.2. Combustor Example

> *Rarified Research operates a ram-fed incinerator for destruction of select wastes at its large, centralized research facility, including liquid flammable solvents in small plastic containers. The incinerator is fired by natural gas and is brick-lined. Temperatures are closely monitored, and stack emissions are routinely sampled.*

Referring to the questions in Chapter 3, Question 1 (“Is intentional chemistry performed at your facility?”) should be answered YES for this example.

TABLE 5.1
Intentional Chemistry Example Documentation (All Questions Answered)

FACILITY: Charbroiled Chemicals

Do the answers to the following questions indicate chemical reactivity hazard(s) are present? [1] YES

AT THIS FACILITY:	YES, NO, or NA	BASIS FOR ANSWER; COMMENTS
1. Is intentional chemistry performed?	YES	Batch chlorination; waste neutralization
2. Is there any mixing or combining of different substances?	YES	Raw materials combined in reactor
3. Does any other physical processing of substances occur?	YES	Purification steps
4. Are there any hazardous substances stored or handled?	YES	Organic feed materials; concentrated hydrochloric acid; oxygen
5. Is combustion with air the only chemistry intended?	NO	Chlorination
6. Is any heat generated during the mixing or physical processing of substances?	NO	No indication of exothermic behavior
7. Is any substance identified as spontaneously combustible?	NO	No indication from MSDS or literature
8. Is any substance identified as peroxide forming?	YES	Organics in feed have propensity to form organic peroxides under right conditions
9. Is any substance identified as water reactive?	NO	No indication from MSDS or literature
10. Is any substance identified as an oxidizer?	YES	Oxygen feed; chlorine gas intermediate
11. Is any substance identified as self-reactive?	NO	No indication from MSDS or literature
12. Can incompatible materials coming into contact cause undesired consequences?	NO	No scenarios identified beyond those for intentional chemistry abnormal situations

[1] Use Figure 3.1 with answers to Questions 1–12 to determine if answer is YES or NO

Raw materials (wastes) are processed such that a chemical reaction is intended to take place, with products (combustion gases, ash and slag) being of a different chemical composition than the starting materials.

Question 5 (“Is combustion with air the only chemistry intended at your facility?”) can be answered YES in this case, assuming the “facility” being addressed is limited to the incinerator system. Due to the great number of combustion systems in operation, many other resources are available for ensuring safe design and operation of the combustion part of the incinerator facility. However, it should be noted that many combustors now have effluent treatment systems, such as selective catalytic reduction (SCR) systems, that involve intentional chemistry beyond the combustion reaction.

Question 2 should be answered YES if there is any combining of wastes before being fed to the combustion chamber. Question 6 will likely be answered NO if similar wastes are combined, such that no significant heat effects (such as heat of solution) are experienced.

The answers to Questions 7 through 11 will likely determine whether chemical reactivity hazards are present. For example, a jar of liquid ether that is a peroxide former may be brought to the facility for incineration. If it had been stored a long time and the contents had been exposed to air, unstable peroxides may be present that could explode when handled or fed to the incinerator. The information in Section 3.3 may be helpful in identifying whether any reactive chemicals are present.

If the answer to all of Questions 7 through 11 are NO, then Question 12 (“Can incompatible materials coming into contact cause undesired consequences?”) should be addressed. This involves the three steps described at the end of Section 3.3: decide on undesired consequences of concern, identify mixing scenarios, and document mixing scenario consequences. The bottom rows of Table 5.2 give a couple of mixing scenarios that may be possible for this system.

If NO mixing scenarios with undesired consequences are identified that have a reasonable likelihood of occurring during the lifetime of the facility, then it can be concluded that operation of the incinerator does not involve chemical reactivity hazards. In this case, the information in Chapter 4 will not need to be applied.

If the answer to any of the Questions 7 through 12 is YES, then one or more chemical reactivity hazards are present. The information in Chapter 4 should be used to identify and manage the hazards.

Figure 5.2 indicates the path taken through the screening flowchart for the combustor example, as documented in Table 5.2.

TABLE 5.2

Combustor Example Documentation

FACILITY: Rarified Research/Incinerator

Do the answers to the following questions indicate chemical reactivity hazard(s) are present?[1] YES

AT THIS FACILITY:	YES, NO, or NA	BASIS FOR ANSWER; COMMENTS
1. Is intentional chemistry performed?	YES	Combustion is a chemical reaction
2. Is there any mixing or combining of different substances?	YES	Wastes are mixed before feeding to incinerator
3. Does any other physical processing of substances occur?	NA	
4. Are there any hazardous substances stored or handled?	NA	
5. Is combustion with air the only chemistry intended?	YES	Designed for controlled combustion
6. Is any heat generated during the mixing or physical processing of substances?	NO	No indication of exothermic behavior when premixing wastes
7. Is any substance identified as spontaneously combustible?	NO	No indication from MSDS or literature
8. Is any substance identified as peroxide forming?	NO	No indication from MSDS or literature
9. Is any substance identified as water reactive?	NO	No indication from MSDS or literature
10. Is any substance identified as an oxidizer?	NO	No indication from MSDS or literature
11. Is any substance identified as self-reactive?	NO	No indication from MSDS or literature
12. Can incompatible materials coming into contact cause undesired consequences, based on the following analysis?	YES	See analysis on the next page

TABLE 5.2 (*continued*)

SCENARIO	CONDITIONS NORMAL?[2]	R, NR, or ?[3]	INFORMATION SOURCES; COMMENTS
1. Acetone from leaking bottle contacts paper material in feeder	No—feeder is enclosed and above ambient temperature	NR	Acetone not reactive with paper material by common experience; feeder is hot but below autoignition temperatures; seal should prevent flashback
2. Container of dicumyl peroxide powder breaks in feeder and contacts residual combustible solids or liquids	No—feeder is enclosed and above ambient temperature	R	May ignite and burn rapidly in feeder; however, analysis indicates feeder design will contain material and flame, and no significant undesired consequences are expected; also, this material would not normally be put into incinerator

[1] Use Figure 3.1 with answers to Questions 1–12 to determine if answer is YES or NO

[2] Does the contact/mixing occur at ambient temperature, atmospheric pressure, 21% oxygen atmosphere, and unconfined? (IF NOT, DO NOT ASSUME THAT PUBLISHED DATA FOR AMBIENT CONDITIONS APPLY)

[3] R = Reactive (incompatible) under the stated scenario and conditions
NR = Nonreactive (compatible) under the stated scenario and conditions
? = Unknown; assume incompatible until further information is obtained

5.3. Repackaging Example

Eastown Industries conducted a Management of Change review for switching to a new propylene dichloride supplier. The propylene dichloride was purchased in railcar quantities and unloaded into a large storage tank, from which it was metered into 55 gal drums for sale to customers. During the Management of Change review, it was identified that the supplier sometimes used aluminum railcars for other products. The shift supervisor raised the question of what would happen if the propylene dichloride was received in an aluminum railcar and remained on the siding for a few days before unloading its contents into the storage tank.

Referring to the questions in Chapter 3, Question 1 ("Is intentional chemistry performed at your facility?") can be answered NO for this example, since the unloading, storage and repackaging operation involves no intended chemical reactions. Likewise, Questions 2 and 3 can be answered NO, since mixing and physical processing are also not intended. Question

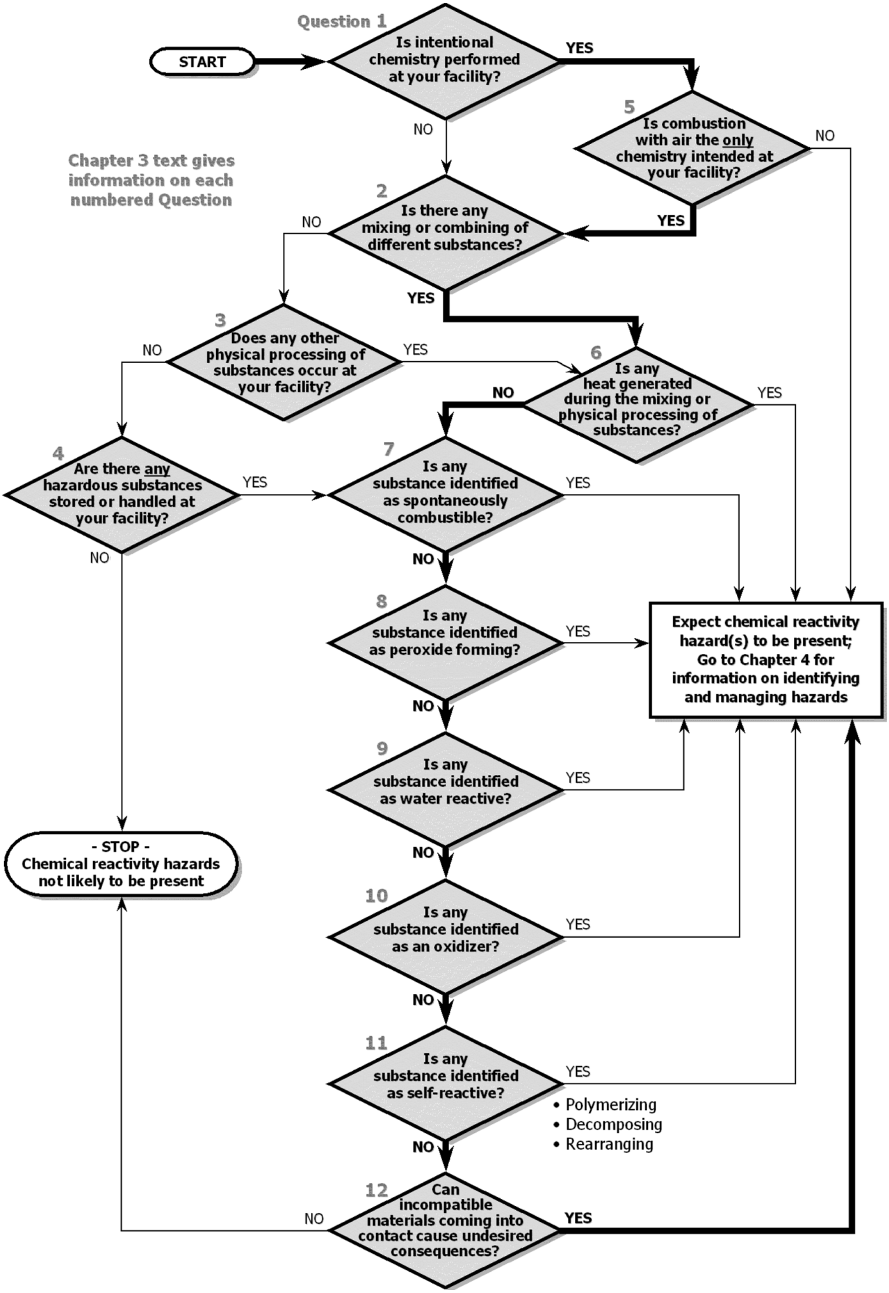


Figure 5.2. **Screening flowchart path for combustor example.**

4 should be answered YES, since propylene dichloride (1,2-dichloropropane) is a flammable liquid, having a flash point of 60°F (16°C).

A review of material safety data and standard references for propylene dichloride would result in answering NO to Questions 7 through 11, since this material is not indicated to be spontaneously combustible, peroxide forming, water reactive, an oxidizer, or self-reactive. Addressing the scenario for Question 12 of the consequences of receiving the material in an aluminum railcar, it would be found that propylene dichloride will react with oxidizing materials, alkalis, and alkali and other metals such as aluminum (NFPA 2002). The consequences of such a reaction might range from causing a leak and a fire if ignited, to a more catastrophic railcar incident.

Group compatibility data indicates no reaction between propylene dichloride and aluminum oxide (which would form an outside layer on the aluminum metal). However, "heat generation, may cause pressurization" and "forms very unstable explosive metallic compounds" are the results of combining propylene dichloride and aluminum powder (NOAA 2002).

A literature review of previous incidents found a reported incident where an aluminum railcar filled with this material leaked from the railcar within 24 hours. Based on this information, it was decided that positive steps needed to be taken to:

- Convey and retain this information throughout the lifetime of the facility
- Ensure propylene dichloride is never received in an aluminum railcar
- Conduct tests to determine all possible consequences under the full range of ambient conditions which could be experienced
- Contact the supplier to communicate the hazard and ensure provisions are in place for avoidance.

If more severe consequences than a leaking railcar were found, then even greater precautions would likely be warranted. These precautions would need to ensure no material is received in an aluminum container. Also, aluminum must be excluded from the facility as a material of construction in pipes, tanks, valves, pumps, and especially any container in which product would be transferred to a customer.

Table 5.3 shows what the documentation of the screening might look like for this example.

TABLE 5.3

Repackaging Example Documentation

FACILITY: Eastown Industries

Do the answers to the following questions indicate chemical reactivity hazard(s) are present? [1] YES

AT THIS FACILITY:	**YES, NO, or NA**	**BASIS FOR ANSWER; COMMENTS**
1. Is intentional chemistry performed?	NO	Repackaging only
2. Is there any mixing or combining of different substances?	NO	Repackaging only
3. Does any other physical processing of substances occur?	NO	Repackaging only
4. Are there any hazardous substances stored or handled?	YES	Propylene dichloride is a flammable liquid
5. Is combustion with air the only chemistry intended?	NA	
6. Is any heat generated during the mixing or physical processing of substances?	NA	
7. Is any substance identified as spontaneously combustible?	NO	No indication from MSDS or literature
8. Is any substance identified as peroxide forming?	NO	No indication from MSDS or literature
9. Is any substance identified as water reactive?	NO	No indication from MSDS or literature
10. Is any substance identified as an oxidizer?	NO	No indication from MSDS or literature
11. Is any substance identified as self-reactive?	NO	No indication from MSDS or literature
12. Can incompatible materials coming into contact cause undesired consequences, based on the following analysis?	YES	See analysis below

SCENARIO	**CONDITIONS NORMAL?** [2]	**R, NR, or ?** [3]	**INFORMATION SOURCES; COMMENTS**
1. Propylene dichloride received in aluminum railcar	No—confinement within railcar	R	Previous incident resulted in leak within 24 hours. NOAA Chemical Reactivity Worksheet indicates combining propylene dichloride with aluminum powder results in “heat generation, may cause pressurization” and “forms very unstable explosive metallic compounds.”

[1] Use Figure 3.1 with answers to Questions 1–12 to determine if answer is YES or NO

[2] Does the contact/mixing occur at ambient temperature, atmospheric pressure, 21% oxygen atmosphere, and unconfined? (IF NOT, DO NOT ASSUME THAT PUBLISHED DATA FOR AMBIENT CONDITIONS APPLY)

[3] R = Reactive (incompatible) under the stated scenario and conditions

NR = Nonreactive (compatible) under the stated scenario and conditions

? = Unknown; assume incompatible until further information is obtained

5.4. Physical Processing Example

In a Downstream Decomposing facility not the subject of this example, intentional chemistry is performed as ammonium dichromate is heated to decomposition to make chromium dioxide, which is used in the production of magnetic tape products. In the Upstream Feeds facility under study, physical processing is performed as ammonium dichromate is fed through a screw conveyor. The Preliminary Screening Method is to be used as a first-cut determination whether chemical reactivity hazards will need to be managed in the physical processing facility.

Referring to the questions in Chapter 3, Question 1 can be answered NO for this example, since the physical processing involves no intended chemical reactions. Question 2 is answered NO, since mixing or combining of different substances is not intended. Question 3 should be answered YES, since the operation involves physical processing. The input of mechanical energy to the ammonium dichromate raises its temperature somewhat in the screw conveyor, so Question 6 should be answered YES. Consequently, the Preliminary Screening Method indicates that a chemical reactivity hazard should be expected. The information in Chapter 4 would be useful in both identifying and managing any chemical reactivity hazards that are present. Questions 7 through 12 of the Preliminary Screening Method could be used to give an indication of what chemical reactivity hazards to expect. Table 5.4 shows what the documentation of the Preliminary Screening might look like for this example.

5.5. Mixing Example

This example presents a simplified retrospective of the 1995 explosion and fire at the Napp Technologies facility in Lodi, New Jersey (EPA 1997). The intent is to illustrate the Preliminary Screening Method for the type of process involved in the incident.

A contract manufacturer is contracted to prepare one 8100 lb batch of a gold precipitating agent. Ingredients are mixed in a 125 ft^3 (6 m^3) cone blender which is insulated and has a steel jacket to allow cooling and heating with a water/glycol mixture. The precipitating agent consists of approximately 66% sodium hydrosulfite, 22% aluminum powder and 11% potassium carbonate by weight. After blending these dry ingredients, a small amount of liquid benzaldehyde is added for odor control. The product blend is packaged into eighteen 55 gal drums for shipment.

TABLE 5.4
Physical Processing Example Documentation

FACILITY: Upstream Feeds

Do the answers to the following questions indicate chemical reactivity hazard(s) are present?[1] YES

AT THIS FACILITY:	YES, NO, or NA	BASIS FOR ANSWER; COMMENTS
1. Is intentional chemistry performed?	NO	Physical processing only
2. Is there any mixing or combining of different substances?	NO	Ammonium dichromate only
3. Does any other physical processing of substances occur?	YES	Mechanical screw conveyor
4. Are there any hazardous substances stored or handled?	NA	
5. Is combustion with air the only chemistry intended?	NA	
6. Is any heat generated during the mixing or physical processing of substances?	YES	Some temperature increase due to mechanical energy of screw conveyor
7. Is any substance identified as spontaneously combustible?	NO	No indication from MSDS or literature
8. Is any substance identified as peroxide forming?	NO	No indication from MSDS or literature
9. Is any substance identified as water reactive?	NO	Ammonium dichromate is water soluble
10. Is any substance identified as an oxidizer?	YES	Listed in NFPA 430 as Class 3 Oxidizer
11. Is any substance identified as self-reactive?	YES	Decomposes at 170°C, generating gas, swelling dramatically, rupturing closed containers; may also be shock sensitive
12. Can incompatible materials coming into contact cause undesired consequences?	NO	No scenarios identified

[1] Use Figure 3.1 with answers to Questions 1–12 to determine if answer is YES or NO

Referring to the questions in Chapter 3, Question 1 ("Is intentional chemistry performed at your facility?") would be answered NO for this example, since the operation consists only of loading, blending, and packaging, with no intended chemical reactions.

Question 2 ("Is there any mixing or combining of different substances?") would be answered YES, since the blending operation involves mixing of the ingredients. Assuming no indication of heat generation is reported for the intended operation, Question 6 would be answered NO.

A review of material safety data and standard references for the ingredients may result in answering Questions 7 through 11 as shown in Table 5.5. Two of the ingredients, aluminum powder and sodium hydrosulfite, are known to be reactive chemicals, so a chemical reactivity hazard is obviously present. At this point, the Preliminary Screening Method would point the user to the information in Chapter 4, for identifying and managing chemical reactivity hazards.

Two example scenarios for Question 12 are also shown in Table 5.5. A third scenario that could be investigated would be the addition of excess benzaldehyde to the mixture. The group contribution method of the NOAA Chemical Reactivity Worksheet (NOAA 2002) predicts the generation of heat and flammable gases if benzaldehyde and sodium hydrosulfite were combined. A fourth scenario might be found by a literature review. For example, *Bretherick's Handbook* (Urben 1999) indicates an equimolar mixture of potassium carbonate and magnesium gives an explosive substance. Since aluminum and magnesium have analogous hazards, potassium carbonate and aluminum might likewise pose a reactivity hazard. Other scenarios are also possible.

The Preliminary Screening Method is not intended to identify all conditions under which reactive chemicals and incompatibilities may lead to uncontrolled reactions. However, it should give an indication whether chemical reactivity hazards exist, as well as what to investigate more closely by analysis and testing.

TABLE 5.5
Mixing Example Documentation

FACILITY: Napp Technologies, Inc., Lodi, New Jersey

Do the answers to the following questions indicate chemical reactivity hazard(s) are present? [1] YES

AT THIS FACILITY:	YES, NO, or NA	BASIS FOR ANSWER; COMMENTS
1. Is intentional chemistry performed?	NO	Loading, blending, and packaging only
2. Is there any mixing or combining of different substances?	YES	Blending of ingredients in cone blender
3. Does any other physical processing of substances occur?	NA	
4. Are there any hazardous substances stored or handled?	NA	
5. Is combustion with air the only chemistry intended?	NA	
6. Is any heat generated during the mixing or physical processing of substances?	NO	No indication of heat generation from previous batch or from nature of blend
7. Is any substance identified as spontaneously combustible?	YES	Sodium hydrosulfite is DOT/UN Hazard Class 4.2, Spontaneously Combustible Material; finely divided aluminum powder is pyrophoric without oxide coating
8. Is any substance identified as peroxide forming?	NO	No indication from MSDS or literature
9. Is any substance identified as water reactive?	YES	Sodium hydrosulfite is water reactive; uncoated aluminum powder is DOT/UN Hazard Class 4.3, Dangerous When Wet
10. Is any substance identified as an oxidizer?	NO	No indication from MSDS or literature
11. Is any substance identified as self-reactive?	YES	Heating of sodium hydrosulfite can initiate self-sustaining exothermic decomposition
12. Can incompatible materials coming into contact cause undesired consequences, based on the following analysis?	YES	See analysis on the next page

TABLE 5.5 (*continued*)

SCENARIO	**CONDITIONS NORMAL?**[2]	**R, NR, or ?**[3]	**INFORMATION SOURCES; COMMENTS**
1. Vacuum seal cooling water enters blender, reacts with aluminum powder and sodium hydrosulfite, and initiates exothermic decomposition	No—N_2 atmosphere, confinement in blender	R	Both aluminum powder and sodium hydrosulfite are water reactive
2. Glycol/water mixture leaks from jacket into blender, reacts with aluminum powder and sodium hydrosulfite, and initiates exothermic decomposition	No—N_2 atmosphere, confinement in blender	R	NOAA Worksheet indicates combining sodium hydrosulfite with ethylene glycol is "explosive due to vigorous reaction or reaction products may produce detonation," "may cause fire," and indicates "flammable gas generation" and "heat generation by chemical reaction, may cause pressurization"

[1] Use Figure 3.1 with answers to Questions 1–12 to determine if answer is YES or NO

[2] Does the contact/mixing occur at ambient temperature, atmospheric pressure, 21% oxygen atmosphere, and unconfined? (IF NOT, DO NOT ASSUME THAT PUBLISHED DATA FOR AMBIENT CONDITIONS APPLY)

[3] R = Reactve (incompatible) under the stated scenario and conditions
NR = Nonreactive (compatible) under the stated scenario and conditions
? = Unknown; assume incompatible until further information is obtained

5.6. Oxygen System Example

A University Lab expansion includes installation of a distribution system to provide gaseous oxygen from manifolded cylinders to a biological laboratory. No chemical reactivity hazards have been previously identified for the lab facilities.

Referring to the questions in Chapter 3, Questions 1, 2, and 3 can be answered NO for this example, assuming chemical reactions, mixing, and physical processing are not intended to be part of the laboratory facilities. Question 4 should be answered YES, since oxygen is considered hazardous as an oxidizing gas.

With respect to Questions 7 through 11, a review of material safety data and standard references for oxygen would result in answering YES only to Question 10. Table 5.6 shows how this example might be documented, including an incompatibility scenario.

TABLE 5.6

Oxygen System Example Documentation

FACILITY: University Lab Oxygen Distribution System

Do the answers to the following questions indicate chemical reactivity hazard(s) are present? [1] YES

AT THIS FACILITY:	YES, NO, or NA	BASIS FOR ANSWER; COMMENTS
1. Is intentional chemistry performed?	NO	Not part of laboratory procedures
2. Is there any mixing or combining of different substances?	NO	Not part of laboratory procedures
3. Does any other physical processing of substances occur?	NO	Not part of laboratory procedures
4. Are there any hazardous substances stored or handled?	YES	Oxygen is an oxidizing compressed gas
5. Is combustion with air the only chemistry intended?	NA	
6. Is any heat generated during the mixing or physical processing of substances?	NA	
7. Is any substance identified as spontaneously combustible?	NO	Noncombustible gas
8. Is any substance identified as peroxide forming?	NO	No indication from MSDS or literature
9. Is any substance identified as water reactive?	NO	No indication from MSDS or literature
10. Is any substance identified as an oxidizer?	YES	Oxygen is a strong oxidizing agent
11. Is any substance identified as self-reactive?	NO	No indication from MSDS or literature
12. Can incompatible materials coming into contact cause undesired consequences, based on the following analysis?	YES	See analysis below

SCENARIO	CONDITIONS NORMAL?[2]	R, NR, or ?[3]	INFORMATION SOURCES; COMMENTS
1. Oxygen gas contacts oil film remaining in oxygen distribution system after installation	No—pressurized, enclosed	R	NOAA Worksheet indicates mixing O_2 with petroleum lubricating oil may cause fire; reaction may cause pressurization

[1] Use Figure 3.1 with answers to Questions 1–12 to determine if answer is YES or NO

[2] Does the contact/mixing occur at ambient temperature, atmospheric pressure, 21% oxygen atmosphere, and unconfined? (IF NOT, DO NOT ASSUME THAT PUBLISHED DATA FOR AMBIENT CONDITIONS APPLY)

[3] R = Reactive (incompatible) under the stated scenario and conditions

NR = Nonreactive (compatible) under the stated scenario and conditions

? = Unknown; assume incompatible until further information is obtained

Future Work on Chemical Reactivity Hazards

6

To push toward the goal of having no incidents in facilities with chemical reactivity hazards, a concerted effort will be required between companies, universities, governmental organizations, and professional societies. Further development of the means to achieve this goal will require the talents and expertise of a wide diversity of backgrounds. The Center for Chemical Process Safety expects to continue work in this area through its Reactive Chemicals Subcommittee and through future projects.

This effort is expected to center on two of the primary thrusts introduced in Chapter 2: *inform* and *communicate*. The tables in this chapter list some areas where future work may be beneficial.

6.1. Inform

Key Consideration	Areas for Future Work
Know if you have the potential for uncontrolled reaction(s) to take place within your facility	Improve tools like CHETAH so people can identify chemical reactivity hazards without detailed knowledge; develop genuine expert system? Develop advanced computer-based predictive tools Develop a comprehensive, systematic, generalized approach to evaluating chemical reactivity hazards, giving step by step details of the different levels of experimental and theoretical evaluation work required and specifying the limitations of each step or level of evaluation, and revealing the most efficient results while requiring minimum advanced analysis Improve undergraduate curriculum offerings related to chemical reactivity hazards Encourage and facilitate the sharing of reactivity test data within and between companies

Key Consideration	Areas for Future Work
Know how such reactions might be initiated (e.g., heat, contamination, inadvertent mixing, impact, friction, electrical short, lightning)	Develop guidance for specific situations, such as • Loss of control • Materials of construction issues • Management of change issues • Frequent product changeover • Contaminants • Air/water/cleaning chemical sensitivity • Mixing hazards / mixing loss hazards • Inhibitor/catalyst issues (lack of, timing, excess) • Scale/inventory issues • Unit operations commonly related to reactive chemistry, such as distillation
Know what the consequences would be if such a reaction took place (e.g., toxic gas release, fire, explosion)	Develop guidance for specific situations, such as • Energy density • Rate of energy release Develop tools for predicting uncontrolled reaction byproducts such as toxic or flammable gases
Know what safeguards are (or need to be) in place to prevent uncontrolled reactions from taking place, including how to avoid them altogether (inherently safer design/ operations) and how to control them within safe limits (automatic controls, procedures, etc.)	Develop new less-energetic chemical reaction systems for product manufacture, including alternate catalytic and biological routes where appropriate Emphasize need to develop economically viable inherently safer systems at the research and development stages of new process development Develop new process equipment and strategies for product manufacture using lower inventories of reactive chemicals, error tolerant approaches, and process conditions further from limits of control where appropriate Develop or apply advanced technologies for inferring chemical reaction rates and nearness to control limits (e.g., maximum cooling capacity) from process measurements using a combination of real-time computerized algorithms and reactivity test data
Know how to respond properly if an uncontrolled reaction takes place (including operator actions, emergency response plans, community alerting plans, etc.)	Develop emergency strategies specific to actual chemical reaction systems Encourage wider use of emergency response preplanning for chemical reactivity incidents; integrate consequence analyses for chemical reaction systems with emergency response scenarios

6.2. Communicate

Key Consideration	Areas for Future Work
Tell all affected personnel of the potential hazards involved with the operation (including normal operating instructions, emergency procedures, etc.)	Determine better means of seeking out and conveying existing hazard information—over 90% of chemical reactivity incidents reviewed by CSB had reactive hazard information that was documented in the literature (CSB 2002b) Develop an understanding of consequences of the various chemical reactivity incident types Develop an information repository of past experience and lessons learned, such as a chemical reactivity incident database Develop training delivery methods specific to communicating an understanding of chemical reactivity hazards associated with operations
Tell all affected personnel what to do to avoid chemical reactivity hazards, recognize when an uncontrolled chemical reaction is taking place, and respond properly if an uncontrolled reaction occurs	Determine hiring qualifications or training requirements for understanding of chemical reactivity hazards at facilities where such hazards must be controlled, appropriate to the nature of the hazards Employ plant simulators for better operator training in learning how to detect, diagnose and respond to abnormal situations
Tell customers, suppliers, trade and technical associations of any relevant information regarding the chemical reactivity hazards posed by raw materials, intermediates and products	Provide information on-line, with user databases, for more rapid and comprehensive alerting Initiate short courses and other means of disseminating expertise in reactivity hazard identification, reduction and control Develop and implement examples, self-assessment checklists and simplified tools Develop and implement effective means of communicating this information for use by small and medium enterprises
Tell emergency responders and other potentially affected persons what to expect, and how to respond to a chemical reactivity incident if one occurs at your facility	Employ improved data logging and recall capabilities with new instrumentation

Glossary

Presented here is a glossary of terms related to the subject of this Concept Book. Several glossary entries are not used elsewhere in this publication. They have been included in case the user comes across an unfamiliar term in the course of managing chemical reactivity hazards. The Sources in the last column are all included in the reference list in the Reference section of this publication. Words in square brackets have been added to referenced definition.

Term	Definition	Source
Accelerating rate calorimetry (ARC)	A technique in which a substance is heated in stages until very slow decomposition [or other reaction] is detected. The substance is then held under adiabatic conditions and the course of the decomposition [or other reaction] is monitored. (Also the name of a commercial test apparatus.)	Barton and Rogers 1997
Activation energy	The constant *E* in the exponential part of the Arrhenius equation, associated with the minimum energy difference between the reactants and an activated complex (transition state), which has a structure intermediate to those of the reactants and the products, or with the minimum collision energy between molecules that is required to enable a reaction to occur. It is a constant that defines the effect of temperature on reaction rate.	CCPS 1995a, Barton and Rogers 1997
Adiabatic	No heat transfer occurs to or from the environment surrounding the sample, including the sample container.	HSE 2000
Adiabatic decomposition temperature rise	An estimation of the computed temperature which a specimen would attain if all of the enthalpy (heat) of decomposition reaction were to be absorbed by the sample itself. High values represent high hazard potential.	ASTM E 1445

Term	Definition	Source
Arrhenius equation	$k = Z\, e^{-E/RT}$ where k is the specific reaction rate constant in reciprocal minutes for first order, Z is the pre-exponential factor in reciprocal minutes, E is the Arrhenius activation energy in J/mol, R is the gas constant, 8.32 J/mol K, and T is the temperature in kelvin.	ASTM E 1445
Autocatalysis	The increase of the rate of reaction due to the catalyzing effect of the reaction products.	HSE 2000
Autodecomposition	The sustained decomposition of a substance without introduction of any other apparent ignition source besides thermal energy and without air or other oxidants present. Autodecomposition is the result of a thermal self-decomposition reaction for given initial conditions (temperature, pressure, volume) at which the rate of heat evolution exceeds the rate of heat loss from the reacting system, thus resulting in an increasing reaction temperature and reaction rate.	CCPS 1995b
Autodecomposition temperature	The minimum temperature for a specified test method, test apparatus (including material of construction and test volume) and initial pressure required to initiate self-sustained decomposition of a solid, liquid or gaseous substance without any other apparent source of ignition and without air or other oxidants present.	CCPS 1995b
Autoxidation	Also *autooxidation* or *auto-oxidation.* A slow, easily initiated, self-catalyzed reaction, generally by a free-radical mechanism, between a substance and atmospheric oxygen. Initiators of autoxidation include heat, light, catalysts such as metals, and free-radical generators. Davies (1961) defines autoxidation as interaction of a substance with molecular oxygen below 120°C without flame. Possible consequences of autoxidation include pressure buildup by gas evolution, autoignition by heat generation with inadequate heat dissipation, and the formation of peroxides.	CCPS 1995b
Catalyst	A chemical substance that accelerates the rate of a chemical reaction by lowering the energy of activation required for the chemical reaction to occur.	CCPS 1998a
Chemical	Any element, chemical compound or mixture of elements and/or compounds.	OSHA 1994
Chemical reactivity	The tendency of substances to undergo chemical change.	NOAA 2002
Chemical reactivity hazard	A situation with the potential for an uncontrolled chemical reaction that can result directly or indirectly in serious harm to people, property or the environment. The uncontrolled chemical reaction might be accompanied by a temperature increase, pressure increase, gas evolution or other form of energy release.	

Term	Definition	Source
Compatibility	The ability of materials to exist in contact without specified (usually hazardous) consequences under a defined scenario.	ASTM E 1445
Cool-flame ignition	A relatively slow, self-sustaining, barely luminous gas-phase reaction of the sample or its decomposition products with an oxidant. Cool flames are visible only in a darkened area.	NFPA 325 2001
Critical half thickness	An estimation of the half thickness of a sample in an *unstirred container,* in which the heat losses to the environment are less than the retained heat. This buildup of internal temperature leads to a thermal-runaway reaction.	ASTM E 1445
Decomposition	To undergo chemical breakdown, separating into constituent parts or elements or into simpler compounds.	NFPA 49 2001
Decomposition energy	The maximum amount of energy which can be released upon decomposition. The product of decomposition energy and total mass is an important parameter for determining the effects of a sudden energy release—for example, in an explosion. The decomposition energy can occasionally be obtained from the literature or calculated theoretically.	Barton and Rogers 1997
Decomposition temperature	See *autodecomposition temperature.*	
Deflagration	A release of energy caused by the propagation of a chemical reaction in which the reaction front advances into the unreacted substance at less than sonic velocity in the unreacted material. Where a blast wave is produced with the potential to cause damage, the term *explosive deflagration* may be used.	CCPS 1995b
Detonation	A release of energy caused by the propagation of a chemical reaction in which the reaction front advances into the unreacted substance at greater than sonic velocity in the unreacted material.	CCPS 1995b
Differential scanning calorimetry (DSC)	A technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature, while the substance and the reference material are subjected to a controlled temperature program.	ASTM E 1445
Differential thermal analysis (DTA)	A technique in which the temperature difference between a substance and reference material is measured as a function of temperature while the substance and the reference material are subjected to a controlled temperature program.	ASTM E 1445

Term	Definition	Source
Disproportionation	A chemical reaction in which a single compound serves as both oxidizing and reducing agent and is thereby converted into a more oxidized and a more reduced derivative; e.g., a hypochlorite upon appropriate heating yields a chlorate and a chloride.	CCPS 1995b
Endothermic	A physical or chemical change that requires or is accompanied by the absorption of heat.	CCPS 1998a
Exothermic	A process or chemical reaction that is accompanied by release of heat.	NFPA 49 2001
Explosion	A release of energy sufficient to cause a pressure wave; a rapid or sudden release of energy that causes a pressure discontinuity or blast wave.	HSE 2000; CCPS 1999a
Explosive	A chemical that causes a sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden shock, pressure, or high temperature.	OSHA 1994
Extrinsic factor	As used in this publication, a factor that is not an intrinsic property of a material being handled (see *intrinsic property*).	
Hazard	A chemical or physical condition that has the potential for causing damage to people, property or the environment.	CCPS 1999b
Hazardous chemical	Any chemical which is a physical hazard or a health hazard.	OSHA 1994
Hazardous material	In a broad sense, any substance or mixture of substances having properties capable of producing adverse effects on health, safety or the environment. These dangers may arise from but are not limited to [flammability, explosibility,] toxicity, reactivity, instability or corrosivity.	CCPS 1999a
Health hazard	A chemical for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees.	OSHA 1994
Heat of reaction	The total quantity of thermal energy liberated or absorbed during a chemical reaction.	HSE 2000
Hot-flame ignition	A rapid, self-sustaining, sometimes audible gas-phase reaction of the sample or its decomposition products with an oxidant. A readily visible yellow or blue flame usually accompanies the reaction.	NFPA 325 2001
Hydration	The incorporation of molecular water into a complex molecule with the molecules or units of another species. The complex may be held together by relatively weak forces or may exist as a definite compound.	Parker 1997

Term	Definition	Source
Hypergolic	Hypergolic behavior is characterized by immediate, spontaneous ignition of an oxidation reaction upon mixing of two or more substances.	CCPS 1995b
Incompatible	The term can refer to any undesired results occurring when substances are combined. In the context of this publication, it refers to incompatible substances giving an undesired chemical reaction when combined, posing a chemical reactivity hazard under a defined scenario.	
Inhibitor	A chemical substance used to prevent or stop a chemical reaction, such as polymerization, from occurring.	CCPS 1998a
Instability	The degree of intrinsic susceptibility of a material to release energy through self-reaction (polymerizing, decomposing or rearranging).	
Intentional chemistry	Processing of substances such that a chemical reaction is intended to take place.	
Intrinsic property	In relation to materials, a property of the material itself, regardless of use or environmental conditions.	
Isomerization	The conversion of a chemical with a given molecular formula to another compound with the same molecular formula but a different molecular structure, such as from a straight-chain to a branched-chain hydrocarbon or an alicyclic to an aromatic hydrocarbon. Examples include the isomerization of ethylene oxide to acetaldehyde (both C_2H_4O) and butane to isobutane (both C_4H_{10}).	CCPS 1995b
Isoperibolic system	A system in which the controlling external temperature is kept constant.	CCPS 1995a
Isothermal	A system condition in which the temperature remains constant.	HSE 2000
Minimum ignition energy (MIE)	Electrical energy discharged from a capacitor, which is just sufficient to effect ignition of the most ignitable mixture of a given fuel-mixture under specific test conditions.	ASTM E 1445
Monomer	A simple molecule that is capable of combining with a number of other molecules to form a polymer.	NFPA 49 2001
Near miss	An unplanned sequence of events that could have caused harm or loss if conditions were different or were allowed to progress, but actually did not.	CCPS 1989
Onset temperature	The temperature at which a deflection from the established baseline is first observed.	ASTM E 1445
Organic peroxide	An organic compound that contains the bivalent –O–O– structure and which may be considered to be a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms has been replaced by an organic radical.	OSHA 1994

Term	Definition	Source
Oxidation	Depending on the context, oxidation can either refer to (a) a reaction in which oxygen combines chemically with another substance or (b) any reaction in which electrons are transferred. For the latter definition, *oxidation* and *reduction* always occur simultaneously (redox reactions), and the substance that gains electrons is termed the *oxidizing agent.* Electrons might also be displaced within a molecule without being completely transferred away from it.	CCPS 1995b
Oxidizer	Any material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials. More generally, an oxidizer is any oxidizing agent.	NFPA 430 2000
Oxidizing agent	See definition for *oxidation.*	
Partial oxidation	The combination of oxygen with a material in an oxygen-deficient atmosphere that generally results in carbon monoxide being one of the combustion products.	CCPS 1995b
Peroxide	A chemical compound that contains the peroxy (–O–O–) group, which may be considered a derivative of hydrogen peroxide (HOOH).	CCPS 1995b
Peroxide former	A material that reacts with oxygen or hydrogen peroxide to produce a peroxide of the reactant.	CCPS 1995b
Physical hazard	A chemical for which there is scientifically valid evidence that it is a combustible liquid, a compressed gas, explosive, flammable, an organic peroxide, an oxidizer, pyrophoric, unstable (reactive) or water-reactive.	OSHA 1994
Polymer	Substance made of giant molecules formed by the union of simple molecules (monomers); for example, polymerization of ethylene forms a polyethylene chain, or condensation of phenol and formaldehyde (with production of water) forms phenol-formaldehyde resins.	Parker 1997
Polymerization	A chemical reaction generally associated with the production of plastic substances. The individual molecules of the chemical (liquid or gas) react with each other to produce what can be described as a long chain.	DOT 2000
Pyrophoric	A chemical that will ignite spontaneously in air at a temperature of 130°F (54.4°C) or below. [Note that definitions of *pyrophoric* from other sources may specify a time frame, usually seconds or minutes, within which ignition must be observed.]	OSHA 1994
Quenching	Abruptly stopping a reaction by severe cooling or by catalyst inactivation in a very short time period; used to stop continuing reactions in a process thus preventing further decomposition or runaway.	CCPS 1995a

Term	Definition	Source
Reaction	Any transformation of material accompanied by a change of enthalpy which may be endothermic or exothermic.	ASTM E 1445
Reaction induction time (RIT) value	The time a chemical compound or mixture may be held under isothermal conditions until it exhibits a specific exothermic reaction.	ASTM E 1445
Reactive chemical	A substance that can pose a chemical reactivity hazard by readily oxidizing in air without an ignition source (spontaneously combustible or peroxide forming), initiating or promoting combustion in other materials (oxidizer), reacting with water, or self-reacting (polymerizing, decomposing or rearranging). Initiation of the reaction can be spontaneous, by energy input such as thermal or mechanical energy, or by catalytic action increasing the reaction rate.	
Reactive groups	Categories of chemicals that react in similar ways, often because they are similar in their chemical structure.	NOAA 2002
Reactivity, chemical	See *chemical reactivity.*	
Rearrangement	Disproportionation, isomerization or tautomerization.	
Runaway reaction	A reaction that is out of control because the rate of heat generation by an exothermic chemical reaction exceeds the rate of cooling available.	HSE 2000
Scenario	[In the context of identifying incompatibilities:] A detailed physical description of the process whereby a potential inadvertent combination of materials may occur.	ASTM E 1445
Self-accelerating decomposition temperature (SADT)	Certain compounds, such as organic peroxides, when held at moderate ambient temperatures for an extended period of time, may undergo an exothermic reaction that accelerates with increase in temperature. If the heat liberated by this reaction is not lost to the environment, the bulk material increases in temperature, which leads to an increase in the rate of decomposition. Unchecked, the temperature grows exponentially to a point at which the decomposition cannot be stopped or slowed. The minimum temperature at which this exponential growth occurs in a material packed in its largest standard shipping container is defined as the self-accelerating decomposition temperature. Self-accelerating decomposition temperature is a measure of the ease in which decomposition occurs under normal storage conditions. It is not an indicator of the violence of any decomposition reaction under conditions of fire exposure or contact with incompatible materials.	NFPA 49 2001

Term	Definition	Source
Self-reactive	Capable of polymerization, decomposition or rearrangement. Initiation of the reaction can be spontaneous, by energy input such as thermal or mechanical energy, or by catalytic action increasing the reaction rate.	
Shock sensitive	A relatively unstable material, the energetic decomposition of which can be initiated by merely the input of mechanical energy at normal ambient conditions. Materials are considered as shock sensitive if they are more easily initiated than dinitrobenzene in a standard drop-weight test.	CCPS 1995b
Spontaneously combustible	Capable of igniting and burning in air without the presence of an ignition source. *Pyrophoric* materials are spontaneously combustible, although some pyrophorics require the presence of a minimum amount of moisture (humidity) to spontaneously ignite. Other spontaneously combustible substances and mixtures may require more time or an insulating environment to self-heat to the point of ignition.	
Stable materials	Those materials that normally have the capacity to resist changes in their chemical composition, despite exposure to air, water, and heat as encountered in fire emergencies.	NFPA 704 2001
Tautomerizing	Converting from one isomer into another in organic compounds that differ from one another in the position of a hydrogen atom and a double bond.	CCPS 1995b
Temperature of no return	The temperature at which the rate of heat generation of a reaction or decomposition is equal to the maximum rate of cooling available.	Barton and Rogers 1997
Thermally unstable	A material that will undergo an exothermic, self-sustaining or accelerating self-reaction (decomposition, polymerization or rearrangement) when heated to a specific temperature for given conditions of pressure, volume, composition and containment. Thus, the self-reaction can be initiated by thermal energy alone.	CCPS 1995b
Time to thermal runaway	An estimation of the time required for an exothermic reaction, in an adiabatic container, (that is, no heat gain or loss to the environment), to reach the point of thermal runaway.	ASTM E 1445
Toll manufacturer	Contract manufacturer (external manufacturer).	
Unstable material	A material that, in the pure state or as commercially produced, will vigorously polymerize, decompose or condense, become self-reactive, or otherwise undergo a violent chemical change under conditions of shock, pressure, or temperature.	NFPA 704 2001

Term	Definition	Source
Water reactive	A material that will react upon contact with water under normal ambient conditions. Includes materials that react violently with water and other materials that react slower but can generate heat or gases that can result in elevated pressure if contained.	CCPS 1995b

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Further Reading and Other Resources

An extensive list of articles and references related to chemical reactivity is included on the CD-ROM.

CCPS 1995b (referenced above) includes, as its Appendix A, an annotated bibliography of chemical reactivity hazards literature sources, grouped as:

- Procedures for Hazard Evaluation and Testing
- Accident and Loss Prevention

- Data Sources and Compilations
- Material Safety Data Sheets
- Computerized On-line Databases
- Educational and Training Materials.

Case Histories

A-1

Part of learning everything possible from previous incidents (so as not to repeat them!) is to study case histories that have been made available. For chemical reactivity incidents, many case histories have been published by the sources listed below. Also given in this appendix are extended abstracts of several recent incidents that are particularly instructive.

Barton and Rogers, *Chemical Reaction Hazards: A Guide to Safety*

Barton and Rogers (1997) gives a compilation of 100 brief case histories related to chemical reactivity incidents. These incidents are grouped according to the following summary causes:

- Inadequate understanding of the process chemistry and thermochemistry
- Inadequate plant design
- Inadequate plant safety and control systems
- Inadequate operating procedures and instructions.

The positive side of each summary cause (*adequate understanding of the process chemistry and thermochemistry,* etc.) is an important aspect of chemical reactivity safety, particularly in facilities where intentional chemistry is practiced.

Lees, *Loss Prevention in the Process Industries*

Lees (1996) gives detailed descriptions and analysis of many process incidents that have had catastrophic consequences, dating back to the early

1900s. Separate appendices are devoted to the 1976 dioxin release near Seveso, Italy and the 1984 methyl isocyanate release in Bhopal, India. The following description is given by Lees of the 1992 Hickson and Welch Ltd. fire at Castleford.

Hickson and Welch, Castleford, UK: Runaway Reaction and Jet Fire

> At about 1:20 p.m. on Monday, 21 September, 1992 a jet flame erupted from a manway on the side of a batch still on the Meissner plant at Hickson and Welch Ltd. at Castleford. The flame cut through the plant control/office building, killing two men instantly. Three other employees in these offices suffered severe burns from which two later died. The flame also impinged on a much larger four-story office block, shattering windows and setting rooms on fire. The 63 people in this block managed to escape, except for one who was overcome by smoke in a toilet; she was rescued but later died from the effects of smoke inhalation.
>
> The flame came from a process vessel, the "60 still base," used for the batch distillation of organics, which was being raked out to remove semi-solid residues, or sludge. Prior to this, heat had been applied to the residue for three hours through an internal steam coil. The UK Health and Safety Executive (HSE) investigation concluded that this had started self-heating of the residue and that the resultant runaway reaction led to ignition of evolved vapors and to the jet flame.
>
> The 60 still base was a 45.5 m^3 horizontal, cylindrical, mild steel tank 7.9 m long and 2.7 m diameter. The still was used to separate a mixture of the isomers of mononitrotoluene (MNT), two of which (*o*-nitrotoluene and *m*-nitrotoluene) are liquids at room temperature and third (*p*-nitrotoluene) a solid. Other byproducts were also present, principally dinitrotoluene and nitrocresols. It is well known in the industry that these nitro compounds can be explosive in the presence of strong alkali or strong acid, but in addition explosions can be triggered if they are heated to high temperatures or held at moderate temperatures for a long period.
>
> The still base had not been opened for cleaning since it was installed in 1961. Following a process change in 1988, a build-up of sludge was noticed. The general consensus was that it was about 1820 liters, equivalent to a depth of about 10 cm, though readings had been reported of 29 cm and, the day before the incident, of 34 cm. One explanation of this high level was that on September 10 the still base had been used as a 'vacuum cleaner' to suck out sludge left in the "whizzer oil" storage tanks 162 and 163. This resulted in the transfer of some 3640 liters of a jelly-like material. The intent had been to pump this material to the 193 storage but transfer was slow and was not completed because the material was thick. The batch still was used for further distillation operations, which were completed on September 19. The still base was then allowed to cool and on September 20 the remaining liquid was pumped to the 193 storage.

On September 17, the shift and area managers discussed cleaning out the still base. The former had been told by workers that the still had never been cleaned out and he realized that the sludge covered the bottom steam heater battery. It was agreed to undertake a clean-out. The area manager gave instructions that preparations should be made over the weekend, but when he arrived on the Monday morning nothing had been done. He was concerned about the downtime, but was assured that this could be minimized and gave instructions to proceed.

At 9:45 a.m. the area manager gave instructions to apply steam to the bottom battery to soften the sludge. Advice was given that the temperature in the still base should not be allowed to exceed 90°C. This was based solely on the fact that 90°C is below the flash point of MNT isomers. However, the temperature probe in the still was not immersed in the liquid but in fact recorded the temperature just inside the manway. Further, the steam regulator which let down the steam pressure from 400 psig (27.6 bar) in the steam main to 100 psig (6.9 bar) in the batteries was defective. Operators compensated for this by using the main isolation valve to control the steam. This valve was opened until steam was seen whispering from the pressure relief valve on the battery steam supply line. This relief valve was set at 100 psig but was actually operating at 135 psig (9 bar), at which pressure the temperature of the steam in the battery tubes would be about 180°C.

The clean-out operation, which had not been done in the previous 30 years, was not subjected to a hazard assessment to devise a safe system of work, and there were defects in the planning of and permit-to-work system of the operation. The task was largely handled locally with minimal reference to senior management and with lack of formal procedures, although such procedures existed for cleaning other still bases on the site. The permits were issued by a team leader who had not worked on the Meissner plant for 10 years prior to his appointment on September 7. At 10:15 a.m., he made out a permit for a fitter to remove the manlid. The fitter signed on about 11:10 a.m. and shortly after went to lunch. Operatives who were standing by offered to remove the manlid and the same team leader made out a permit for them to do so. When the fitter returned from lunch, it was realized that the still base inlet had not been isolated and a further permit was issued for this to be done.

Meanwhile, the manlid had been removed. The area manager asked for a sample to be taken. This was done using an improvised scoop. He was told the material was gritty with the consistency of butter. He did not check himself and mistakenly assumed the material was thermally stable tar. No instructions were given for analysis of the residue or the vapour above it. Raking out began, using a metal rake that had been found on the ground nearby. The near part of the still base was raked. The rake did not reach to the back of the still and there was a delay while an extension was procured. The employees left to get on with other work and it was at this point that the jet flame erupted.

The HSE report states that analysis of damage at the Meissner control building at 13.4 m from the manway source indicated that at this building the jet flame was 4.7 m diameter. The jet lasted some 25 seconds and had a surface emissive power of about 1000 kW/m^2. The temperature at 6 m from the manway would have been about 2300°C.

The company employed some highly qualified staff with considerable expertise in the manufacture of organic nitro compounds. The HSE report describes some of the investigations of thermal stability, safety margins, etc., in which these staff were involved. It also comments in relation to the incident in question, "Regrettably this level of understanding was not reflected in the decision which was made on 21 September when it was decided that the 60 still base would be raked out."

As soon as the personnel at the gate office saw the flame, one of them made a "999" emergency call. The employee requested the ambulance and fire services, but spoke only to the former before the call was terminated at the exchange. Thereafter incoming calls prevented further outgoing calls for assistance.

Just over a year before the incident, the management structure had been reorganized. This involved replacing a hierarchical structure with a matrix management system, eliminating the role of plant manager and instituting a system in which production was coordinated through senior operatives acting as team leaders. The area managers had a significant workload. In addition to their production duties they had taken over responsibility for the maintenance function, which had previously been under the works engineering department. Managers were not meeting targets for planned inspections under the safety programme, and this was said to be due to lack of time.

U.S. Environmental Protection Agency

Occasionally, the U.S. EPA issues a process safety alert or study that is related to chemical reactivity hazards. The following incident summaries are from a Case Study on phenol-formaldehyde reaction hazards (EPA 1999a) and from an Alert urging the use of multiple data sources when developing emergency response strategies (EPA 1999b).

Georgia-Pacific Resins, Columbus, Ohio: Runaway Reaction and Explosion

Approximately 10:42 a.m. on Wednesday, Sept. 10, 1997, an explosion occurred in a resins production unit at Georgia-Pacific Resins, Inc. in Columbus, Ohio. The blast was reported to be felt at least 2 miles and possibly as far as 7 miles away according to various news accounts and other reports. As a result of the explosion, one worker was killed and four others injured. The explosion extensively damaged the plant. Local news reported that a vocational school and several homes and businesses within a ¾-mile radius were evacuated as a precaution by the local fire department for several hours. The explosion also resulted in the release of a large quantity of liquid resin and smaller quantities of other chemicals within the facility. Three fire fighters were injured during the response, treated for first-degree chemical burns, and released.

Georgia-Pacific was manufacturing a phenolic resin in an 8000 gal batch reactor when the incident occurred. An operator charged raw materials and catalyst to the reactor and turned on steam to heat the contents. A high temperature alarm sounded and the operator turned off the steam. Shortly after, there was a large, highly energetic explosion that separated the top of the reactor from the shell. The top landed 400 ft away. The shell of the reactor split and unrolled, and impacted against other vessels. A nearby holding tank was destroyed and another reactor was partially damaged.

The investigation revealed that the reactor explosion was caused by excessive pressure generated by a runaway reaction. The runaway was triggered when, contrary to standard operating procedures, all the raw materials and catalyst were charged to the reactor at once followed by the addition of heat. Under the runaway conditions, heat generated exceeded the cooling capacity of the system and the pressure generated could not be vented through the emergency relief system, causing the reactor to explode.

Arkansas Warehouse: Azinphos Methyl Explosion

In May 1997, a massive explosion and fire occurred at an agricultural chemical facility in eastern Arkansas. Prior to the explosion, employees observed smoke in a back warehouse and evacuated. The facility called local responders and asked for help to control smoldering inside a supersack of azinphos methyl, a pesticide. The local fire department rapidly responded and reviewed the MSDS of the smoldering product. The MSDS lacked information on decomposition temperatures or explosion hazards. The firefighters decided to investigate the building. While they were approaching, a violent explosion occurred. Fragments from a collapsing cinder block wall killed three fire fighters and seriously injured a fourth.

Napp Technologies, Lodi, New Jersey: Explosion and Fire

In April 1995, an explosion and fire at a manufacturing facility in Lodi, New Jersey caused the death of five responders. The explosion occurred while the company was blending aluminum powder, sodium hydrosulfite, and other ingredients.

Although the material was water reactive, the MSDS for the product advised the use of a "water spray . . . to extinguish fire." The recommendation in the MSDS for "small fires" was to flood with water. However, "small fire" was not defined, the amount of water necessary was not specified, and no information dealt with how to respond to large fires (which can occur during blending processes).

The MSDS only described the hazards associated with the blended product. Incident responders needed information on the chemical reactivity hazards during the blending process, which were significantly different in this case from the hazards associated with the finished product.

U.S. Chemical Safety Board

The U.S. Chemical Safety and Hazard Investigation Board (CSB) has conducted detailed investigations into a few chemical reactivity incidents. Case studies and full investigation reports are available from the CSB (Washington, DC) or its website (www.chemsafety.gov). Extracts from three CSB publications (1998, 2002a, 2002c) are given here.

Morton International, Paterson, New Jersey: Runaway Reaction, Explosion, and Fire

On Wednesday, April 8, 1998, at 8:18 p.m., an explosion and fire occurred during the production of Automate Yellow 96 Dye at the Morton International, Inc. (now Rohm & Haas) Plant in Paterson, New Jersey. The explosion and fire were the consequence of a runaway reaction, which overpressurized a 2000 gal reactor vessel and released flammable material that ignited.

Yellow 96 Dye was produced by the mixing and reaction of two chemicals, *ortho*-nitrochlorobenzene (*o*-NCB) and 2-ethylhexylamine (2-EHA). The dye was used to tint petroleum fuel products.

The investigation team determined that the reaction accelerated beyond the heat-removal capability of the kettle. The resulting high temperature led to a secondary runaway decomposition reaction, causing an explosion that blew the hatch off the kettle and allowed the release of the kettle contents. The initial runaway reaction was most likely caused by a combination of the following factors: (1) the reaction was started at a temperature higher than normal, (2) the steam used to initiate the reaction was left on for too long, and (3) the use of cooling water to control the reaction rate was not initiated soon enough.

The explosion ejected flammable vapors from the kettle into the second floor of the production building. The explosion and flash fires inside the building injured nine workers. The flashing eruption of chemicals broke through the building roof, ignited and formed a large fireball above the building, and spattered the adjacent neighborhood with a yellow-brown mixture of compounds that included Yellow 96 Dye and *o*-NCB. Workers' injuries included burns, contusions, and twisted joints. Two employees were badly burned and required extended hospitalization. All of the employees were able, some with assistance, to escape the site of the explosion.

Neither *o*-NCB nor 2-EHA, individually, demonstrates exothermic activity at the normal Yellow 96 process temperatures. Morton's initial research and development for the Yellow 96 process identified the existence and described the two exothermic chemical reactions that can occur when the chemicals used to produce Yellow 96 are mixed and heated. The desired exothermic reaction to form Yellow 96 is initiated at an onset temperature of 38°C (100°F) and begins to proceed rapidly at a temperature of approximately 75°C (167°F). The undesired, exothermic reaction that results from the thermal decomposition of the Yellow 96 product is initiated at an onset temperature 195°C (383°F).

The Paterson facility was not aware of the decomposition reaction. The Process Safety Information (PSI) package, which was used at the Paterson plant to design the Yellow 96 production process in 1990, served as the basis for a Process Hazard Analysis (PHA) conducted in 1995. The PSI noted the desired exothermic reaction but did not include information on the decomposition reaction.

Concept Sciences, Allentown, Pennsylvania: Hydroxylamine Explosive Decomposition

At 8:14 p.m. on February 19, 1999, a process vessel containing several hundred pounds of hydroxylamine exploded at the Concept Sciences, Inc. (CSI), production facility near Allentown, Pennsylvania, USA. Employees were distilling an aqueous solution of hydroxylamine and potassium sulfate, the first commercial batch to be processed at CSI's new facility. After the distillation process was shut down, the hydroxylamine in the process tank and associated piping explosively decomposed, most likely due to high concentration and temperature.

Four CSI employees and a manager of an adjacent business were killed. Two CSI employees survived the blast with moderate-to-serious injuries. Four people in nearby buildings were injured. Six firefighters and two security guards suffered minor injuries during emergency response efforts. The production facility was extensively damaged. The explosion also caused significant damage to other buildings in the Lehigh Valley Industrial Park and shattered windows in several nearby homes.

Hydroxylamine is an oxygenated derivative of ammonia, represented by the chemical formula NH_2OH. Hydroxylamine is usually handled as an aqueous solution or as salts. The concentrated free base is susceptible to explosive decomposition.

Only salts of hydroxylamine were available until the 1980s, when Nissin Chemical Company, Ltd., of Japan, commercialized aqueous free-base hydroxylamine by adding a proprietary stabilizer to prevent decomposition. Hydroxylamine is commercially available in solutions up to 50% (all percentages are by weight).

Over the past decade, the semiconductor manufacturing industry has used hydroxylamine solutions in cleaning formulations to strip process residues from integrated circuit devices. Hydroxylamine and its derivatives are also used in the manufacture of nylon, inks, paints, pharmaceuticals, agrochemicals, and photographic developers.

The current market for concentrated hydroxylamine solutions is expanding. If not for the explosion, CSI would have been the first company in the United States to manufacture this product in commercial quantities. Nissin Chemical Company was the sole global supplier of hydroxylamine up to that time. In early 1999, BASF Aktiengesellschaft started up a new production facility in Germany. Fourteen months following the CSI incident, a catastrophic explosion at the Nissin plant in Japan further decreased the availability of hydroxylamine.

CSI began development of its own hydroxylamine production process through laboratory-scale experimentation in 1997. Development continued with the construction of a 10 gal pilot plant, which was operational in early 1998. In July 1998, CSI leased approximately 20,000 square feet in a multiple-tenant building and began to set up the production facility.

Ashland Chemical Company, a division of Ashland Inc., was CSI's primary customer for purified hydroxylamine solutions. Ashland used the hydroxylamine solutions in residue cleaners for the semiconductor industry. Ashland planned to purchase 2 million pounds of 50% hydroxylamine from CSI. In exchange for discounted pricing of future deliveries of hydroxylamine solutions, Ashland provided CSI with financial support ($350,000) to purchase production equipment. By February 1999, CSI had approximately twenty full-time employees, ten of whom were assigned to the new production facility.

On the day of the incident, CSI was producing its first batch of 50% hydroxylamine solution at the new facility. CSI's production process involved the four basic steps of reaction, filtration, distillation, and ion exchange purification.

CSI's distillation process included a 2500 gal charge tank, a vacuum distillation system and two product receivers. The distillation is performed in two phases. The first phase of the process begins as a pump circulates the 30% hydroxylamine from the charge tank to the heating column, a vertical tube-in-shell glass heat exchanger. The hydroxylamine enters the top of the column and is heated by 120°F (49°C) distilled water as it cascades through the tubes back to the charge tank. Vapor from the column is condensed using a chilled water condenser (condenser column). The distillate, initially consisting primarily of water with some hydroxylamine, is directed into the forerun tank.

When the concentration of hydroxylamine reaches 10% in the forerun tank, the distillate is diverted to the final product tank, where it is collected until the concentration of the liquid phase in the charge tank is 80 to 90% hydroxylamine. At this point, the first phase of distillation is complete. The charge tank and column are cleaned using a 30% hydroxylamine solution, and the charge tank is taken out of service.

In the second phase of distillation, the 45% hydroxylamine solution collected in the final product tank is further concentrated by redistillation. It is fed back to the top of the heating column and flows through the tubes, where it is heated by 140°F (60°C) water. The distillate is directed back to the final product tank. Water is removed from the hydroxylamine solution until the material in the final product tank reaches 50% hydroxylamine, at which point the distillation is complete.

CSI began its first distillation to produce 50% hydroxylamine in the new facility on Monday afternoon, February 15, 1999. The charge tank contained approximately 9000 lb of 30% hydroxylamine. About 30 hours of distillation was required to complete the batch under normal conditions.

By Tuesday evening, the concentration of liquid solution in the charge tank was approximately 48%, and the product was being collected in the forerun tank. CSB was unable to determine exactly when the product was diverted from the forerun tank to the final product tank. The process was shut down Tuesday evening for maintenance when it was determined that water had leaked into the charge tank through broken tubes in the heater column. The necessary repairs were made by Thursday afternoon, and the distillation process was restarted. At 11:15 p.m., the concentration of liquid solution in the charge tank was 56%, and the concentration of the material collected was 15%. The distillation continued until approximately 11:30 p.m. that evening.

On Friday, February 19, a 1.5-inch feed line to the heater column was replaced with a 2-inch line, which delayed startup until later in the morning. The concentration of liquid solution in the charge tank at that time was about 57% hydroxylamine. It steadily increased throughout the day. Between 7:00 and 7:15 p.m., the concentration of liquid solution in the charge tank was recorded as 86% hydroxylamine.

From laboratory distillations, CSI management knew that crystals formed with hydroxylamine concentrations greater than 80%. Crystals of hydroxylamine are unstable and potentially explosive.

Management was also aware of the hazards associated with concentrating hydroxylamine. As described in CSI's material safety data sheet (MSDS): "Danger of fire and explosion exists as water is removed or evaporated and hydroxylamine concentration approaches levels in excess of about 70%."

CSI personnel visually monitored the distillation system for the formation of crystals. At approximately 7:45 p.m. Friday, the still was shut down and cleaned with 30% hydroxylamine to wash away crystals that may have formed. The second phase of distillation was never started.

A manufacturing and engineering supervisor was called at his home and arrived at the facility shortly after 8:00 p.m. The explosion occurred at 8:14 p.m. The events during the minutes prior to the explosion could not be conclusively determined.

BP Amoco, Augusta, Georgia: Thermal Decomposition Incident

On March 13, 2001, three people were killed as they opened a process vessel containing hot plastic at what was then the BP Amoco Polymers plant in Augusta, Georgia. They were unaware that the vessel was pressurized. The workers were killed when the partially unbolted cover blew off the vessel, expelling hot plastic. The force of the release caused some nearby tubing to break. Hot fluid from the tubing ignited, resulting in a fire.

The Augusta facility produced plastics, including Amodel, a hard but moldable high-performance nylon. Amodel is manufactured by passing a solution of diamines and dicarboxylic acids through a series of reactors. The reaction is completed in an extruder, and the material is then formed and cooled into solid pellets.

Workers were attempting to open a cover on a process vessel when the incident occurred. The vessel, referred to as the polymer catch tank (KD-502), was designed to receive partially reacted waste Amodel diverted from a chemical reactor during periods of startup and shutdown. Twelve hours prior to the incident, an attempt was made to start the production unit. After approximately one hour, the startup was aborted due to problems with the extruder downstream of the reactor, but not before an unusually large amount of partially reacted material had been sent to the polymer catch tank. Hot molten plastic inside the tank continued to react and also began to slowly decompose, thereby generating gases and causing the contents of the tank to foam. The material expanded as foaming continued, and eventually the entire tank was filled. The material then forced its way into connecting pipes, including the normal and emergency vents. Once in the pipes, the plastic solidified as it cooled, resulting in a hardened layer 3 to 5 inches thick around the entire inner wall of the tank. The core of the plastic mass remained hot and molten, and likely continued to decompose over several hours, generating gases that pressurized the vessel. Before opening the polymer catch tank, personnel may have relied on a pressure gauge and a transmitter on the vent piping from the vessel to ascertain whether it was under pressure. They also knew that the process was shut down. However, any reading from the pressure gauge would likely have been unreliable because plastic had entered the vent line and solidified. On previous occasions, the polymer catch tank contained no pressure when it was opened. Varying amounts of plastic were found inside; sometimes the plastic was hot, but it was always solid. Expecting that to be the case again, the workers proceeded to remove the 44 bolts from the cover. When half of the bolts had been removed, the cover suddenly blew off. Hot plastic spewed throughout the area, traveling as far as 70 ft. The cover and the expelled plastic struck the workers, killing them. The force created by the ejection of gas and plastic propelled the polymer catch tank backward and bent the attached piping. A section of hot oil (370°C) supply tubing for a heating jacket on the inlet line from the reactor knockout pot to the catch tank broke, and the fluid spilled into the area. A flammable vapor cloud formed and ignited within a few minutes. Several hours of fire-fighting efforts were required to extinguish the fire.

Operations and technical support staff at the manufacturing site were unaware that the Amodel could decompose and generate high pressure when held at elevated temperatures for an extended time. Product performance testing conducted by the company's research and development group demonstrated that the plastic was susceptible to thermal decomposition at processing temperatures. However, the manufacturing process was not subjected to a specialized design review to identify hazards from unintended and uncontrolled reactions, and the risks posed by decomposition of the plastic were not recognized.

In earlier years, large lumps of solidifying waste plastic removed from the polymer catch tank had burst, hurtling fragments a considerable distance. Investigations were not thorough enough to determine that the hot, molten material within the lumps was most likely continuing to react and decompose, creating gas and pressure.

On one occasion after the polymer catch tank was opened, the waste plastic inside spontaneously caught fire. This also happened when a companion vessel was opened. On two other occasions, waste plastic removed from these vessels spontaneously caught fire after being placed in a dumpster. Investigations did not identify that the fires were likely related to the formation of volatile and flammable substances from thermal decomposition of the plastic. During inspections, the pressure relief device was found to be fouled with solid plastic, which could have rendered it inoperative. The potential consequences of such fouling were not analyzed, and no adequate measures were developed to prevent recurrence.

An Inherently Safer Process Checklist

A-2

This checklist may be used to stimulate the thinking of inherent safety review and process hazard analysis teams, and any other individuals or groups working on process improvements. It is intended to promote "blue-sky" or "out-of the-box" thinking, and to generate ideas that might be usable in an existing facility or a "plant of the future" concept.

This checklist should not be used in a rote "yes/no" manner, nor is it necessary to answer every question. The idea is to consider what might be possible, and then determine what is feasible. The checklist should be reviewed periodically throughout the life cycle of the process. As technology changes, what was once impossible becomes possible, and what was once infeasible becomes feasible.

Users of this checklist may find it helpful to rephrase questions in order to prompt maximum creativity; for example "how might it be possible to . . .?" This approach can lead users to consider alternative means for reducing the hazard level inherent in the process.

The topics for this checklist have been taken from CCPS (1993b) and Bollinger et al. (1996). Every effort was made to ensure that this checklist is comprehensive; therefore, there may be some redundancy or overlap in questions among the different sections. It should be noted that some of the items in this checklist employ a very broad concept of inherent safety, as presented by Bollinger et al. (1996). As such, they may address inherent aspects of passive, engineered or even administrative controls, rather than the narrower inherent safety conception of reducing the underlying process hazards that must be contained and controlled to safely operate a facility.

1. Intensification/Minimization

1.1. Do the following strategies reduce inventories of hazardous raw materials, intermediates, and/or finished products?

- Improved production scheduling
- Just-in-time deliveries
- Direct coupling of process elements
- Onsite generation and consumption

1.2. Do the following actions minimize in-process inventory?

- Eliminating or reducing the size of in-process storage vessels
- Designing processing equipment handling hazardous materials for the smallest feasible inventory
- Locating process equipment to minimize the length of hazardous material piping runs
- Reducing piping diameters

1.3. Can other types of unit operations or equipment reduce material inventories? For example:

- Wiped film stills in place of continuous still pots
- Centrifugal extractors in place of extraction columns
- Flash dryers in place of tray dryers
- Continuous reactors in place of batch
- Plug flow reactors in place of continuous-flow stirred tank reactors
- Continuous in-line mixers in place of mixing vessels

1.4. Can thermodynamic or kinetic efficiencies of reactors be improved by design upgrades (e.g., improved mixing or heat transfer) to reduce hazardous material volume?

1.5. Can equipment sets be combined (e.g., replacing reactive distillation with a separate reactor and multi-column fractionation train; installing internal reboilers or heat exchangers) to reduce overall system volume?

1.6. Can pipeline inventories be reduced by feeding hazardous materials as a gas instead of a liquid (e.g., chlorine)?

1.7. Can process conditions be changed to avoid handling flammable liquids above their flash points?

1.8. Can process conditions be changed to reduce production of hazardous wastes or by-products?

2. Substitution/Elimination

2.1. Is it possible to eliminate hazardous raw materials, process intermediates, or by-products by using an alternative process or chemistry?

2.2. Is it possible to eliminate in-process solvents by changing chemistry or processing conditions?

2.3. Is it possible to substitute less hazardous raw materials? For example:

- Noncombustible rather than flammable
- Less volatile
- Less reactive
- More stable
- Less toxic

2.4. Is it possible to use utilities with lower hazards (e.g., low-pressure steam instead of combustible heat transfer fluid)?

2.5. Is it possible to substitute less hazardous final product solvents?

2.6. For equipment containing materials that become unstable at elevated temperatures or freeze at low temperatures, is it possible to use heating and cooling media that limit the maximum and minimum temperature attainable?

3. Attenuation/Moderation

3.1. Is it possible to keep the supply pressure of raw materials lower than the design pressure of the vessels to which they are fed?

3.2. Is it possible to make reaction conditions (e.g., pressure or temperature) less severe by using a catalyst or by using a better catalyst?

3.3. Can the process be operated at less severe conditions using any other route? For example:

- Improved thermodynamic or kinetic efficiencies of reactors by design upgrades (e.g., improved mixing or heat transfer) to reduce operating temperatures and/or pressures
- Changes to the order in which raw materials are added
- Changes in phase of the reaction (e.g., liquid/liquid, gas/liquid, or gas/gas)

3.4. Is it possible to dilute hazardous raw materials to reduce the hazard potential? For example, by using the following:

- Aqueous ammonia instead of anhydrous
- Aqueous HCl instead of anhydrous
- Sulfuric acid instead of oleum
- Dilute nitric acid instead of concentrated fuming nitric acid
- Wet benzoyl peroxide instead of dry

4. Limitation of Effects

4.1. Is it possible to design and construct vessels and piping to be strong enough to withstand the largest overpressure that could be generated within the process, even if the "worst credible event" occurs (eliminating the need for complex, high-pressure interlock systems and/or extensive emergency relief systems)?

4.2. Is all equipment designed to totally contain the materials that might be present inside at ambient temperature or the maximum attainable process temperature (i.e., higher maximum allowable working temperature to accommodate loss of cooling, simplifying reliance on the proper functioning of external systems, such as refrigeration systems, to control temperature such that vapor pressure is less than equipment design pressure)?

4.3. Can passive leak-limiting technology (e.g., blowout resistant gaskets and excess flow valves) be utilized to limit potential for loss of containment?

4.4. Can process units be located to reduce or eliminate adverse effects from other adjacent hazardous installations?

4.5. Can process units be located to eliminate or minimize the following?

- Off-site impacts
- On-site impacts on employees and other plant facilities

4.6. For processes handling flammable materials, is it possible to design the facility layout to minimize the number and size of confined areas and to limit the potential for serious overpressures in the event of a loss of containment and subsequent ignition?

4.7. Can the plant be located to minimize the need for transportation of hazardous materials?

4.8. Can materials be transported in the following ways?

- In a less hazardous form
- Via a safer transport method
- Via a safer route

5. Simplification/Error Tolerance

5.1. Is it possible to separate a single, procedurally complex, multipurpose vessel into several simpler processing steps and processing vessels, thereby reducing the potential for hazardous interactions when the complexity of the number of raw materials, utilities, and auxiliary equipment is reduced for specific vessels?

5.2. Can equipment be designed so that it is difficult to create a potentially hazardous situation due to an operating or maintenance error? For example:

- Simplifying displays
- Designing temperature-limited heat transfer equipment
- Lowering corrosion potential by use of resistant materials of construction
- Lowering operating pressure to limit release rates
- Using higher processing temperatures (to eliminate cryogenic effects such as embrittlement failures)
- Using passive vs. active controls (e.g., stronger piping and vessels)
- Using buried or shielded tanks
- Using fail-safe controls if utilities are lost
- Limiting the degree of instrumentation redundancy required
- Using refrigerated storage vs. pressurized storage
- Spreading electrical feed over independent or emergency sources
- Reducing wall area to minimize corrosion/fire exposure
- Reducing the number of connections and paths
- Minimizing the number of flanges in hazardous processes
- Valving/piping/hose designed to prevent connection error

- Using fewer bends in piping
- Increasing wall strength
- Using fewer seams and joints
- Providing extra corrosion/erosion allowance
- Reducing vibration
- Using double-walled pipes, tanks, and other containers
- Minimizing the use of open-ended valves
- Eliminating open-ended, quick-opening valves in hazardous service
- Improving valve seating reliability
- Eliminating unnecessary expansion joints, hoses, and rupture disks
- Eliminating unnecessary sight glasses/glass rotameters

5.3. Can procedures be designed so that it is difficult to create a potentially hazardous situation due to an operating or maintenance error? For example:

- Simplifying procedures
- Reducing excessive reliance on human action to control the process

5.4. Can equipment be eliminated or arranged to simplify material handling?

- Using gravity instead of pumps to transfer liquids
- Siting to minimize hazardous transport or transfer
- Reducing congestion (i.e., easier to access and maintain)
- Reducing knock-on effects from adjacent facilities
- Removing hazardous components early in the process rather than spreading them throughout the process
- Shortening flow paths

5.5. Can reactors be modified to eliminate auxiliary equipment (e.g., by creating a self-regulatory mechanism by using natural convection rather than forced convection for emergency cooling)?

5.6. Can distributed control system (DCS) modules be simplified or reconfigured such that failure of one module does not disable a large number of critical control loops?

This checklist courtesy of Art Burk, E. I. du Pont de Nemours & Co., Inc.

Executive Summary of CSB Investigation Report

A-3

Reproduced in this appendix is the Executive Summary of a hazard investigation report entitled "Improving Reactive Hazard Management" (CSB 2002b). The report, issued by the U.S. Chemical Safety and Hazard Investigation Board (CSB), documents a review of uncontrolled chemical reactivity incidents, U.S. regulations related to chemical reactivity hazards, and related topics. Recommendations were made to governmental, industry and labor organizations. Literature references have been changed to match the Reference list in this publication.

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.

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.

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

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).

OSHA develops and enforces standards to protect employees from workplace hazards. In the aftermath of the reactive incident that caused 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.

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]

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[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. The incident resulted in an estimated 2000 deaths within a short period (Lees 1996 A5-1).

[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.

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.

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 chemical incidents.
- Examine how industry, OSHA, and EPA currently address reactive chemical 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 chemical incidents.

ES.2. Investigative Process

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, and/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]

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

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 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.
6. As a result of the joint OSHA-EPA chemical accident investigation of the Napp Technologies incident in April 1995, a recommendation was made by EPA and OSHA to consider adding more reactive chemicals to their respective lists of chemicals covered by process safety regulations. To date, neither OSHA nor EPA 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

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[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 materials in themselves are 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.

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) account for over 65 percent of the equipment involved; chemical reaction vessels account for only 25 percent.

Reactive incidents can result in a variety of consequences, including fire and explosions (42 percent of incidents) as well as toxic gas emissions (37 percent).

8. 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.
9. 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.
10. 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]
11. 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]
12. 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.
13. 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

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[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 of CSB (2000b) for a list of selected literature.

[13] National Oceanic and Atmospheric Administration Chemical Reactivity Worksheet (NOAA 2002), American Society for Testing and Materials CHETAH (Balaraju et al. 2002), and *Bretherick's Reactive Chemical Hazards Database* (Urben 1999).

test data, such as thermal stability data—which can be valuable in identifying reactive hazards—are not typically shared.

14. 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.
15. 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, 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.
16. Several voluntary industry initiatives, such as ACC's Responsible Care and NACD's 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.
17. 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 its proposed revisions of the Toxic Catastrophe Prevention Act (TCPA) regulations.

ES.4. Conclusions

1. Reactive incidents are a significant chemical safety problem.

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[14] This CCPS publication, *Essential Practices for Managing Chemical Reactivity Hazards*, may address this gap in industry guidance.

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 Requirements (40 CFR 68) 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 focus 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 performing a process hazard analysis. Given that reactive incidents are often caused by inadequate recognition and evaluation of reactive hazards, improving reactive hazard management involves defining and requiring relevant factors (e.g., rate and quantity of heat and gas generated) to be examined 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.
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.

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

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.

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., ASTM's CHETAH, NOAA's The Chemical Reactivity Worksheet).
     - 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.

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[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.

- 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 identifica-

   tion, 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 Firefighters
Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE)
The United Steelworkers of America
Union of Needletrades, Industrial, and Textile Employees (UNITE)
United Food and Commercial Workers International Union
American Society of Safety Engineers (ASSE)
American Industrial Hygiene Association (AIHA)

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

Contents of CD-ROM

The following can be found on the CD-ROM included with this Concept Book:

- CCPS Safety Alert, "Reactive Material Hazards: What You Need To Know" (CCPS 2001a). Steps through how to identify if you have reactive chemicals or can have reactive interactions, what data and safeguards are needed to control reactivity hazards, and where to get additional information. Can be downloaded from the AIChE website at www.aiche.org/ccps/pdf/reactmat.pdf.
- U.S. National Oceanic and Atmospheric Administration (NOAA) Chemical Reactivity Worksheet, Version 1.5. As described elsewhere in this publication, the Worksheet can be used to identify chemical reactivity hazards and the general consequences of combining incompatible materials. Can be downloaded from the NOAA website at http://response.restoration.noaa.gov/chemaids/react.html.
- Documentation of example chemical reactivity hazard management programs from CCPS sponsor companies that practice intentional chemistry.
- Table 3.1, Example Form to Document Screening of Chemical Reactivity Hazards, with the accompanying flowchart of Figure 3.1, for use with the preliminary screening method of Chapter 3.
- Table 4.1, Gap Analysis: Chemical Reactivity Hazard Management System, and Table 4.2, Basic Chemical Reactivity Data to Collect.
- Bibliography of articles and publications related to chemical reactivity and intentional chemistry processes.
- English translation of "Guide for the Identification and Control of Exothermic Chemical Reactions" (TAA-GS-05 1994), a document in German by the Technischer Ausschuss für Anlagensicherheit (Tech-

nical Committee for Plant Safety) of the Federal Ministry of the Environment, Nature Conservation and Reactor Safety.

- Text of the U.S. Chemical Safety and Hazard Investigation Board report, “Improving Reactive Hazard Management” (CSB 2002b).

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CCPS
CENTER FOR
CHEMICAL PROCESS SAFETY
An AIChE Industry
Technology Alliance

Reactive Material Hazards

What You Need To Know

SAFETY ALERT

Introduction

❶ How Do We Handle Reactive Materials?

❷ Can We Have Reactive Interactions?

❸ What Data Do We Need To Control These Hazards?

❹ What Safeguards Do We Need To Control These Hazards?

Where Can We Get More Help?

October 1, 2001

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

REACTIVE MATERIAL HAZARDS

What You Need To Know

Many facilities have chemically reactive materials and systems without knowing the hazards they pose. Others are aware of the hazards, but have inadequate safeguards. Still others have situations where materials are adequately controlled individually, but the potential for a major incident exists if materials are inadvertently combined. Here are five examples:

- Rainwater leaked into a room where hundreds of drums of dry swimming pool chemicals were stored, causing an explosion. The explosion and resulting fire set off the sprinkler system that soaked the remaining drums. The fire, explosions and chlorine releases lasted three days. Over 25,000 people were evacuated, and 275 people went to the hospital with skin burns and respiratory problems.

- Twenty-three people were sent to the hospital after a chemical release at a resort casino. Two cleaning agents were apparently mixed together in the basement of the building, generating vapors that permeated part of the resort.

- A runaway reaction and reactor explosion occurred in a resins production facility that killed one worker and injured four others. To control the reaction rate, an operating procedure called for the slow addition of one of the raw materials to the reactor. The runaway was triggered when the raw materials and catalysts were improperly charged to the reactor simultaneously, followed by heat addition.

- A massive explosion and fire occurred at an agricultural chemical packaging facility in Arkansas, killing three firefighters and injuring a fourth. The likely cause was a supersack of azinphos-methyl (an insecticide) being placed near a hot compressor exhaust pipe.

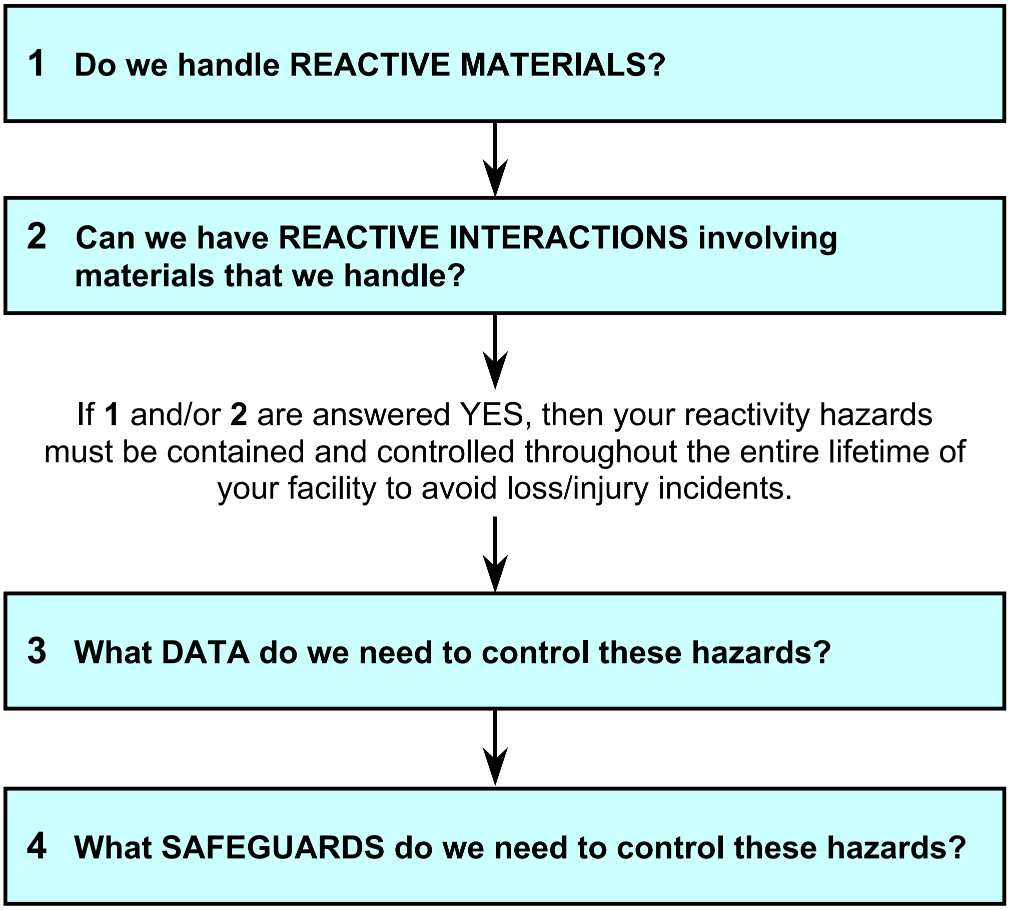
- Five workers were killed when a blender exploded. The blender was used to mix several dry powders, including aluminum powder and sodium hydrosulfite. The likely cause of the explosion was the unintentional introduction of water into the blender, possibly through a leaking water-cooled seal.

This document is intended as an introduction to reactive material issues for people whose main business is ***not*** reactive materials and systems. Further, it does ***not*** replace any of the more extensive guides and references that deal with this topic in detail, or eliminate the need for competent expert analysis in dealing with these issues. The last section of this document lists references and sources of information that readers are strongly encouraged to use.

Reactivity is the tendency of a material or combination of materials to undergo chemical change under the right conditions. Chemical reactivity is a highly desirable trait that permits a wide variety of useful materials to be synthesized. It also allows products to be made under relatively moderate conditions of pressure and temperature, saving energy and reducing the physical risks of high-temperature and/or high-pressure equipment. Even some consumer products such as swimming pool chemicals have reactive properties. On the other hand, it is these properties that make reactive materials so useful that also pose hazards to health and property, and reactions are not limited to intended and controlled situations.

You may find it helpful to identify and control reactivity hazards in two broad categories: ***reactive materials*** and ***reactive interactions.*** ***Reactive materials*** are commonly regarded as those materials that can be hazardous by themselves when caused to react by heat, pressure, shock, friction, a catalyst, or by contact with air or water. ***Reactive interactions*** require the combining of two or more materials to pose a hazardous situation by chemical reaction.

So, what *do* you need to know about reactive materials and interactions? The following diagram will guide you through the four key questions that you must be able to answer. The best time to consider these questions is when designing a new operation or facility, but they should be answered for existing operations as well, particularly when making changes or bringing in new materials.



These questions are addressed in turn on the following pages.

1 Do We Handle Reactive Materials?

Chemical reactivity has many different names, such as reactive materials, runaway reaction hazards, instability, thermal sensitivity, and incompatibility. Flammability, toxicity, and corrosion are also forms of reactivity. Since these topics are addressed elsewhere, our focus here will be on those reactions that fall outside the normal definitions of flammable or toxic and that generally occur far more rapidly than corrosion.

To decide if we handle reactive materials, we want to identify those materials that can cause a dangerous release, such as of heat, blast energy, toxic vapors, or gases that could rupture a container, when exposed to conditions that may reasonably occur in normal or abnormal situations. This step is sometimes called an *intrinsic* evaluation, as the information we are seeking relates to a property of the material itself.

Material Safety Data Sheets (MSDSs) are a good place to begin identifying reactive materials. You should have an MSDS from your supplier for every hazardous material you have on hand. While formats vary, there should be a section titled “Reactivity Data,” “Stability and Reactivity,” or similar, which outlines the material’s main reactivity hazards. This will not tell you everything you need to know, but it should give you an immediate warning of a major reactivity hazard associated with the material. Other clues may be found in MSDS sections dealing with fire fighting measures or explosion data.

Be aware that MSDSs for the same material but from different sources can vary considerably in what they report as hazards. For this reason, it is wise to consult multiple MSDSs and other sources before concluding that a material is or is not hazardous. In addition to MSDSs, there are many other readily available references that can provide similar information, often in more detail than the MSDS. Several are listed in the “Where Can I Get More Help?” section of this document, under Reactive Materials.

Here are some intrinsic reactivity hazards and their definitions. *Incompatible materials* will be considered in the next section of this document, as reactive interactions.

Reactivity Hazard	General Definition	Examples
UNSTABLE (DECOMPOSING, THERMALLY SENSITIVE, SHOCK SENSITIVE, EXPLOSIVE)	Has the tendency to break down (decompose) over time or when exposed to conditions such as heat, sunlight, shock, friction, or a catalyst with the resulting decomposition products often being toxic or flammable. Decomposition can be rapid enough to give an explosive energy release and can generate enough heat and gases for fires/explosions.	Trinitrotoluene (TNT), dibenzoyl peroxide, ethylene oxide, acetylene, picric acid, hydrogen peroxide (concentrated)
POLYMERIZING	Has the tendency to self-react to form larger molecules, while possibly generating enough heat/gases to burst a container	Acrylic acid, styrene, 1,3-butadiene
PYROPHORIC	Will ignite spontaneously when exposed to air	Phosphorus, silane
PEROXIDE FORMER	Has the tendency to slowly react with oxygen, such as from being exposed to air, to form unstable organic peroxides	1,3-Butadiene, isopropyl ether
WATER REACTIVE	Will react with water or moisture. Some react slowly; others violently. Heat and flammable/toxic gases may be produced.	Sodium, sulfuric acid, acetic anhydride
OXIDIZER	Will give up oxygen easily or readily oxidize other materials.	Chlorine, nitric acid

2 Can We Have Reactive Interactions?

Many materials that are not considered “reactive materials” can nevertheless react dangerously with other, incompatible materials. The other material may be there intentionally (addition of the right material, but in the wrong amount) or by accident (such as contaminants like rust or lubricants). Conditions under which the materials are used (pressure, temperature, humidity, concentration, etc.) can also change the reactive behavior dramatically. For these reasons, identifying reactivity hazards involving the mixing of two or more materials is highly situation-dependent and not readily addressable using a “cookbook” list, or rule-based prescriptive approach. This section presents an *extrinsic* approach to identifying reactive interactions that goes beyond the intrinsic properties of the individual materials that may be associated with your business.

Determining the potential for dangerous interactions is not always easy. Take concentrated sulfuric acid as an example. By itself, it is very stable unless heated to high temperatures. It is non-flammable, and has a fairly low vapor pressure. However, mix it with water, or worse, a caustic solution, and it can rupture a tank in seconds. The key to evaluating the reactive hazard in this example is to first **identify** that both concentrated sulfuric acid and caustic are present. Then, safeguards can be put in place to ensure the two materials do not come into uncontrolled contact.

The first thing to do is determine what you have on site, and then determine which materials are reactive with which other materials. There are some easy-to-use tools that can help in this analysis, and one of the best is called a *compatibility chart*. Other references may call this a *chemical compatibility chart*, a *chemical interactivity chart*, or a *chemical interaction matrix*.

A hypothetical example of such a chart is shown below. All intended chemicals and common contaminants (such as utility streams that might leak in) are listed on both the horizontal and vertical axes. Each box in the chart represents the interaction of the two gridded components. Each half of the chart represents all possible binary (two-component) mixtures. Therefore, only one half of the matrix needs to be filled out to assess possible two-component combinations. This kind of simple analysis does not consider order of mixing (X mixing into Y is treated the same as Y mixing into X), which may be an important consideration such as when handling strong acids.

Example Compatibility Chart for an Acetic Anhydride Handling Facility

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

Note that some of the "reactions" indicated by the chart are combinations where the heat generated by diluting a material may cause pressurization of an enclosure. Note also that more information is needed about the chemical composition of the cleaning solution before its compatibility with the other materials can be determined.

At this point, we are not trying to decide how likely it is for the two materials to come together. We are only identifying what combinations pose a reactivity hazard. The questions addressed in the next two sections of this document will lead you to consider what data are needed to determine the severity of an interaction and whether safeguards are adequate to keep incompatible materials from being combined in an uncontrolled manner.

Completing a compatibility chart often requires persistence and determination. You or someone in your organization may be able to readily answer whether most combinations are reactive or not. A few combinations may take more work. One way to do a quick check on chemical combinations is to use a method such as the **Chemical Reactivity Worksheet**, available free of charge (see the Where Can We Get More Help? section of this document under Reactive Interactions). This program has over 6,000 chemicals in its database, and predicts the results of two-chemical mixtures by reactive group combinations. The Worksheet not only indicates possible hazardous interactions, it also sets up a compatibility chart and indicates potential consequences of the interactions (e.g., "Heat generation by chemical reaction, may cause pressurization").

Some other important considerations at this stage:

- MSDSs and the literature may not provide the information needed, especially if the chemicals being used are not common or are new materials under development. In these situations, specific testing may be needed to provide enough information to accurately fill out the compatibility chart.

- A compatibility chart only considers two-component mixtures. Consider also whether any interactions among three materials are hazardous; e.g., one acting as a catalyst for the reaction of two others.

- Check with your purchasing people to find out what materials are brought on site.

- Do not overlook materials that are produced on site, including chemical intermediates.

- Be careful about ruling out materials on the basis of quantity alone. Mixing liquid waste materials in 55-gallon drums has resulted in numerous incidents. Acetylene in contact with copper can produce shock-sensitive copper acetylides, which can be dangerous in very small quantities.

- Consider materials such as air, water, oil, or foreign objects that could be left inside equipment during cleaning or maintenance operations. Physical processing conditions, such as temperature, pressure, humidity, and oxygen content should also be considered.

- Be sure to consider the possibility of mixing materials in your waste disposal or sewer system.

3 What Data Do We Need to Control These Hazards?

Now that you know where the reactive material and interaction hazards are at your facility, you will need to ensure all of the hazards are contained and controlled on an ongoing basis.

Reactive Materials. You can get most of the data you need to safely handle many reactive materials from material suppliers. Depending on the nature of the material and how you will be storing and using it, the needed data for each reactive material will likely include:

- Materials of construction to use and to avoid
- Common materials and contaminants to avoid (e.g., air, water, rust, oil, acids, caustic)
- Storage configurations, maximum quantities, and minimum/maximum storage temperatures
- Shelf life considerations
- What to do in the event of a leak or spill
- What to do if an unwanted reaction starts
- How to fight a fire involving the material
- Possible toxic/corrosive/flammable products of reaction or decomposition
- Any special considerations (e.g., “light-sensitive” or “forms unstable byproducts over time”)

You should be able to find some of this information on the MSDS, such as how to respond to a spill or fire. In some cases, suppliers have developed technical bulletins that provide very detailed engineering information. You should ask for and use these bulletins if they are available.

If you are producing a unique material, you or an experienced reactive materials testing company will need to do your own material assessments. This may include testing for water reactivity, shock sensitivity, dust explosivity, and thermal stability in actual storage and handling configurations, as well as finding out all of the items in the list above.

Reactive Interactions. Likewise, your material supplier may not be much help for reactive interactions on your compatibility chart. For these combinations, the first thing you need to know is how much heat or gas can be generated. In some cases, this can be as simple as using the heat of mixing published in a technical reference book. In others, it may involve use of special equipment to accurately measure the amount of heat and pressure generated during a complex chemical reaction.

In addition, you will need to know under what conditions a reaction will occur, whether an explosive mixture can result, and whether the reaction products (e.g., off-gases) are hazardous.

A number of sophisticated tools can be of assistance in these areas. Two of the more common tools are the Differential Scanning Calorimeter (DSC) and the Accelerating Rate Calorimeter (ARC). The resulting data can then be used to properly size heat transfer equipment and relief devices, as well as establish safe limits of operation. You may need to get professional assistance to gather the data you require.

A word of warning: be very careful in the use of information from small-scale tests. For example, the maximum storage temperature for a temperature-sensitive material will vary, depending on the storage quantity and configuration. Safe operating limits may also change such as with differing sizes and shapes of mixing vessels.

4 What Safeguards Do We Need to Control These Hazards?

Many materials in common use today have obvious reactivity hazards, for example, explosives, laboratory chemicals, and raw materials to make plastics and other useful products. Yet they are handled safely every day. How? Their hazards have been recognized and controlled so that undesirable events (those which can cause loss and harm) do not happen. Your first source of information for controlling hazards should always be your material supplier.

Inherently Safer. If you can eliminate the use of reactive materials, substitute materials with less reactivity potential, reduce inventories of materials, and/or reduce the severity of operating conditions, then you will be moving in the direction of an inherently safer operation. Be very careful that one hazard is not just substituted for another when making these kinds of changes.

Codes and Standards. Where some reactivity hazards have been handled for many years by companies in similar ways, industry codes and standards have been developed that specify needed safeguards. After your material supplier, these codes and standards should be your next point of reference for controlling hazards. For example, organic peroxides are commonly used as initiators and curing agents. If you handle organic peroxides, NFPA 432 (formerly NFPA 43B), *Code for the Storage of Organic Peroxide Formulations,* gives safe storage and handling considerations.

Reactivity Safeguards. When reactivity hazards are unavoidable, multiple safeguards can be set up as lines of defense. These safeguards can prevent abnormal situations, keep abnormal situations from leading to incidents such as fires and explosions, and reduce the severity of consequences if an incident does occur. To be effective, safeguards, such as those listed below, must be carefully designed, properly installed, and maintained in working order throughout the lifetime of your facility.

- Train all personnel to be aware of reactivity hazards and incompatibilities and to know maximum storage temperatures and quantities
- Design storage and handling equipment with all compatible materials of construction
- Avoid heating coils, space heaters, and all other heat sources for thermally sensitive materials
- Avoid confinement when possible; otherwise, provide adequate emergency relief protection
- Avoid the possibility of pumping a liquid reactive material against a closed or plugged line
- Locate storage areas away from operating areas in secured and monitored locations
- Monitor material and building temperatures where feasible with high temperature alarms
- Clearly label and identify all reactive materials, and what must be avoided (e.g., heat, water)
- Positively segregate and separate incompatible materials using dedicated equipment if possible
- Use dedicated fittings and connections to avoid unloading a material to the wrong storage tank
- Rotate inventories for materials that can degrade or react over time
- Pay close attention to housekeeping and fire prevention around storage and handling areas
- Some operations will need to be contained within special blast-resistant enclosures
- Have an emergency response plan in place and conduct periodic drills

Each of these considerations will not, of course, apply to every material and situation. To look at your operation in a systematic, rigorous way with a knowledgeable group of people, a *process hazard analysis* can be conducted. Books and outside consulting resources are available that can provide guidance and professional assistance when needed.

Where Can We Get More Help?

You may find the following references useful in getting the information you need to identify and control reactivity hazards. References marked with an asterisk (*) can be obtained from the American Institute of Chemical Engineers – Center for Chemical Process Safety, 1-800-AIChemE, www.aiche.org/ccps/products.

Reactive Materials	MSDSs from suppliers and via internet; www.ilpi.com/msds links to many MSDS sites Lewis, _Sax's Dangerous Properties of Industrial Materials,_ ISBN 0471354066 _NFPA 49: Hazardous Chemicals Data,_ www.nfpa.org U.S. Dept. of Transportation. _Emergency Response Guidebook_, http://hazmat.dot.gov
Reactive Interactions	_Bretherick's Handbook of Reactive Chemical Hazards,_ can be searched from www.chemweb.com after free registration _NFPA 491: Guide for Hazardous Chemical Reactions,_ www.nfpa.org U.S. National Oceanic and Atmospheric Administration (NOAA), _Chemical Reactivity Worksheet_, http://response.restoration.noaa.gov/chemaids/react.html American Society for Testing and Materials (ASTM), _Guide E2012-00, Standard Guide for Preparation of Binary Chemical Compatibility Chart_, www.astm.org
Reactivity Data	*_Guidelines for Chemical Reactivity Evaluation and Application to Process Design_ Yoshida, Wada and Foster, _Safety of Reactive Chemicals and Pyrotechnics,_ ISBN 0444886567
Analysis and Safeguards	*Lees, _Loss Prevention in the Process Industries_ ISBN 0750615478 *_Guidelines for Safe Storage and Handling of Reactive Materials_ *_Guidelines for Process Safety in Batch Reaction Systems_ *_Guidelines for Hazard Evaluation Procedures, Second Edition with Worked Examples_
Professional Assistance	_Professional Assistance Directory of Process Safety Consultants_. See the CCPS website at www.aiche.org/ccps/pdad/profdr.asp
Government Agencies	The U.S. Environmental Protection Agency (www.epa.gov/ceppo) shares information on preventing and preparing for chemical emergencies. The U.S. Occupational Safety and Health Administration (_www.osha.gov_) has additional information related to process safety management. The U.S. Chemical Safety and Hazard Investigation Board (www.chemsafety.gov) publishes investigation reports, such as on major incidents and reactive chemical hazards

The Center for Chemical Process Safety was established by the American Institute of Chemical Engineers in 1985 to focus on the engineering and management practices to prevent and mitigate major incidents involving the release of hazardous chemicals and hydrocarbons. CCPS is active worldwide through its comprehensive publishing program, annual technical conference, research, and instructional material for undergraduate engineering education.

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A final word, quoted from The Dow Chemical Company, a leader in the field of reactive chemistry:

"We recognized long ago that virtually any chemical can be reactive if involved in the wrong situation or scenario. We therefore do not limit our hazard assessments to any specific list of chemicals. Some companies limit the scope of their reactive chemicals hazard assessments to scenarios that involve only inadvertent mixing of chemicals. While this type of scenario is an important part of any reactive chemicals program, it is far from all of what needs to be considered in a total reactive chemicals hazard assessment effort. Companies whose work is just chemical handling may find it appropriate to only address inadvertent mixing, but additional dimensions need to be included for companies involved with processing or reacting chemicals. Some additional types of scenarios beyond inadvertent mixing of chemicals that need to be included in a comprehensive Reactive Chemicals program include:

- Reactor loss of control scenarios and lines of defense
- Inadvertent lack of mixing of things like reaction inhibitors in reactors or storage tanks
- Accelerated corrosion and loss of containment due to material incompatibility
- Special scenarios that result in loss of stability of chemicals."

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Lyondell Chemical Co.
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SUBSECTION 3.1
UNIT CHEMICAL LIST

The site should have a complete listing of chemicals used in each unit. The list is to identify process chemicals including:

- Raw Materials
- Intermediates When Stored Even Briefly as an Isolated Material
- Final Products(s)
- By-Product(s)
- Catalysts
- Solvents
- Fuels & Waste Fuels

Incidental materials such as lubricants are not intended to be listed unless that material is specified for process safety reasons.

For each material listed, the maximum intended inventory is to be listed along with the intended use (i.e. raw, intermediate, product, lab, etc.).

ACTIONS NECESSARY TO COMPLETE OR MAINTAIN THIS SUBSECTION

- Develop the chemical list, associated maximum inventory figures, and intended use.
- Add to or update this listing as process materials or storage capacity changes.

SUBSECTION 3.2
MATERIAL SAFETY DATA SHEETS

The site will have the current Material Safety Data Sheet (MSDS) for all chemicals identified in Subsection 3.1 of this file. Vendors or supplies of chemicals are responsible to supply an MSDS upon request.

ACTIONS NECESSARY TO COMPLETE OR MAINTAIN THIS SUBSECTION

- Collect a Material Safety Data Sheet for each material on the unit chemical list (Subsection 3.1).
- When no Material Safety Data Sheet exists, obtain what descriptive chemical information is available and contact your HS&E resource to initiate the production of the necessary MSDS.
- Maintain a current file for all chemicals.

SUBSECTION 3.3
MATERIAL TECHNICAL SHEETS

Material Technical Sheets are to be generated when MSDS information is not sufficient to adequately determine the hazards of a chemical. The site will establish and document a rationale for determining when Material Technical Sheets are needed. It is recommended that potential hazards of the chemicals will be a determining factor in the rationale.

The Material Technical Sheet provides a document to list data specific to the technology of a process chemical and the reference of the source of the data. Sources may include MSDS, vendor literature, standard reference handbooks, or design tests or experiments.

Following this page is a blank material technical sheet used to accumulate technical data on the materials used within the unit. It is not intended that new data be generated for all our chemicals just to fill in the blanks on the sheet. It is intended that data necessary to support the Process Hazard Analysis of this unit, the design, and the operation of the unit be consistent, accurate, and available.

The data to be listed on the Material Technical Sheet needs to be comprehensive enough for an accurate assessment of the fire and explosion characteristics, reactivity hazards, corrosion or erosion effects, and safety, health, and environmental hazards.

ACTIONS NECESSARY TO COMPLETE OR MAINTAIN THIS SUBSECTION

- Develop a rationale for determining when Material Technical Sheets are needed.
- Develop a Material Technical Sheet for chemicals per the developed rationale.
- As new or revised data becomes available, this information should be included on the material technical sheet.
- In preparation of safety files consider the appropriate data which may need to be collected to support the PHA.
- Provide references of the sources of data entered into the Material Technical Sheet. Typical references include vendor literature, technical reference handbooks, and MSDS.

RHODIA INC.

MATERIAL TECHNICAL SHEET	**Global Formula**	
UNIT PRODUCTION:	**Name:** **Structural Formula:** **M.W.**	
PROPERTIES		**REF. or APPEND.**
- State at 20° C	gas, liquid, paste, powder, solid	
- Melting point		
- Boiling point		
- Vapor pressure		
- Critical temperature		
- Critical pressure		
- Specific gravity		
- Vapor density		
SOLUBLE IN		
- Insoluble in		
- Heat of formation		
- Heat of fusion		
- Heat of vaporization		
- Heat of solution		
- Heat of combustion		
- Heat of polymerization		
COMBUSTION		
- Flash point		
- Auto-ignition temp.		
- Flammable limits (air)		
- Flammable limits (operating conditions)		
- Ignition energy		
- KST dust class		
- Resistivity		
- Pyrophoricity		
- % 0_2 min. to maintain combustion		
- Extinguishing agents	water, foam, CO_2, halogens, dry chemical	
- Incompatible extinguishing agents		
CORROSION		
- Recommended materials		
- Prohibited materials		
INCOMPATIBLE WITH		
- Water		
- Heat transfer fluids		
- Metals		
- Plastic materials, others...		

PROPERTIES		**REF. or APPEND.**
STABILITY: HAZARDS - Thermal - Impact - Friction **CATALYSTS FOR:** - Polymerization, decomposition **INHIBITORS OF:** - Polymerization, decomposition	Peroxidation, polymerization, electrostatic charging	
INDUSTRIAL HYGIENE		**REF. or APPEND.**
- Olfactory limits - Toxicity limit value - Toxicity		
ENVIRONMENT		**REF. or APPEND.**
- Absorption - desorption - N-octanol/water coefficient - Henry constant - Biodegradation and/or abiotic degr.: disappearance coef. - Bioaccumulation - Aquatic Ecotox Fish 24 to 96 hours Daphnia 24 to 48 hours - Air/soil/sediment Ecotox		
REGULATIONS		**REF. or APPEND.**
- Classification - Labeling - Occupation diseases - Medical attention - Poisons - Transportation	N. N. N. in chart (special) List: Class - Group - Ident. code	
STORAGE		**REF. or APPEND.**
- Precautions		
DISPOSAL		**REF. or APPEND.**
- Spills - Unusable material		

SUBSECTION 3.4
OTHER CHEMICAL REFERENCES

Often additional information pertaining to specific unit chemicals is available and useful. Such information might consist of (for example):

- P_4 Handling Manual
- Chlorine Manual (Chlorine Institute)
- Manufacturer's Booklets & Brochures, Etc.

ACTIONS NECESSARY TO COMPLETE OR MAINTAIN THIS SUBSECTION

- Maintain file of other chemical references.

Table 3.1 **Example Form to Document Screening of Chemical Reactivity Hazards**

FACILITY:			**COMPLETION DATE:**
COMPLETED BY:			**APPROVED BY:**
Do the answers to the following questions indicate chemical reactivity hazard(s) are present? [1] ___________			
AT THIS FACILITY:		***YES, NO*** **or** ***NA***	**BASIS FOR ANSWER; COMMENTS**
Question 1. Is intentional chemistry performed?			
2. Is there any mixing or combining of different substances?			
3. Does any other physical processing of substances occur?			
4. Are there any hazardous substances stored or handled?			
5. Is combustion with air the only chemistry intended?			
6. Is any heat generated during the mixing or physical processing of substances?			
7. Is any substance identified as spontaneously combustible?			
8. Is any substance identified as peroxide forming?			
9. Is any substance identified as water reactive?			
10. Is any substance identified as an oxidizer?			
11. Is any substance identified as self-reactive?			
12. Can incompatible materials coming into contact cause undesired consequences, based on the following analysis?			
SCENARIO	**CONDITIONS NORMAL?**[2]	***R, NR*** **or** ***?***[3]	**INFORMATION SOURCES; COMMENTS**
1			
2			
3			

[1] Use Figure 3.1 with answers to Questions 1-12 to determine if answer is YES or NO

[2] Does the contact/mixing occur at ambient temperature, atmospheric pressure, 21% oxygen atmosphere, and unconfined? (IF NOT, DO NOT ASSUME THAT PUBLISHED DATA FOR AMBIENT CONDITIONS APPLY)

[3] **R** = Reactive (incompatible) under the stated scenario and conditions
NR = Non-reactive (compatible) under the stated scenario and conditions
? = Unknown; assume incompatible until further information is obtained

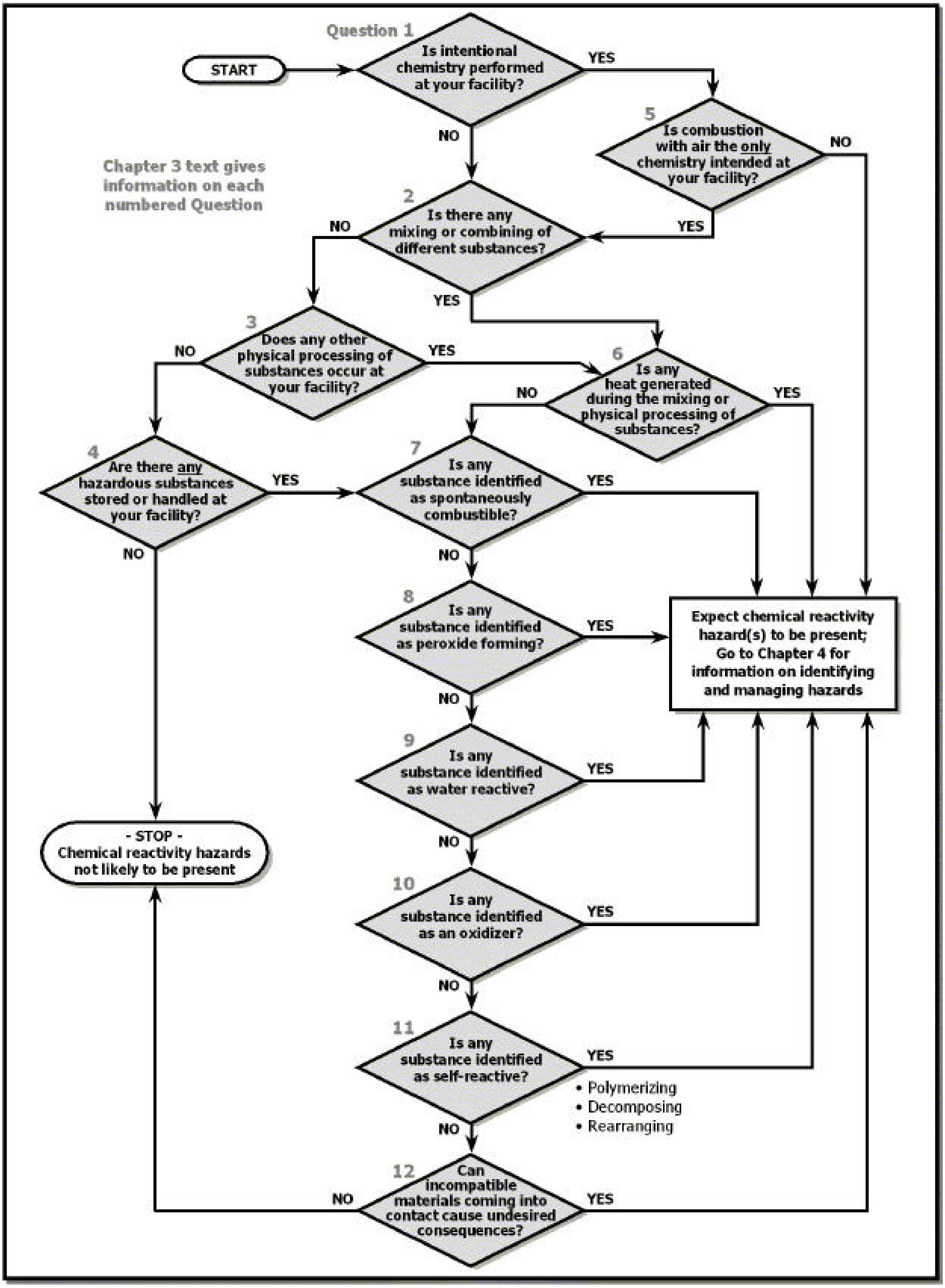

Figure 3.1 **Preliminary Screening for Chemical Reactivity Hazards: Summary Flowchart**

Table 4.1

Gap Analysis: Chemical Reactivity Hazard Management System

____ **Top management commitment has been expressed in written form and personally communicated to site management and employees.**

____ **Business decisions and allocation of resources are consistent with this expressed top management commitment.**

____ **Ownership of the facility or process involving chemical reactivity hazards is clearly established.**

____ **Line management is committed to managing chemical reactivity hazards, from the chief executive officer to first-level supervisors.**

____ **An appropriate system to manage chemical reactivity hazards has been developed and formally documented.**

____ **This system includes clear, written statements of what needs to be done and documented, when, how, how often, and by whom.**

____ **Means and resources have been permanently allocated, and training to the appropriate level is conducted and verified, to equip every person throughout the organization with the knowledge and skills needed to carry out his/her responsibilities.**

____ **It is understood by every person that following all established procedures for managing chemical reactivity hazards is a condition of employment.**

____ **Technical resources are readily available to identify chemical reactivity hazards, acquire needed data, assess risks, and develop safeguards.**

____ **The design basis of the facility and its safety systems, including operating and maintenance procedures, are established and documented.**

____ **All process, equipment and personnel changes are managed such that the safety of the facility is not compromised by any change.**

____ **Line management participates in regularly scheduled audits to ensure the procedures and practices for managing chemical reactivity hazards are being consistently followed.**

____ **Line management participates in the investigation of all chemical reactivity incidents and near misses, and makes resources available to implement corrective actions.**

____ **An attitude and practice of continuous improvement is cultivated within the organization, including looking outside to keep abreast of new or updated information and striving to make the facility inherently safer.**

Table 4.2 **Basic Chemical Reactivity Data to Collect** (see Glossary for definitions)

CAS Number ________________

NFPA Instability Rating ______

Oxidizer? __________

Water reactive? __________

Polymerizes? __________

Decomposes? __________

Sensitive to heat? __________

Name[1] ____

Chemical Formula ____________________________

Forms unstable peroxides? __________

Spontaneously combustible? __________

Inhibitor required? __________

Shock or friction sensitive? __________

Temperature control required? __________

Incompatibilities? ____

____

Reaction products? ____

Rate of reaction? ____

Quantitative data (onset temperature, heat of reaction, maximum pressure rise…) may be needed later.

[1] Also include form, concentration range and diluent, as appropriate.

From “Essential Practices for Managing Chemical Reactivity Hazards”, CCPS, American Institute of Chemical Engineers, 2003

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Technical Committee for Facility Safety of the
German Federal Ministry for the Environment, Conservation of Nature and Reactor Safety.

Guideline for the Identification and Control of Exothermic Chemical Reactions.

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The technical committee for facility safety (TAA[1]) is a committee that is organized under the auspices of § 31a of the BundesImmissionsschutzgesetzes (German environmental legislation) by the (German) Federal Ministry for the Environment, Conservation of Nature and Reactor Safety.

The committee has been established by the Institute for Facility and Reactor Safety (German: GRS).

Preface:

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The "Guideline for the Identification and Control of Exothermic Chemical Reactions" is the English translation of the (German) Guideline TAA – GS – 05. Dr-Ing Jan C A Windhorst prepared this English translation for the CCPS of the AIChE (2002) for inclusion in the CCPS book *Essential practices for Managing Reactivity Hazards*. In case of conflict between the English version and the original German TAA – GS – 05 Guideline the original German guideline shall be used. The translator assumes no liabilities with respect to the use, interpretation, multiplication or reproduction of this English guideline.

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[1] TAA: *Technischer Ausschuß für Anlagensicherheit* beim Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit - *Technical Committee for Facility Safety* of the Federal Ministry for the Environment, Conservation of Nature and Reactor Safety.

Guideline for the Identification and Control of Exothermic Chemical Reactions.

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A study group on behalf of the Technical Committee for Facility Safety of the Federal Ministry for the Environment, Conservation of Nature and Reactor Safety prepared this guideline.

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A Introduction/Problem Definition

Chemical facilities have to be operated safely during normal operation as well as during deviations from the specified process and equipment parameters. Chemical reactions that go to completion can only become a hazard for humans and the environment when process pressures or temperatures rise beyond the equipment design parameters of a facility; e.g., as result of a runaway reaction. For example unacceptable pressure increases can develop as a result of exothermic processes with inadequate heat sinks or reactions that produce gaseous products (e.g., decompositions).
The potential hazards of such chemical reactions are primarily determined by the quantity of energy or gas that is generated and released and/or by the type and quantity of the materials involved. These hazards are the result of the interaction between the properties of individual components and mixtures, the process and equipment parameters and possible failure values. Since this interaction can be influenced by reaction rates it is necessary to consider the conversion of the reactant(s) over time.

Process hazards associated with a process need first of all to be identified and subsequently assessed in order to arrive at a process concept that gives due consideration to safety and environmental protection. The assessment will determine to what an extent safeguarding measure are required.

In the remainder of this guideline the discussion is limited to reactions in a narrow sense; i.e., conversions of materials. Other process-technical operations; e.g., physical processes such as drying and distillations, can be treated in the same fashion.

B Process hazard assessment of reactions during normal operations

A chemical reaction can, as a rule, be described by reaction equations that show the reactants participating in the reaction. Furthermore the reaction equations provide information about intermediates, byproducts and possible gaseous products. The possible hazard level as a result of exothermic chemical reactions is identified with a series of physical and chemical parameters that are characteristic for the reactants and equipment parameters. Especially important are the following parameters:

1. The reaction enthalpy ΔH_R for both the desired reaction as well as possible secondary reactions (e.g., decomposition)
2. The possible gas evolution M and the rate of gas evolution (dM/dt) (or corresponding derived parameters) of the reaction or possible decomposition
3. The rate of heat production (dQ_R/dt, reaction output), where applicable as a function of temperature
4. The total heat removal capacity of the system (dQ_K/dt)

5 The maximum permissible temperature T_{exo} for the thermal stability of the reactants and reaction mixtures under process conditions[2].

These parameters need to be considered for reactions that go towards the intended completion as well as for possible upsets (see section C). Measuring methodologies for determining characteristic material property values (Stoffkenngrößen), e.g., differential thermal analysis ("DTA"), calorimetry, and adiabatic experiments, and their possible use and applications are given in the literature /1, 2, 3, 4/.

Materials and mixtures that are capable of a deflagration or a detonation occupy a special position. For such materials the rate of heat and gas production is no longer a function of the process temperature. Measures taken to control an exothermic process, which are based on such functionality will therefore be futile. This concerns predominantly explosive materials, organic peroxides, and decomposing materials (classes 1, 5.2 and 4.1 of the German regulations for the transport of hazardous goods). Usually additional measures are required to control reactions in which such materials and their intermediates /5/ participate; these additional measures are beyond the scope of this study. Criteria and test methods for testing such materials can be found, for example, in the UN test manual /6/ and other relevant regulations. However, this guideline is suitable for studying the other properties that need to be considered.

Furthermore knowledge of the boundary conditions under which reactions have to run their course is an essential condition for the safety assessment of exothermic reactions. This includes especially:

- reaction management, e.g.
    - continuous/intermittent with batch/semi-batch operation
    - specified components/metering rate
    - temperature and pressure range
    - phase conditions during the reaction

- equipment technical parameters, e.g.
    - reactor vessel size
    - ancillary equipment
    - heat removal capacity of equipment

A flowchart (**Figure 1**) shows a decision-making flow for the determination and safety assessment of the hazard potential.

---

[2] $\mathbf{T_{exo}}$ depends not only on the material properties but is to a large extent determined by the difference between $\mathbf{(dQ_R/dt)}$ and $\mathbf{(dQ_K/dt)}$. $\mathbf{T_{exo}}$ is therefore not unequivocally determined for a single material by a measuring process. This temperature can be obtained in different ways which need to be adjusted for the process and equipment, therefore different values can be found for $\mathbf{T_{exo}}$. For each individual case a measuring methodology for $\mathbf{T_{exo}}$ needs to be considered that either simulates actual equipment conditions or can be extrapolated to them. As an alternative an adiabatic measuring process can be considered. The following methodologies for determining $\mathbf{T_{exo}}$ have proven satisfactory:

a. the onset temperature of a runaway as measured by DTA (heating rate 1, ...10 K/min) is reduced by 100 K
b. the temperature for an adiabatic induction period (up to maximum conversion) of 24 hours ("AZT 24"), is reduced by 10 K
c. the temperature at which the heat production of the system reaches 0.1 W/kg is reduced by 10 K.

This procedure is based on typical residence times and onset values for reactions as well as process operations. Where boundary conditions clearly deviate from such values it is necessary to consider these when determining $\mathbf{T_{exo}}$. This can happen for example when materials and mixtures of materials are stored for longer periods of time and for very large inventories.

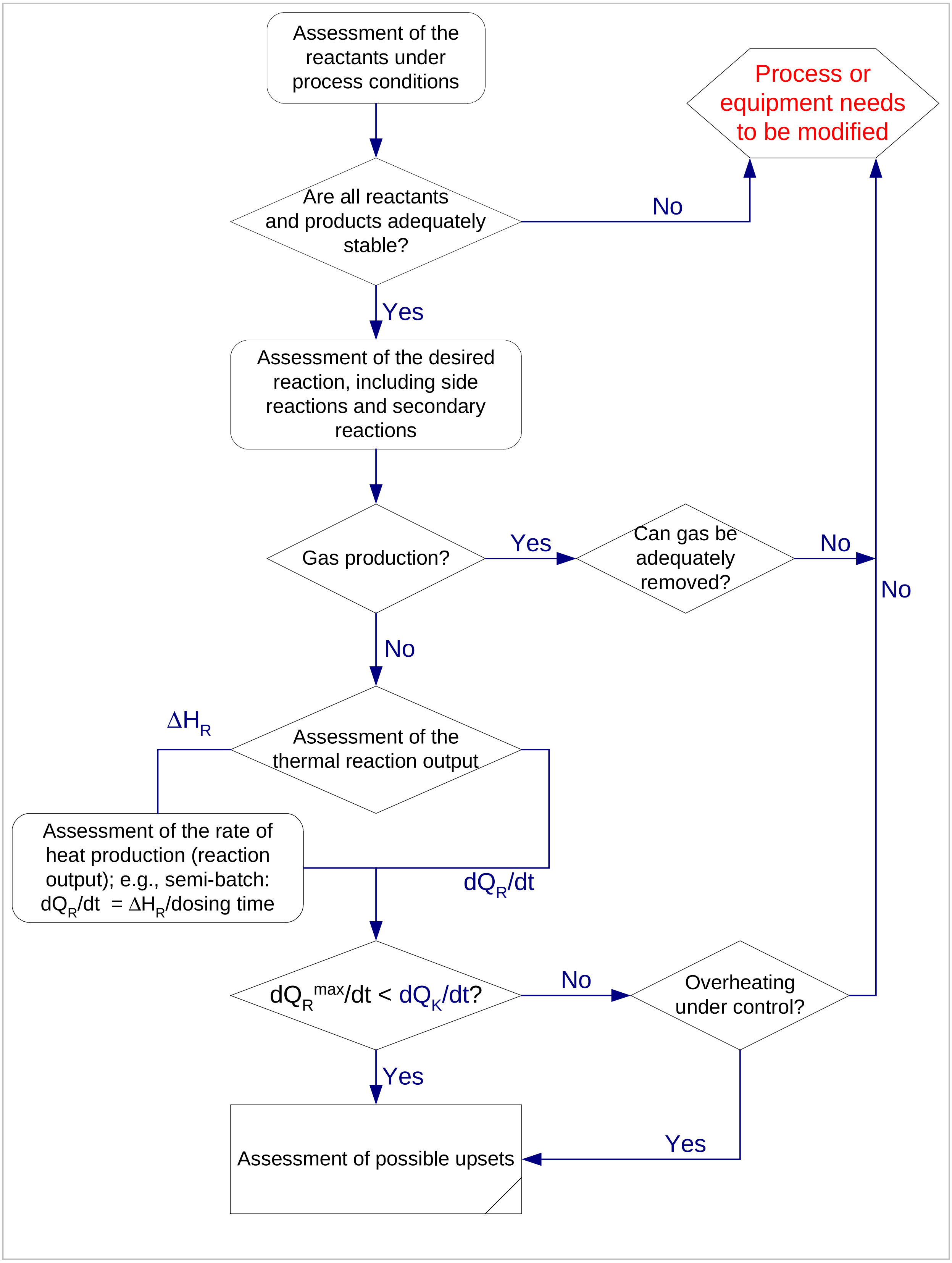

Figure 1: Iterative assessment strategy for normal operations

The assessment begins with an assessment of the reactants. The question is whether all initial process reactants can be regarded as thermally stable within the intended temperature range and time domain. Possible interactions with non-reacting materials need to be considered as part of this assessment.

Information about the thermal stability of materials and mixtures can be obtained with little effort. It is known that when certain functional groups are present an increased probability of exothermic decomposition needs to be accounted for. A list of special compounds and materials are given in the Appendix (section G 1).

Beyond this purely theoretical analysis there is usual a need for experimental screening methods to determine the hazard potential associated with the handling of a material or mixture. References /7,8/ give possible applications and limitations with respect to these screening methods. Application of these screening methods allows first of all information about the stability within the intended temperature range. If significant thermal effects occur within this temperature range then further research needs to be carried out to determine the peak demands (e.g., on cooling water) for the duration of the given reaction and the mixtures under consideration. This research can include adiabatic tests or comparable techniques.

If tests showed that all initial reactants involved in the reaction exhibited adequate stability then the next step is to evaluate the desired reaction, including side and secondary reactions, in a normal operation. The stoichiometric equation of the desired reaction forms the essential backbone for this evaluation. When this equation shows that gas will be an expected reaction product then the facility has to be engineered to remove the resulting gas in a safe and efficient manner.

A key element in the assessment of the reaction is again the thermal evaluation. A tentative decision for the assessment of the safety of normal operation can be derived from knowledge of the heat of reaction ΔH_R from which the adiabatic temperature increase, ΔT_{adiab}, can be determined.

If the adiabatic temperature increase is known then the following estimates can be applied to the process:

- If the adiabatic temperature increase of the reaction is less than 50 K during normal operation and the starting materials, reaction mixture or products have no thermal instabilities within a temperature range of ($T_{process} + \Delta T_{adiab}$); then the normal operation can be regarded as safe. The same applies when secondary decomposition reactions produce so little heat that the sum of this decomposition heat and the heat of reaction does not cause an adiabatic temperature increase of more than 50 K.
- If the starting materials, reaction mixture or products have thermal instabilities within a temperature range of ($T_{process} + \Delta T_{adiab}$) which together with the heat of reaction do cause an adiabatic temperature increase of more than 50 K; then the rate of heat release (heat production as a function of time) needs to be properly evaluated, especially the rate of heat release of the desired reaction.
- The system can be regarded as adequately protected, even for $\Delta T_{adiab} > 50$ K, provided that the boiling point of the system lies in the interval $T_{process} \leq T_{boil} < T_{process} + 50$ K and system properties and the design of the installation prevent the boiling point and the rate of heat production at the boiling point from unacceptable increases.

When assessing the energy output of an exothermic reaction it is advantageous to determine the rate of heat release directly, e.g., by using reaction calorimetry. Alternatively, it is possible to estimate the reaction's energy output from the reaction enthalpy in combination with other measurements and observations. Such an assessment is; however, conditional upon knowledge of the approximate reaction mechanism. For example it might be found after a detailed evaluation that the reaction under consideration can be described by a reaction-kinetic equation with an effective order of reaction that is ≥ 1. In this latter case it is possible to determine for semi-batch operations the heat output from the quotient of reaction enthalpy and addition time, provided the reaction rate is high enough to prevent a dangerous accumulation of reactant (and the order of reaction is ≥ 1). Similar considerations apply to continuous processes where the residence time is used. (Where clearly autocatalytic behaviour is exhibited this method can no longer be used). Furthermore for heterogeneous systems it is necessary to take the extra effect of the different phases into consideration.

The point where the heat production rate reaches its maximum value is of critical importance for a chemical process. This maximum value needs to be compared with the total given maximum heat removal capacity. A reaction going to completion can be considered safe, for normal operation, if the maximum heat removal capacity is greater than the maximum heat production rate. For more precise analysis see the literature /9, 10, 11/.

The evaluation process is completed with a thermal stability assessment of the products within the process temperature and time ranges. This assessment includes possible interactions of the products with the materials of construction of the equipment used. The methodology is the same as the one previously described for the reactants. It needs to be emphasized that depending on the circumstances the investigation cannot be limited to the pure products. Sometimes representative samples of reaction mixtures at different conversion stages need to be assessed as well.

In each case where there is no unequivocal answer to a question in the flowcharts either further investigations or modifications to the process or equipment are required. The next step in the overall evaluation of the process is the determination of the consequences of possible deviations (also known as failures or upsets). If the evaluation of upsets results in process or equipment changes then the normal operation evaluation needs to be revalidated.

C Process hazard assessment of reactions during deviations

When performing chemical reactions it is necessary to consider conceivable deviations (e.g., upsets, abnormal situations, failures) from the normal operation of a process and equipment and their possible effects on the reaction enthalpy ΔH_R, the gas volume M produced and the rate of gas production (dM/dt), the heat flow balance (dQ_R/dt) - (dQ_K/dt) and the maximum permissible temperature T_{exo} for thermal stability under the applicable process conditions. Upsets (abnormal situations, failures) can be divided into two categories, and their consequences can be assessed using the following tables[3]:

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[3] Notes to the use of the tables:
The matrix cells do not represent data fields that require numerical values. In first instance they are to be used as a framework for a thought process: what needs to be considered and which assessment parameters are affected by certain upset (failures) and how. Where applicable it is possible to give relevant cells a checkmark after due consideration/verification. (For the preparation of checklists, see for example /12/).

Table 1: Consequences of deviations in chemical processes

Upset caused by	ΔH_R	dM/dt	$(dQ_R/dt) - (dQ_K/dt)$	T_{exo}	Δn Mat.*
Starting materials (specification, nature, properties), eg.: - Impurities with catalytic effect - Concentration increases/ decreases - Residues (heels) from previous use - Lowering of activator/ inhibitor concentration (e.g. due to storage beyond expiration)					
Presence of reactants and ancillary materials, e.g.: - Solvent used - Solution enhancers - Activator - Inhibitor					
Metering, e.g.: - Wrong material - Wrong quantities/ratios - Changed metering sequence - Erroneous metering rate					
Reaction conditions, e.g.: - Change in pH value - Temperature increase/ decrease - Pressure increase/ decrease - Reaction/Residence time - Delayed reaction start - Increase of by-products/ residues					
Mixing, e.g.: - Insufficient agitation - Stratification of solids/ catalyst					

*Δ**n Mat.**: Formation of new unwanted products or by-products which lead to an increase in the reaction enthalpy or gas formation or reduction of the maximum permissible temperature $\mathbf{T_{exo}}$.

Table 2: Consequences of deviations from normal plant operation

Upset caused by	ΔH_R	dM/dt	$(dQ_R/dt) - (dQ_K/dt)$	T_{exo}	Δn Mat.*
Availability of Utilities, e.g.: - Compressed air - Nitrogen - Electric Power - Heating media - Cooling media - Ventilation					
Heating/cooling media (temperature), e.g.: - Temperature exceeds or falls below the temperatures set for safe process operation					
Process control equipment, e.g.: - Failure					
Material flows, e.g.: - Failure of pumps/valves - Incorrect operation of valves - Plugging of lines/valves/fittings (especially air lines) - Backflow from other equipment					
Level, e.g.: - Overfilling - Leakage from a dump valve - Flooding of condensers (heat exchangers)					
Agitation, e.g.: - Failure - Increased viscosity - Mechanical heat input (internal energy)					
Integrity of components: - Corrosion (in particular with resulting material overflow from/to heat transfer systems) - Mechanical damage					

***Δn Mat.**: Formation of new unwanted products or by-products which lead to an increase in the reaction enthalpy or gas formation or reduction of the maximum permissible temperature $\mathbf{T_{exo}}$.

In addition to the consequences due to deviations in the chemical process or the equipment operation, deviations in storage atmospheres need to be checked (e.g. formation of explosive atmospheres, generation of oxidizing gases such as chlorine or NO_x, loss of stabilizers in gases capable of decomposition).

It is practical to conduct a structured safety analysis, e.g., in accordance with **Figure 2**, for a reaction with a given process in a given facility.

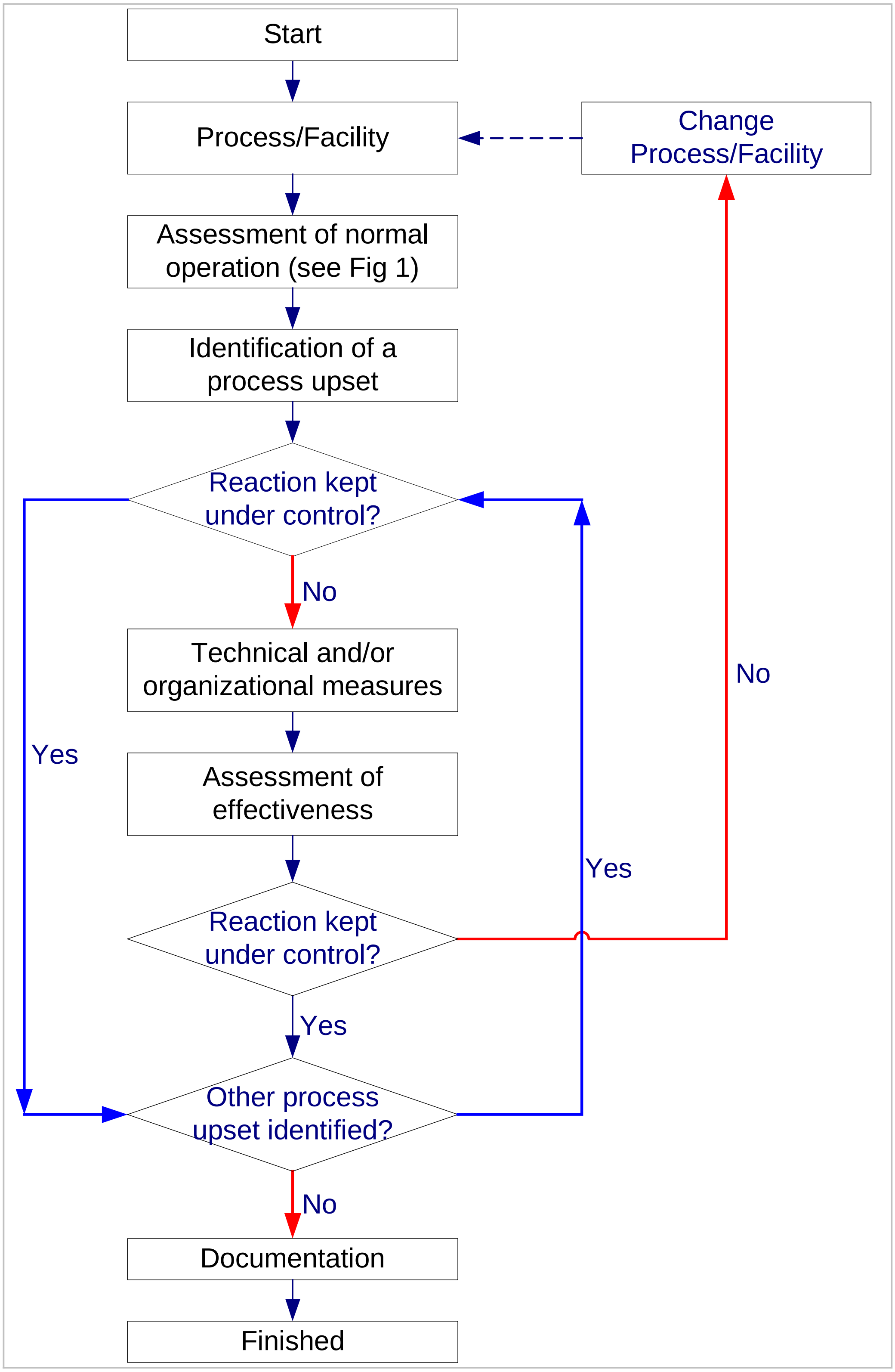

Figure 2: Safety analysis procedure

The result of the safety analysis needs to be documented with an assessment of normal operation as well as the identified upsets and the measures adopted (see section D). Tables 1 and 2 can be used for identification of possible upsets (failures).

D Selection and extent of measures to be implemented

The hazard potential of the intended, side and secondary reactions in terms of exotherms should be assessed with the help of key parameters, especially ΔH_R and dM/dt. Possible consequences of upsets (failures); i.e., the temperature increase $\Delta T_{failure}$ in the system as a result of an energy release and/or an increased gas production $\Delta(dM/dt)_{failure}$ which can cause a pressure build-up need to be considered.

If the following temperature and gas production (which will determine the pressure build-up) apply then the equipment design specifications will not be exceeded, even under upset conditions.

$$T_{process} + \Delta T_{failure} < T_{max.\ design}$$

and

$$(dM/dt)_{process} + \Delta\,(dM/dt)_{failure} < (dM/dt)_{max.\ design}$$

In this case the chemical reaction, in the process under consideration, and the equipment used can be regarded as sufficiently safe for normal as well as upset conditions.

In other cases; i.e., when a review of upset conditions shows that these equations are not satisfied, then additional measures and their reliability (integrity level) should be specified which are expected to exclude a serious hazard with reasonable reliability[4].

The additional measures can be divided into preventive measures to prevent an uncontrolled reaction and design measures to mitigate unacceptable consequences of a runaway reaction. Depending on the circumstances of each individual case the following alternatives or a combination thereof can be considered:

- preventive measures:
  - procedures (organisational measures)
  - process control concepts
  - reaction quench systems
  - emergency cooling
- design measures:
  - pressure-resistant construction
  - pressure relief

Preventive measures are to be preferred; note: the order in which the alternatives have been given does not indicate an order of preference.

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[4] Many limit conditions are already specified and solutions given in technical standards that deal with safeguarding measures. These solutions are recognized as providing an adequate level of safety. The following standards are especially important:

- DruckbehV with TRB 403, TRB 404, AD-Merkblatt A6 *[J Windhorst: this is the German equivalent of ASME and ASME Code Case 2211]*
- BImSchG together with StörfallV
- GefahrstoffV with TRGS 300, ArbeitsstättenV, UVVen
- *[J Windhorst: IEC 61511]*

The reasoning for the selection of measures must be auditable (documented).

Where significant damage is expected the frequency of the undesired event[5] can be reduced as follows:

a. If the event can only occur when ***several independent failures*** have happened then it is necessary to determine whether measures need to be adopted that reduce the frequency of that event. It is essential that the true independence of the contributing failures or upsets that cause the event be verified and to what an extent it is reasonable to assume that they will not occur simultaneously.

   For example, failures which do not initially influence the course of the process might not be corrected without delay. If this is true then it cannot be ruled out that a second failure can occur before the first failure has been corrected. The same applies to “covert” failures. These types of failures should be treated as dependent or common cause failures.

   A failure analysis can result in the conclusion that the occurrence of the event can be ruled out, based on the improbability of a simultaneous occurrence of the necessary contributing failures. Where this happens no additional safeguarding measures need to be implemented.

   Sometimes the event cannot be ruled out with a high enough probability, even when its occurrence requires a special combination of failures. This case requires as a rule a ***single*** additional preventive measure to interrupt the chain of failures leading to the event.

b. When only a *single* failure causes the event to happen then it is crucial to interrupt the causal chain, leading to the event, with a high reliability safeguard. This is achieved by implementing redundant ("single failure tolerance principle" /13/) or single "fault-tolerant" measures. Reliance on procedures (organisational measures) does, as a rule, not suffice for this type of hazard.

Pressure resistant construction or equipment protected by pressure relief devices are considered highly reliable where design measures are adopted to prevent unacceptable consequences of a runaway reaction. Design measures, especially the provision of pressure relief, may be appropriate and also required when a complete and reliable evaluation of deviations, their causes and consequences cannot be achieved. This can happen as a result of the complexity of the contributing causal chains.

Usually it is difficult to justify pressure-resistant construction in the case of extreme operating pressures because of the necessary material strength (JW: wall thickness) needed. In individual cases it can also be difficult and labour-intensive to design a vent system for safe venting via pressure relief devices. This can be the case when catch systems are required. A separate document details the conditions and how safe venting from pressure relief systems can be achieved.

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[5] The term "event" in this guideline should be interpreted as "exceeding design specifications" of process equipment.

E Glossary

Adiabatic temperature increase

The adiabatic temperature increase (ΔT_{adiab}) is defined as the temperature increase that is established in a reactive process system when the process goes to completion without heat or mass exchange with the environment (e.g., following complete failure of cooling in a closed reactor).

Autocatalysis

Autocatalysis happens when a reaction product, formed during reaction, acts as a catalyst which accelerates the progress of the reaction even at constant temperature. An example is the acid-catalysed saponification of various esters and related compounds. Autocatalytic reactions can be easily experimentally identified by means of differential thermal analysis methods.

Calorimetry

Calorimetry is a measuring technique that allows, based on temperature measurements, conclusions to be drawn about the amount of heat produced over time by chemical or physical phenomena. Reaction calorimeters with reaction volumes of 0.1 to 2 litres that can mimic a process under conditions that resemble full-scale conditions have been proven in use.

Deflagration

Deflagration is the continuing conversion of a material after a locally triggered reaction start. The propagation of the reaction occurs with a subsonic velocity. Large quantities of hot gases can be released during a deflagration some of which, dependent on the circumstances, can also be combustible. The rate of deflagration increases with temperature and, as a rule, also with pressure.

Differential thermal analysis

Differential thermal analysis ("**DTA**") is a measuring method which makes it possible to study the heat transfer during physical and chemical reactions. This can be done with small samples (usually a few milligrams). This analysis is suited for studying the thermal stability of materials and can in many cases be used to assess the thermal potential of chemical reactions.

Heat removal capacity

The heat removal power dQ_K/dt describes the total heat removed from the system in a given unit of time. This can be made up of the cooling capacity, the evaporation rate, and other energy removing terms.

Maximum permissible temperature

The maximum permissible temperature ("T_{exo}") is the maximum permissible temperature at which a material or reaction mixture can just be handled without risk. This temperature needs to be defined with due consideration for the process parameters and the measuring methodology that was used to determine the material characteristics. For example, the maximum permissible temperature in a continuous process can be set at a higher level than in a batch process. This is due to the fact that in a continuous process materials are only briefly exposed to high temperatures while in a batch process materials can be exposed to high temperatures for extended periods of time.

Pressure relief

The protection principle of pressure relief is based on limiting the pressure to which equipment might be exposed by the removal of gaseous or multi-phase material flows from. in the case of an explosion or a runaway reaction by allowing certain predetermined openings to be opened in such a way that the pressure in the vessel does not exceed a predetermined permitted value.

Pressure resistant construction

Pressure resistant construction is characterized by a design pressure of a vessel or equipment that is higher than the pressure that can be reached in case of an explosion or runaway reaction. When decomposition of condensed materials need to be considered then it is usually very expensive to realize pressure resistant construction because of the high pressures that can be expected.

Quench

A reaction quench is a system where an inhibiting substance (quench solution; stored in a separate container vessel) can be quickly and effectively fed into the reactor via a pipe which is protected with appropriate isolation valves. This action is independent of other process actions that may be required. The reaction quench can be manually initiated or automatically when certain process parameters are exceeded.

Rate of heat production/reaction power

The rate of heat production dQ_R/dt is the quantity of heat that is produced per unit of time. This rate is proportional to the reaction rate; the latter is a function of the concentrations and the temperature.

Reaction enthalpy

The reaction enthalpy, ΔH_R, is the quantity of heat that is either absorbed by the system (endothermic reaction) or released by the system (exothermic reaction), at constant pressure, as determined by the reaction equation. The reaction enthalpy ΔH_R depends both on the chemical nature of the individual reactants and their physical states.

Single fault tolerance principle

A process or a facility satisfies the single fault tolerance principle when it has been designed or equipped in such a way that a single fault does not lead to the occurrence of the undesired event. This applies also to safety-related systems.

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G Appendix

1 List of special functional groups and materials

2 Examples

2.1 Process and equipment

2.2 azard potential

2.3 Normal operation

2.4 Deviations (failures, upsets)

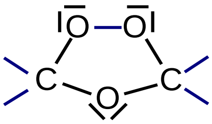
2.5 Various cases with measures proposed

1 List of special functional groups and materials [6]

1.1 Special functional groups

Experience has shown that certain types of functional groups, which are frequently used, have a high thermodynamic instability and can be expected to release large amount of energy.

1.1.1 Typical functional groups in unstable compounds

$-NO_X$	Nitro and nitroso compounds
$-ONO_X$	Esters of nitric and nitrous acid
$>N-X$	Halogenated nitrogen compounds (X = halogen)
$-\overline{N}\equiv N^{+}$	Diazonium salts, also triazene, tetrazene
$-\overline{N}=\overline{N}-$	Azo compounds
$-\underline{\overline{O}}-\underline{\overline{O}}-$	Peroxides, per-acids. Note: Numerous unsaturated hydrocarbons, aldehydes, ketones, ethers and some cyclic hydrocarbons (e.g. Dekalin) tend to form peroxides in the presence of air
	Ozonides
$-C\equiv C-$	Acetylene, acetylides
$-N_3$	Hydrogen nitrides, azides
$-\overline{N}H-\overline{N}H-$	Hydrazides

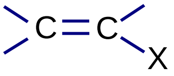
---

[6] This list does not claim to be complete

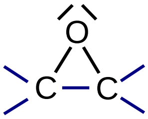
1.1.2

$-ClO_4$	Perchloric acids, perchlorates
$-C\equiv\overset{+}{N}-O^-$	Fulminates, also oximates, salts of aci-nitrogen compounds

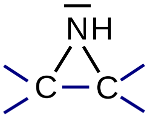
1.1.3 Polymerizable compounds



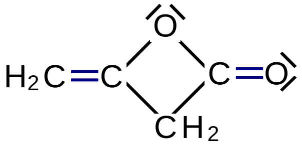
Substituted olefins (X = e.g. -F; -Cl; -CM, -COOR, -CH---CHR; -C6H5)



Epoxides



Aziridines



Diketene

Furthermore: Catalytic effects produced by acids, bases, radical-producing compounds, metals and metal salts need to be considered.

1.2 Oxidizing agents

Frequently used oxidising agents which may liberate significant quantities of energy when mixed with combustible/reducing substances:

HClO4 (conc.)/perchlorates
HNO_3 (conc.)/nitrates
CrO_3/chromates
$KMnO_4$
Chlorates
Nitrating acids
Alkyl nitrites
H_2O_2 organic and inorganic peroxides
SO_3/oleum
Oxygen/ozone

Chlorine

1.3 Reducing agents

Frequently used reducing agents which can lead to significant liberation of energy with oxidising substances:

metals (e.g. sodium, zinc)
organo-metallic compounds
hydrides (e.g. $LiAlH_4$, $NaBH_4$)
silanes
hydrogen

2 Examples

The procedure proposed in this guideline will be illustrated with a few examples of semi-batch reactions.

Three “educational” examples ("cases 1 – 3”) were selected in order to simplify the presentation, clarify the essential steps needed for the evaluation and assessment of a reaction and the decision-making process concerning the type and extent of the necessary measures. The three “educational” examples are characterized by the following constraints:

1. Only single step homogeneous reactions are performed. Side reactions will not go to completion. The reaction mechanisms remain unchanged for the processes under consideration. Interactions of the chemical reactants and/or reaction mixtures with the material of construction are excluded.
2. Relevant material properties as well as process and equipment-specific parameters are completely known for the examples and the solutions proposed. However, the parameters are of a strong abstract nature and are only detailed to the extent needed for the examples. Required calculations were done in accordance with the literature given in the guideline.
3. Only a certain selection (always the same) of the spectrum of possible upsets (faults) is considered.
4. The upsets considered need to be regarded as independent from one another and are not based on "common mode" failure. Furthermore the measures adopted need to be effective and independent of one another.
5. Only preventive solutions based on technical and organizational methods are offered. They represent a single solution from among a number of alternative and equally legitimate solutions. The proposed example solutions do therefore not preclude that inherently safe solutions such pressure-resistant construction or engineered solution such as pressure relief (where necessary with a catch system) can achieve the desired result. More research and more in-depth knowledge than provided here will be necessary to arrive at an optimized solution.
6. It is presupposed that the measures given for the various examples are practical and have also been successfully applied.

The examples and solutions can therefore not be directly applied to each individual real-life situation, without additional study or modifications, where much more complicated facts may need to be considered. The PHA should especially not be allowed to be limited to upsets (faults) selected for the examples moreover possible interdependencies of the upsets need to be investigated and considered appropriately.

2.1 Process and equipment

In a reactor which cannot be isolated from its venting system and which is equipped with a jacket for heating and cooling via an open water circuit the following exothermic reactions of the type

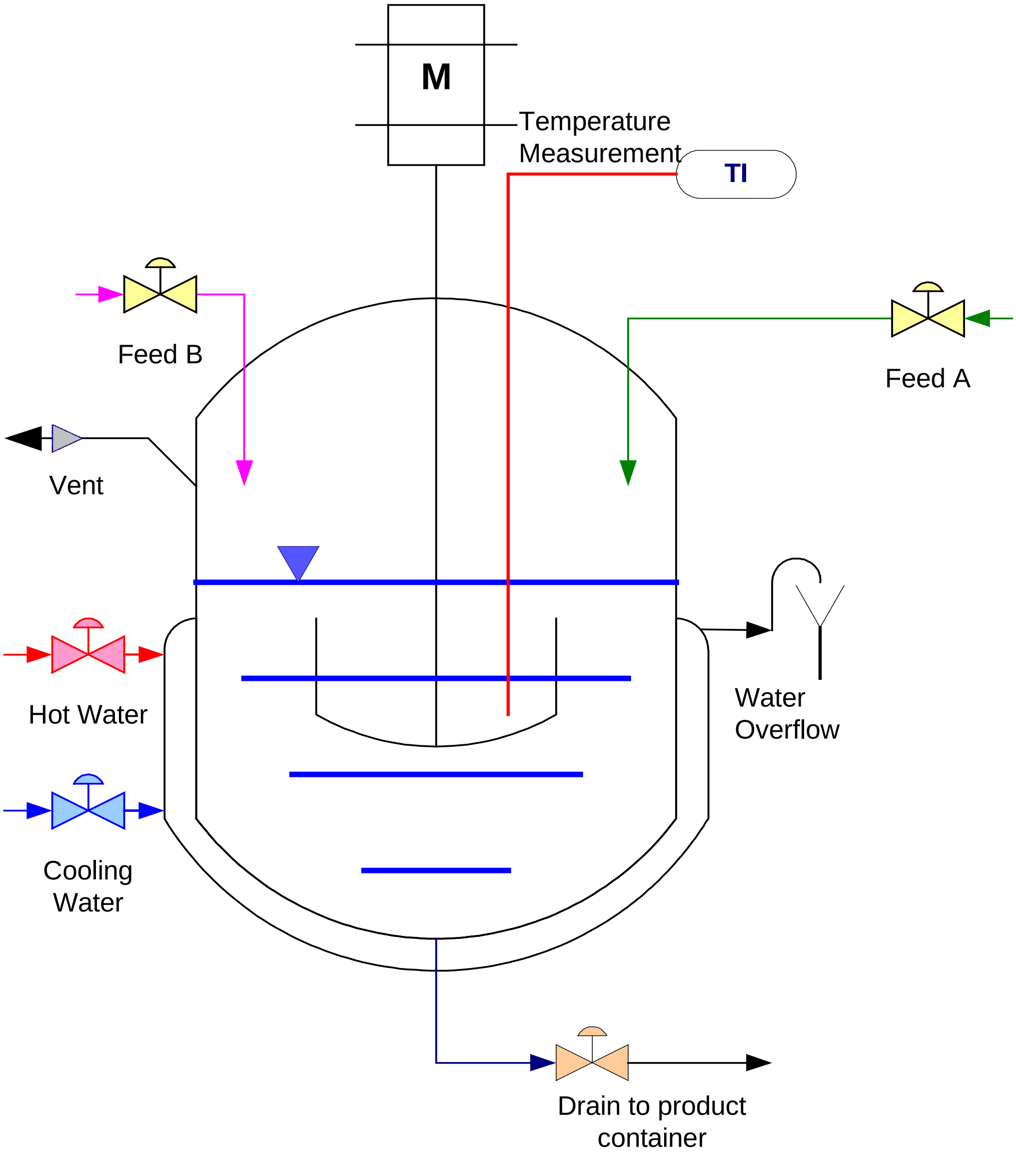
$$A + B \longrightarrow C \qquad \text{(Cases 1 and 3)}$$

and

$$A + B \xrightarrow{D} C \qquad \text{(Case 2)}$$

are to be performed under agitation. In Cases 1 and 3 the reactor is to be charged with compound B at ambient temperature. In Case 2 compound B is dissolved in an inert solvent D that has been placed in the reactor. Afterwards, the vessel is heated to the required process temperature (T_{soll} = 80°C). Compounds A that are supplied cold (at ambient temperature) using a metering system are then supposed to be added over a predetermined period at a constant rate. The heat liberated during the reaction is removed using the water for heating/cooling (see **Figure 3**).

Figure 3: Reactor and ancillary equipment



2.2 Hazard potential

In each case the reaction is exothermic and the reaction enthalpy ΔH_R known; thereby the defining the adiabatic temperature rise which is always greater than $\Delta T_{adiab} > 50$ K. Below 60°C the reaction becomes dormant and an undesirable accumulation of reactants is to be expected. Major reaction energy releases are to be anticipated if the reaction re-initiates.

DTA and caloric measurements have shown that above the maximum permissible temperature T_{exo} the end product decomposes with a strong exotherm by means of an uncontrollable reaction

$$C \longrightarrow \text{decomposition products}$$

This reaction produces copious amounts of gases which would lead to the maximum allowable working pressure (MAWP) of the reactor to be exceeded:

$$(dM/dt)_{decomposition} > (dM/dt)_{max.\ design}$$

T_{exo} was determined for each case 1 - 3 in accordance with the experimental results. For each case T_{exo} is clearly above 100°C. Because of the relationship between T_{exo} and the production of gas, it is necessary to set the design temperature ($T_{max.\ design}$) equal to T_{exo} (unless for example the materials of construction necessitate a lower maximum temperature, a possibility that is not considered here).

2.3 Normal operation

Tests performed on the reactants A and B show an exothermic behaviour and gas formation at temperatures that are in excess of 300°C. The exotherms are in the order of 300 J/g so that explosive properties or a propensity for deflagrations are not anticipated. Testing of reactant mixture samples at different conversion stages of conversion show no need to lower T_{exo} and confirm the reaction enthalpy of the desired process.

Reactants A and B and the reaction mixtures have a negligible vapour pressure below T_{exo}. The solvent D that is used in case 2 is chemically inert over a wide temperature range for the reaction concerned, it has a high boiling point T_s (> 180°C) and is thermally stable at temperatures up to and over 200°C.

A significant gas production need only be anticipated in conjunction with the decomposition reaction of material C. During normal operation the installed equipment can handle all possible vapour/gas volumes that can be produced.

For process reasons, and especially in this case because of the relatively high adiabatic temperature rise ΔT_{adiab} (> 50 K) it is necessary that the heat removal capacity matches (or exceed) the reaction heat capacity. The cooling capacity has therefore been chosen in such a way that the heat of reaction that is released at the intended metering rate can be removed at the required process temperature.

Normal operation may therefore be regarded as safe.

2.4 Deviations (failures, upsets)

Three examples have been used to which the above conditions apply equally, although they differ with regard to certain reaction and processing data.

The following failures may change the temperature level towards T_{exo}:

I *Deviations in reaction conditions (see table 1)*

  a) *reaction temperature too high*
  b) *delayed reaction start (because of too low a temperature, leading to accumulation with subsequent increased reaction power)*
  c) *only half the quantity of component D is used*

II *Deviations in the operation of the installation (see table 2)*

  a) *agitator failure (leading to accumulation with subsequent increase in reaction power)*
  b) *failure of the cooling system at the beginning of the reaction (e.g. failure of the thermal transfer fluid pump)*

2.5 Various cases with measures proposed

2.5.1 Case 1

Reaction $A_1 + B_1 \longrightarrow C_1$

Important data and information for assessment

Material/Reaction	Data and information
A_1	Pure material; thermally stable up and above T_{exo}
B_1	Pure material; thermally stable up and above T_{exo}
C_1	$T_{exo} = 180^{o}C$; $(dM/dt)_{decomposition} > (dM/dt)_{max.\ design}$
$A_1 + B_1 \longrightarrow C_1$	Spontaneous reaction at 80ºC; $T_{exo} = 180^{o}C$; $\Delta T_{adib.} = 75$ K

Evaluation of the given deviation (failure, upset) scenarios

With respect to:

I a) The maximum possible heating temperature is 95ºC, because of the open water circuit. Consequently T_{exo} cannot be reached through external heating.

I b) Reactive power cannot be removed completely by the cooling system so that the temperature temperature increases beyond the required process temperature. The maximum temperature which can be reached is $T_{process} + \Delta T_{adiab}$. With $T_{process} < 80^{o}C$ it remains below T_{exo} (even if the heat removal capacity = 0!)

I c) This failure is not realistic since no solvent D is required.

II a) As under I b), however, $T_{process} = 80^{o}C$. Again, the system remains below T_{exo}.

II b) As under II a).

Each failure on its own satisfies the inequalities

$$T_{process} \quad + \quad \Delta T_{failure} \quad < \quad T_{max.\ design}$$

and

$$(dM/dt)_{process} \quad + \quad \Delta\ (dM/dt)_{failure} \quad < \quad (dM/dt)_{max.\ design}$$

Even the most unfavourable combination, the combination of several failures, and especially I a) with II a) or II b), with a maximum temperature of 170ºC ($<T_{exo}$), does not lead to the design limits being exceeded.

Measures proposed:

With regard to the failures considered, no additional measures pursuant to section D are required.

2.5.2 Case 2

The reaction $A_2 + B_2 \xrightarrow{D} C_2$ is to be performed in solvent D. The component B_2 is supposed to have been dissolved in solvent D in the prescribed quantity. Important data and information for assessment:

Important data and information for assessment

Material/Reaction	**Data and information**
A_2	Pure material; thermally stable up and above T_{exo}
B_2	Pure material; thermally stable up and above T_{exo}
C_2	T_{exo} = 180ºC; $(dM/dt)_{decomposition} > (dM/dt)_{max.\ design}$
D	Chemically inert; T_s > 180ºC; thermally stable up to over 200ºC
$A_2 + B_2 \xrightarrow{D} C_2$	Spontaneous reaction at 80ºC; T_{exo} = 180ºC; $\Delta T_{adib.}$= 75 K $(dQ_R/dt)_{normal\ operation}$ = 95 kW; product of heat transfer coefficient and heat transfer area $k \times F$ = 4.5 kW/K

Evaluation of the given deviation (failure, upset) scenarios:

With respect to:

I a) The maximum possible heating temperature is 95ºC, because of the open water circuit. Consequently T_{exo} cannot be reached through external heating.

I b) Reactive power cannot be removed completely by the cooling system so that the temperature increases above the set point. The maximum temperature which can be reached is $T_{process} + \Delta T_{adiab}$. With $T_{process} <$ 80ºC it remains below T_{exo} (even if the heat removal capacity = 0!)

I c) If only half the solvent quantity D is used, T_{exo} remains unchanged at 180ºC, but the adiabatic temperature increase rises because of the reduced quantity of D, and therefore the changed total heat capacity of the reaction mixture, to ΔT_{adiab} = 112 K. At the same time, the reaction power increases. However, through reactor cooling it can still be reliably removed ($\Delta T_{failure}$ = approx. 17 K). Even with this failure, the system still remains below T_{exo}.

II a) As under I a), but with $T_{process}$ = 80ºC. Here again the system remains below T_{exo}.

II b) As under II a).

Although each individual failure on its own satisfies the inequalities:

$$T_{process} \quad + \quad \Delta T_{failure} \quad < \quad T_{max.\ design}$$

and

$$(dM/dt)_{process} \quad + \quad \Delta\ (dM/dt)_{failure} \quad < \quad (dM/dt)_{max.\ design}$$

the results are different; however, when combinations of two failures are considered, specifically:

α) insufficient solvent quantity D **and** simultaneous failure of stirrer [failures I c) and II a)], T_{exo} may be exceeded:

$(80 + 112)\ ^oC = 192\ ^oC > (T_{exo} = 180\ ^oC)$. Assumption: heat removal power = 0

or

β) solvent quantity D too small **and** cooling failure at the same time at the beginning of the reaction [failures I c) + II b)], T_{exo} may also be exceeded:

$(80 + 112)\ ^oC = 192\ ^oC > (T_{exo} = 180\ ^oC)$. Assumption: heat removal power = 0

Consequence:

The given inequalities are no longer satisfied and additional measures are required. To trigger an event (excess over design limits), at least two failures are necessary. Consequently the causal chain detailed under II a) and II b) must be interrupted by one measure in each case. These measures must be effective independently of one another. The same applies in respect of the measures concerning the failure mode which leads to a reduction in the solvent quantity D.

Measures proposed (see Figure 4):

With respect to:

α) Incorrect starting concentration and stirrer failure:

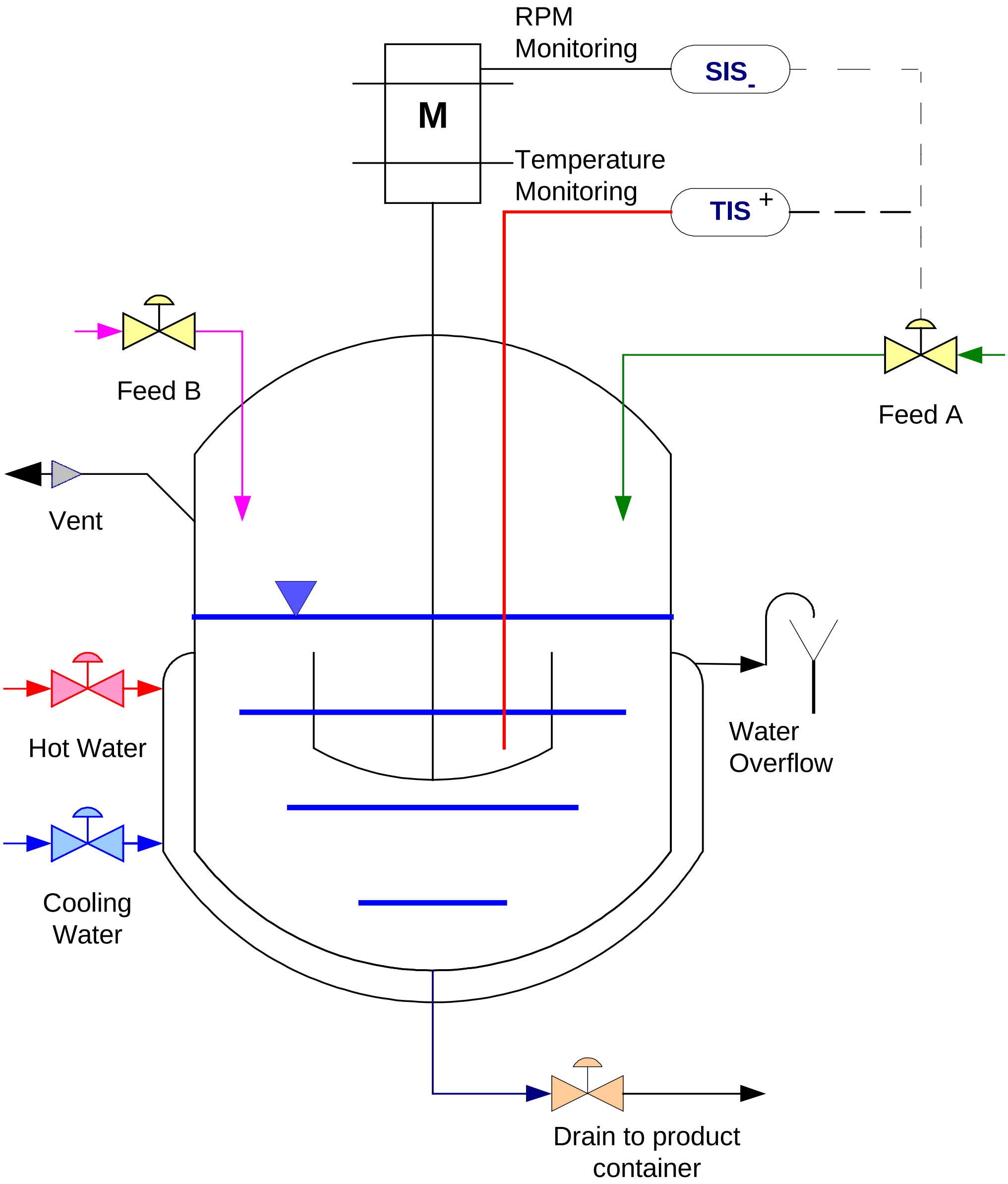
1. Simple interlock of the inlet valve for component A_2 with the stirrer function SIS- (valve closes when the stirrer is stationary), and
2. ensuring that the correct quantity D is added by using a suitable organisational measure (safety operating instruction).

β) Incorrect starting concentration and loss of cooling:

1. Simple interlock of the inlet valve for component A_2 with the temperature controller in the reactor TIS+ (valve closes when a maximum temperature, for example 100 ºC is reached), and
2. ensuring that the correct quantity D is added by using a suitable organisational measure (safety operating instruction).

These measures do not change the parameters for normal operation so that it is not necessary to perform an iterative assessment of normal operation (see schema 2 with schema 1). No further measures are required with regard to the failures considered.

Figure 4: Reactor and ancillary equipment (schematic), case 2



2.5.3 Case 3

Reaction: $A_3 + B_3 \longrightarrow C_3$

Important data and information for assessment

Material/Reaction	Data and information
A_3	Pure material; thermally stable beyond T_{exo}
B_3	Pure material; thermally stable beyond T_{exo}
C_3	T_{exo} = 120ºC; $(dM/dt)_{decomposition} > (dM/dt)_{max.\ design}$
$A_3 + B_3 \longrightarrow C_3$	Spontaneous reaction at 80ºC; T_{exo} = 120ºC; $\Delta T_{adib.}$= 225 K

Evaluation of the given deviation (failure, upset) scenarios

with respect to:

I a) The maximum possible heating temperature is 95ºC, because of the open water circuit. Consequently T_{exo} cannot be reached as a result of external heating.

I b) The cooling system is incapable of removing all the energy of the reaction (heat). The maximum temperature, $T_{process} + \Delta T_{adiab}$, which can now be achieved can exceed T_{exo} (even if $T_{process} <$ 80ºC). A temperature of 160ºC will be reached with the available cooling.

I c) The upset is not realistic since no solvent D is required.

II a) As under I b), but with $T_{process}$ = 80ºC. The system's T_{exo} can also be exceeded for this scenario.

II b) As under II a).

Each upset Ib), IIa) and IIb) individually violates already the prescribed conditions; the following applies:

$$T_{process} \quad + \quad \Delta T_{upset} \quad > \quad T_{max.\ design}$$

and

$$(dM/dt)_{process} \quad + \quad \Delta\ (dM/dt)_{upset} \quad > \quad (dM/dt)_{max.\ design}$$

Consequences:

Additional measures are needed. A single upset will already initiate the event (exceeding of boundary values) in all three cases. The corresponding causal chains need therefore to be interrupted by high availability safeguarding measures (high safety integrity). The implemented measures (see next page) will also break the causal chains of possible fault (upset) combinations.

Recommended measures (see also Figure 5):

I a) A redundant temperature measurement with an emergency block valve (controlled addition of A_3) in case the reactor temperature drops below a set minimum temperature in the vessel, TIS_{-}.

II a) A redundant temperature measurement with an emergency block valve (controlled addition of A_3) in case the reactor temperature drops below a set minimum temperature in the vessel, TIS^{+}.

In order to satisfy the redundancy requirement relating to I a)*, the measurement of the circuit described in case* II a) *is used supplemented with* S_{-}*. Similarly, in order to satisfy the redundancy requirement for* II a), *the measurement for the circuit described in* I a) *is used and supplemented with* S^{+}*.*

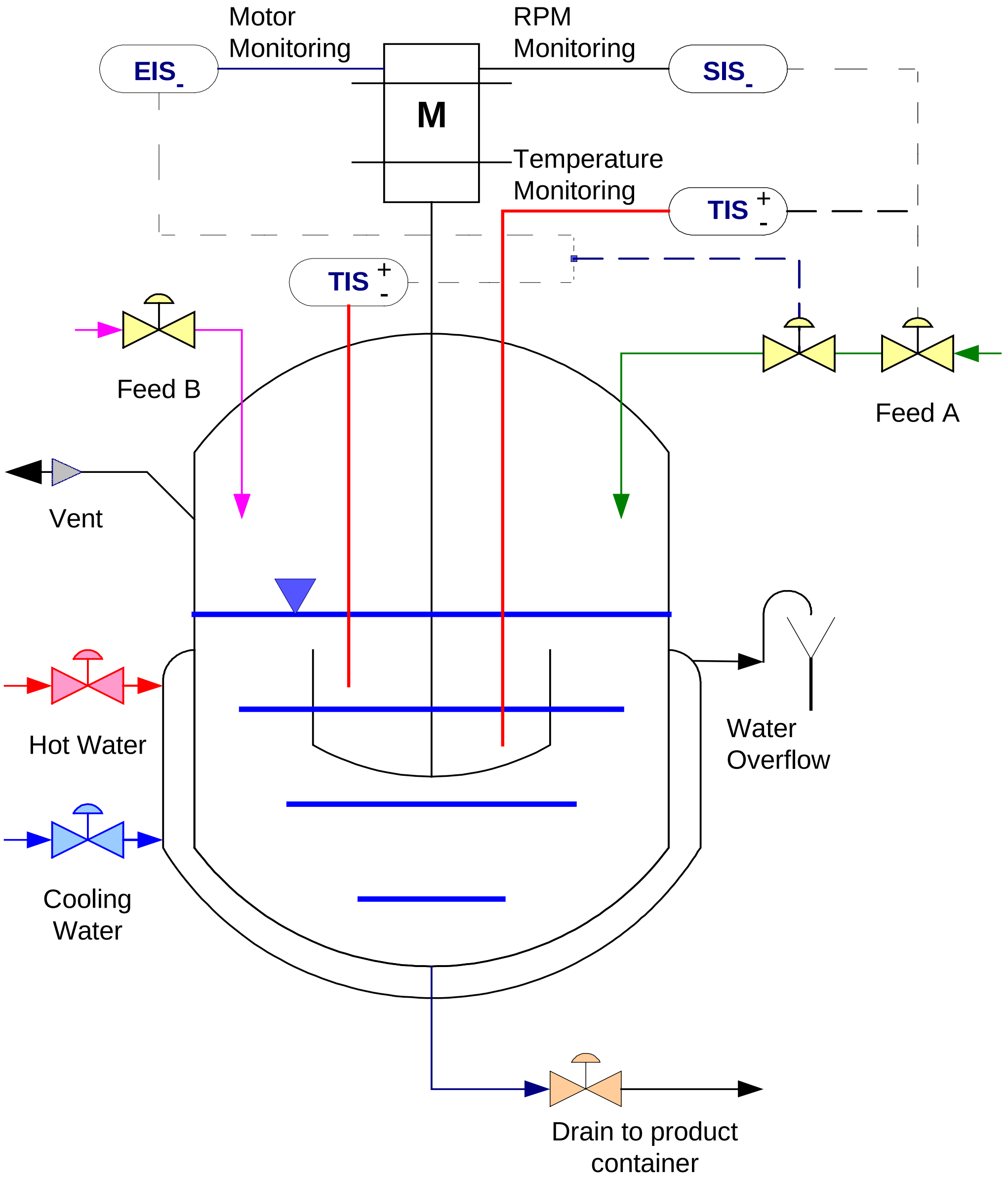
II b) Monitoring of the speed of the agitator, SIS_{-}, and monitoring of the agitator motor, EIS_{-} (diverse redundancy)

The before-mentioned measures do not change the parameters for normal operation, so that iterative assessment of the normal operation (see case 2 and case 1) is not required.

Notes:

The special process feature for case 3 is a relatively high reaction enthalpy in combination with a low "*maximum permissible temperature*" T_{exo}. An alternative safety solution would be to control both these two parameters. For example by adding a pump to the reactor and with solvent makeup the process can be made continuous (CSTR). This allows the adoption of a higher "*maximum permissible temperature*" T_{exo}, because of the short residence time and the dilution effect, and a reduction of the adiabatic temperature increase ΔT_{adiab} because of the dilution effect. Such a (drastic) process and facility change will always require an iterative safety-technical reaction PHA furthermore additional may become necessary.

Figure 5: Reactor and ancillary equipment (schematic), case 3



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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Contents

Figures

*These photographs are not available for website posting. They will be placed in the printed copy.

Tables

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

Acronyms and Abbreviations (cont'd)

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 Communities)
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)

Acronyms and Abbreviations (cont'd)

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)
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-Tricholorophenol
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
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.

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.

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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.

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).

OSHA develops and enforces standards to protect employees from workplace hazards. In the aftermath of the reactive incident that caused 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.

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

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

[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.

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.

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 chemical incidents.

- Examine how industry, OSHA, and EPA currently address reactive chemical 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 chemical incidents.

ES.2 Investigative Process

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, and/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]

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[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).

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 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.

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[8] An NFPA instability rating of "0" means that materials in themselves are 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.

6. As a result of the joint OSHA-EPA chemical accident investigation of the Napp Technologies incident in April 1995, a recommendation was made by EPA and OSHA to consider adding more reactive chemicals to their respective lists of chemicals covered by process safety regulations. To date, neither OSHA nor EPA 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) account for over 65 percent of the equipment involved; chemical reaction vessels account for only 25 percent.

   Reactive incidents can result in a variety of consequences, including fire and explosions (42 percent of incidents) as well as toxic gas emissions (37 percent).

8. 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.

9. 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.

10. 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]

11. 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]

12. 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.

13. 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.

14. 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.

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[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's (NOAA) The Chemical Reactivity Worksheet, American Society for Testing and Materials' (ASTM) CHETAH, and Bretherick's Database of Reactive Chemical Hazards.

15. 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, 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.

16. Several voluntary industry initiatives, such as ACC's Responsible Care and NACD's 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.

17. 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

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

State of New Jersey is also considering similar action in its proposed revisions of the 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 Requirements (40 CFR 68) 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 focus 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 performing a process hazard analysis.

Given that reactive incidents are often caused by inadequate recognition and evaluation of reactive hazards, improving reactive hazard management involves defining and requiring relevant factors (e.g., rate and quantity of heat and gas generated) to be examined 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.

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.

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[15] NOAA's The Chemical Reactivity Worksheet, ASTM's CHETAH, 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., ASTM's CHETAH, NOAA's The Chemical Reactivity Worksheet).

     - 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 Firefighters

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

The United Steelworkers of America

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

United Food and Commercial Workers International Union

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.[17] 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. The 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 on April 8, 1998, at Morton International, Inc., in Paterson, New Jersey, resulted in nine injuries. 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

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

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).

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

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 chemical incidents.
- Examine how industry, the Occupational Safety and Health Administration (OSHA), and the U.S. Environmental Protection Agency (EPA) currently address reactive chemical 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 chemical 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.[18]

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[18] 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.

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 site visits.

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.

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 raised concerns and requested further investigation into reactive hazards–particularly in light of similar incidents since 1995.

Occasionally, in the course of conducting incident investigations, 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 Firefighters.
- 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.
- 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

A public hearing was held 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 chemical 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 public comments were carefully considered before the final report was approved by the Board.

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.

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 (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.

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 create 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 be severe and include fires, explosions, or toxic emissions.

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.

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 throughout this section.

Napp Technologies

On April 21, 1995, an explosion and fire at Napp Technologies in Lodi, New Jersey, killed five employees and destroyed the facility (Figure 1).[19] 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.”

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[19] Photograph not available for website posting; it will appear in the printed copy.

The Napp incident raises questions regarding use of the NFPA rating system as the sole basis for regulating reactive hazards (see Section 5.1.3).

Bartlo Packaging, Inc.

This incident occurred on May 8, 1997 (Figure 2).[20] BPS–a bulk storage and distribution facility in West Helena, Arkansas–was repackaging an organic pesticide, AZM50W. As it 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 cause of the incident was 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.

3.1 Data Sources and Methods

CSB searched over 40 data sources for incidents that met its definition of a reactive incident (Section 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

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[20] Photograph not available for website posting; it will appear in the printed copy.

storage/distribution, waste processing, and petroleum refining.[21] For purposes of this incident search, only reactive incidents that caused serious consequences[22] 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 chemical incident" (Section 1.3).

3.2 Data Limitations

Although the statistics provided in Section 3.3 concerning the number and severity of reactive incidents are grave, existing sources of incident data are inadequate to identify the number, severity, 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;[23] such data are a valuable resource for analyzing incident trends and developing prevention actions at a national level.

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[21] 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).

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

[23] Research indicates that the OSHA Integrated Management Information System (IMIS) identified 70 percent of the reactive incidents 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.

- 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.[24] 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 numbers 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.

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.

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[24] 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 one-fourth of the 12,000 incidents in the database.

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 regional offices	1982-Present	Extensive range of incidents, including those resulting in a chemical release from a reactive incident All states and localities included	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, a third party 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 ARIP	Responses to questionnaires sent by EPA 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**

EPA RMP*Info	Data about chemical releases resulting in specific impacts covered under RMP regulation (40 CFR 68)	1994-Present	Provides further 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**
IChemE Accident Database	Reports about chemical incidents around the world from official government sources, the 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 in the database contain lessons-learned information
HSE MHIDAS	Information taken from public domain sources worldwide; however, majority of the 7,000 incidents occurred either in UK or US	1985 - Present	Scope is beyond incidents reported to or investigated by regulatory agencies or first responders	No extensive description of incidents, including causes and lessons learned
U.S. Fire Administration NFIRS	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 around the world 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.

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.

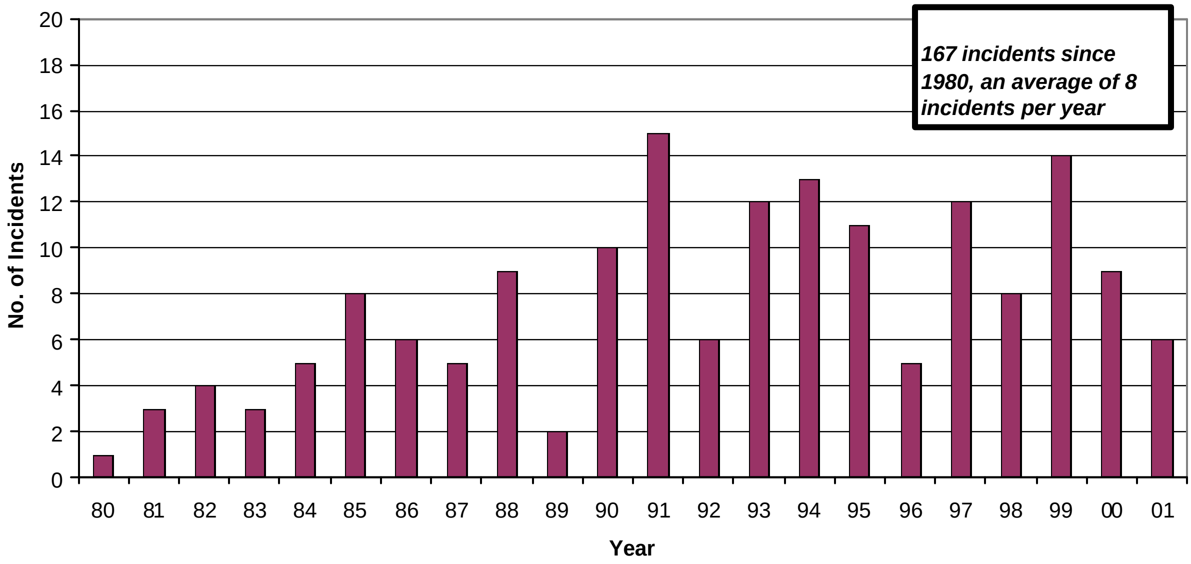

Figure 3. Total incidents by year, 1980–2001.

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).[25] Appendix F presents a 5-year summary of U.S. Bureau of Labor Statistics data on occupational fatalities.

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[25] Photographs not available for website posting; they will appear in the printed copy.

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.

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.

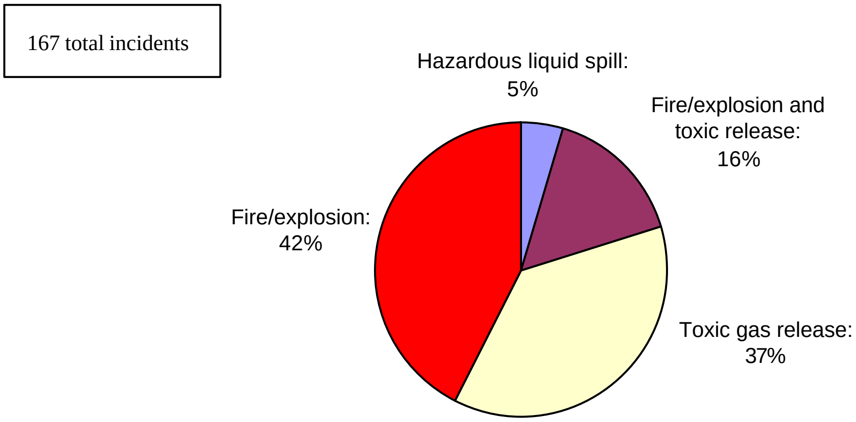

Figure 6. Categorization of consequences of incidents.

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 7).[26] 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.

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[26] Photograph not available for website posting; it will appear in the printed copy.

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 8).[27] These numbers do not include further financial losses due to business interruption or lost market share.

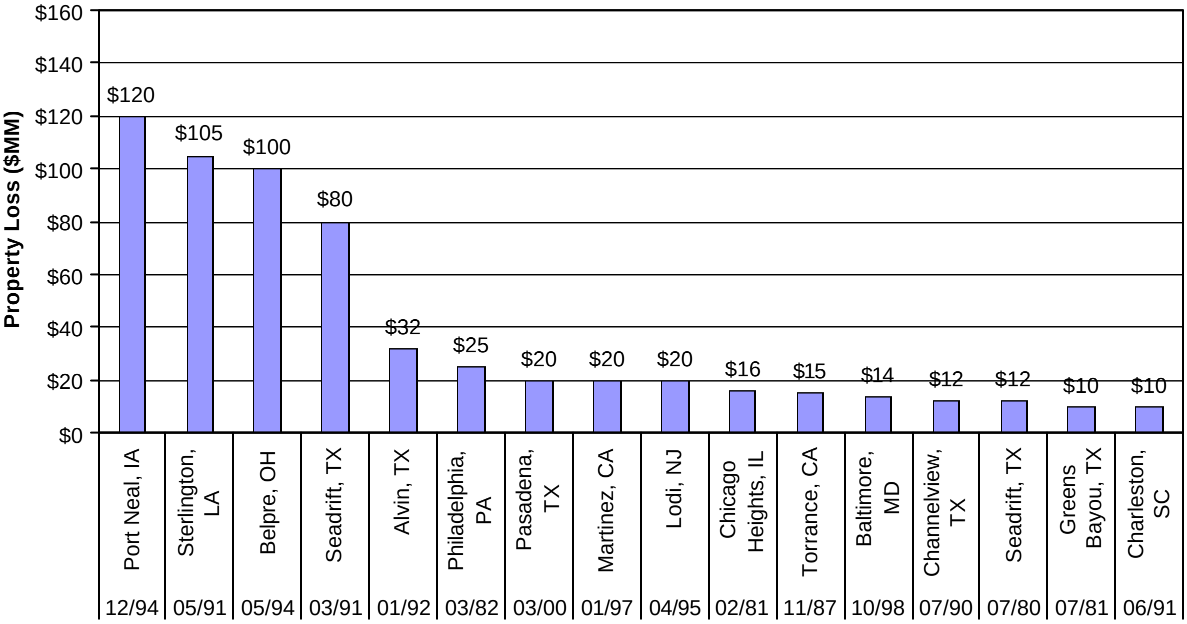

Figure 8. Incidents resulting in large property losses.

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[27] Property loss figures are quoted for the year in which they were incurred. The numbers in Figure 8 are not scaled to represent constant dollar valuation of loss.

Concept Sciences, Inc.

An explosion that occurred 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 9,[28] USCSB, 2002a). Fourteen people were injured. The CSI facility, in Hanover Township, Pennsylvania, was completely destroyed. Several local 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.”

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[28] Photograph not available for website posting; it will appear in the printed copy.

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,[29] 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.

3.4 Profile of Affected Industries

Analysis of CSB data shows that reactive incidents are not unique to the chemical manufacturing industry (Figure 10). Although about 70 percent of the 167 incidents occurred in the chemical 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 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 11).[30]

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[29] The definition of public impact is based on the criteria for reporting offsite incidents in the EPA RMP regulation (40 CFR 68.42a). “Public” includes anyone except employees or contractors at the facility.

[30] Photograph not available for website posting; it will appear in the printed copy.

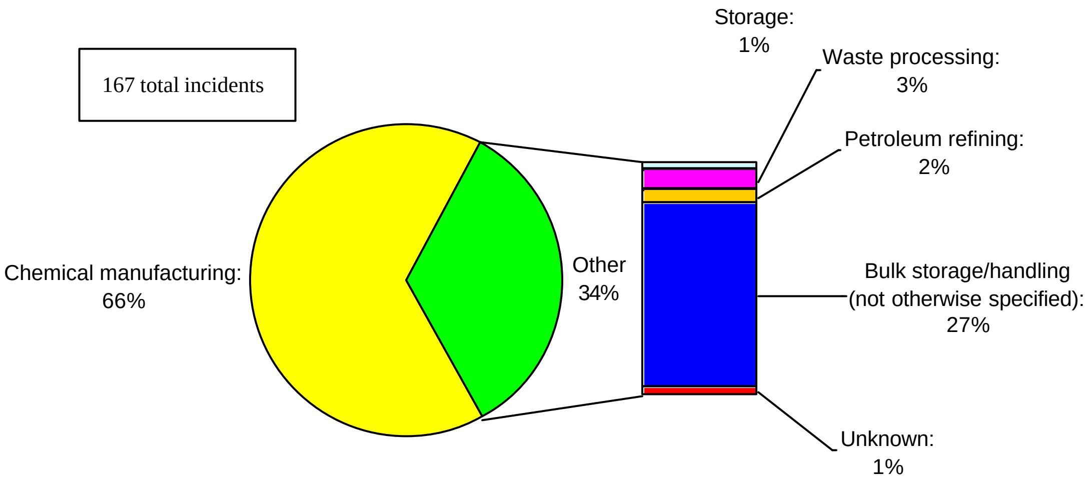

Figure 10. Industry profile, 1980–2001.

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 or 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.

Table 3

Common 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 classes	79

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

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 7.1). 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 12).[31]. 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 13). 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,

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[31] Photograph not available for website posting; it will appear in the printed copy.

waste, separation, and transfer equipment; and 10 percent, bulk storage drums. No particular equipment accounted for 8 percent of the data.

These data contradict a common assumption 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.

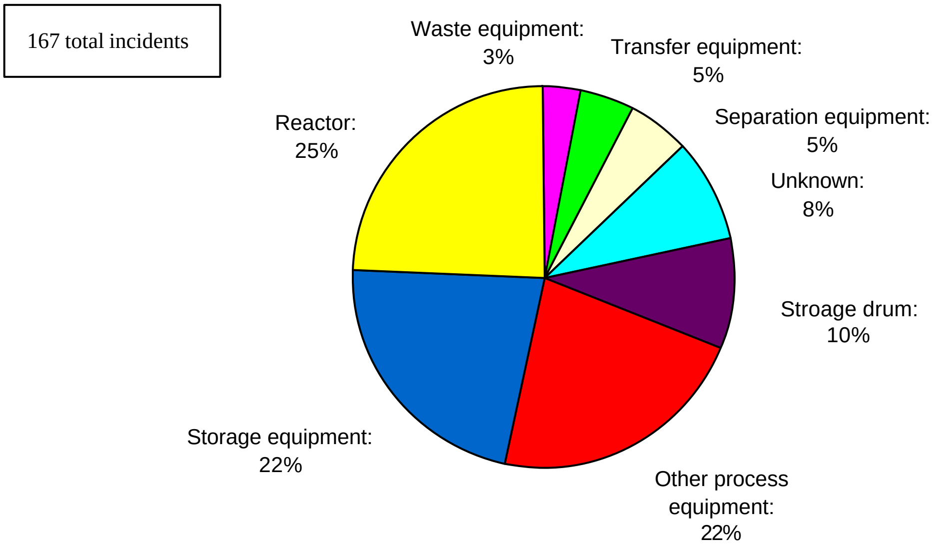

Figure 13. Equipment involved in incidents, 1980–2001.

BP Amoco Polymers, Inc.

On March 13, 2001, three people were killed as the result of a vessel failure and fire at the BP Amoco Polymers plant in Augusta, Georgia (Figure 14,[32] 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. 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.

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[32] Photograph not available for website posting; it will appear in the printed copy.

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.

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.

3.6.2 Causal Information

Causal[33] data are reported for only 37 of the 167 incidents. Analysis of this limited set of data revealed a variety of causes (Table 4). More than 60 percent of reactive incidents for which some causal information was available involved inadequate management systems for identifying or evaluating hazards. In the CSI

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[33] 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.

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).

Table 4

Analysis of Causal Information

Causes	**Frequency of Attribution**	
	No. of Incidents	Incidents With Causal Information (%) (a) (b)
Inadequate hazard identification	9	24
Inadequate hazard evaluation	16	43
Inadequate procedures for storage/handling of reactive chemicals	17	46
Inadequate training for storage/handling of reactive chemicals	10	27
Inadequate management of change (MOC) system to Identify/evaluate reactivity hazards	6	16
Inadequate process design for reactive hazards	6	16
Inadequate design to prevent human error	9	24
Inadequate company-wide communication of hazards	5	14
Inadequate emergency relief system design	3	8
Inadequate safe operating limits	3	8
Inadequate near miss/incident investigation	2	5
Inadequate inspection/maintenance/monitoring of safety critical devices in reactive chemical service	2	5
Previously unknown reactive hazards	1	3

(a) Causal data are reported for 37 of the 167 incidents.
(b) Total greater than 100 percent because each incident may have more than one cause.

4.0 NFPA Hazard Rating System

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

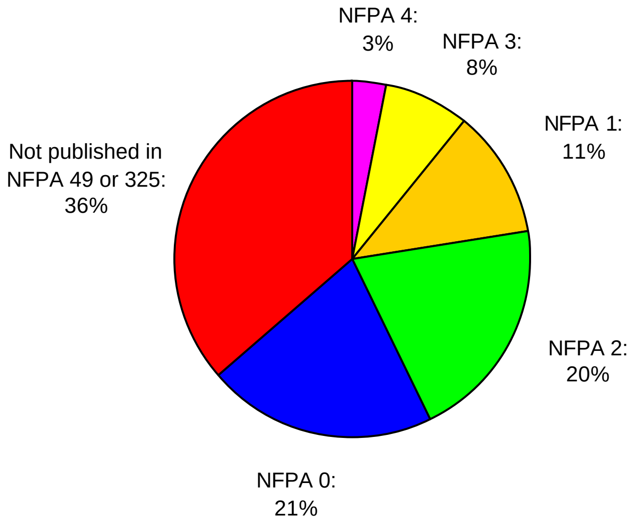

Figure 15. NFPA instability rating analysis (*formerly reactivity rating*) of incident data, 1980–2001.

The OSHA PSM Standard lists 137 highly hazardous chemicals–only 38 of which are considered highly reactive based on NFPA ratings “3” or “4”[34] (as defined in NFPA 704, Standard System for the Identification of the Hazards of Materials for Emergency Response).

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 (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 would address 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. The NFPA hazard rating system primarily relies on qualitative criteria and judgment to assign chemical

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[34] The PSM chemical list is based on ratings in NFPA 49 (1975). 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).

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.[35]

Table 5

NFPA-Defined Degrees of Instability Hazards

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

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

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.

(a) cal/g = calories per gram.

(b) W/mL = watts per milliliter.

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, 1996). Onset temperature, instantaneous power density (IPD; Hofelich et al., 1997),[36] 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 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.

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[36] 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]).

NFPA 49 is no longer issued in the NFPA Fire Code set, and the standard is no longer updated;[37] however, Standard 704 was updated in 2001. NFPA 49 information is available in the *Fire Protection Guide to Hazardous Materials* (NFPA, 1997).

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.

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[37] 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 OSHA 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.

There are OSHA standards 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 hazards associated with the products they produce 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 OSHA 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 OSHA PSM by identifying whether it was listed in PSM or was covered as a flammable chemical by OSHA definition.[38]

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

- In 30 percent of the incidents, the chemicals were covered under PSM.
- In 50 percent of the incidents, the chemicals were not PSM covered.
- In 20 percent of the incidents, it could not be determined whether PSM-covered chemicals were involved.

CSB was unable to determine from the incident data if a process was PSM covered.[39]

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

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[38] Processes that are 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.

[39] 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.

highly hazardous chemicals. Congress specified that highly hazardous chemicals included “toxic, flammable, highly reactive, and explosive substances.”

OSHA relied on several established lists–including the New Jersey Toxic Catastrophe Prevention Act (TCPA), the Delaware Extremely Hazardous Substances Risk Management Act, the European Communities 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 OSHA PSM Standard lists 131 distinct chemicals with toxic or reactive properties.[40] It includes 25 chemicals with an NFPA rating of “3” and 13 chemicals with an NFPA rating of “4.” PSM 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 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.

5.1.2.2 Process Safety Information and Process Hazard Analysis

The 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.

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

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

[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).

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.[41] It does, however, stipulate that an MSDS can be used to compile the data to the extent that it contains the information required. In 1996, OSHA issued a Hazard Information Bulletin cautioning that MSDSs do not always contain information about hazards from mixing or blending chemicals (OSHA, 1996).

Another requirement of the PSM Standard is 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.

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.

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

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 impose a fine. To substantiate a GDC violation, several criteria must be met,[42] 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.

To support a GDC citation, OSHA must establish employer or industry recognition of a hazard. Among other forms of evidence, industry recognition 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.[43]

5.1.4 Other PSM Initiatives

As a result of the joint OSHA-EPA 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

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

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

their respective lists of chemicals covered by process safety regulations. To date, however, neither OSHA nor EPA has modified process safety regulations to better cover reactive hazards.

Following the Napp incident, six labor unions[44] 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.

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[44] 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).

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 (40 CFR 68) to determine whether reactive substances should be added.

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.

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.[45]

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

- In 20 percent of the incidents, the chemicals were covered under RMP.

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

- In 60 percent of the incidents, the chemicals were not RMP listed.
- In 20 percent of the incidents, it could not be determined whether RMP-listed chemicals were involved.

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

5.2.2 Accidental Release Prevention Requirements (40 CFR 68)

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."[46] Consequently, the January 1994 RMP list of 130 chemicals does not contain any substances listed due to reactive hazards.

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

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 OSHA-EPA joint chemical accident investigation team to review the lists of substances subject to the PSM Standard and RMP regulation to determine whether reactive chemicals should be added.

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.

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)[47]. 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.

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.

The EPA 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.

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[47] 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.

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[48] 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 situations.

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[48] " 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.

However, only limited guidance is available on the following aspects of reactive hazards 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.
- 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.

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. 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,[49] 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.

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.

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

- *Rapid Guide to Chemical Incompatibilities*.
- ASTM Chemical Thermodynamic and Energy Release Program (CHETAH).

Responses to the CSB industry survey[50] 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. Such 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 having to conduct chemical testing. Survey responses showed that five of nine companies consider computer-based tools "not valuable." Only two of the surveyed companies use The Chemical Reactivity Worksheet.[51]

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

6.1.2 Chemical Incompatibility

Approximately 36 percent of incidents in the CSB data are related to chemical incompatibility. CCPS provides information on managing chemical incompatibility hazards in guidelines for chemical reactivity. It emphasizes the need to systematically examine possible chemical incompatibilities and describes the use of interaction matrices (CCPS, 1995a, p. 7; 1995b, p. 108).[52], [53] This guidance applies to chemical manufacturers as well as to other industries.

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[50] Appendix B describes the CSB industry survey.

[51] 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.

[52] 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).

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

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 or 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).

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 various 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.

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[54] use reactive chemical test data to identify hazards. (SOCMA membership includes many small- and medium-sized companies.)

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.

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[54] 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.

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, a substantial amount of test data have been generated by the chemical industry. One company visited by CSB had compiled a database of over 60,000 reactive chemical test results. Survey participants were asked if such data are shared with other companies.

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. 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.

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,[55] are attributed to inadequate hazard evaluation. In several cases, the hazard was known, but its

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

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.[56]

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 a general recommendation to evaluate any scenario not protected by high

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[56] 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).

integrity shutdown systems.[57] 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 that can be used 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.

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

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[57] 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.

procedural steps as opposed to deviations from intended equipment design. One company uses a "what-if" PHA protocol specifically designed to address reactivity hazards.

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 employ qualitative hazard evaluations.[58]

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.

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

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

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, changes in raw material specifications, concentration changes, process time changes, and changes in 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.

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.

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 case, 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.

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.

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 reactive hazard management.

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.[59] In 1989, ACC developed the Responsible Care Process Safety Code[60] to prevent fires, explosions, and accidental chemical releases. The code and its accompanying resource guidelines include a series of recommended 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.

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[59] 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.

[60] 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 each member company.

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.

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 to ACC annual reports on process safety incidents that meet specific criteria.[61] The ACC Process Safety Code Measurement System (PSCMS), established in 1996, contains data on

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[61] 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.

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.

7.1.2 SOCMA Guidance on Implementation

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 NACD Responsible Distribution Process

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.[62] 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.

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

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.

NACD (1997) has published an RDP implementation guide to assist member companies in developing programs. A self-evaluation and a third-party onsite MSV audit are required. In the last 3 years, NACD has expelled 20 companies because of noncompliance.

RDP 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 ensures 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 (i.e., addressing reactive mixtures of substances as well as single substances) of reactive hazards covered under the OSHA PSM Standard and EPA RMP regulation. However, there is no consensus on how the problems should be addressed–for example, by regulatory means, by voluntary efforts such as ACC's 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.)

8.1 Improved Coverage Under OSHA PSM

8.1.1 Highly Reactive Substance Classification

One approach to improve 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). Alternatively, multiple criteria such as heat of reaction and total pressure may be a better indicator of reactivity.

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.

8.1.2 Coverage Based on 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.

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[63] 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 concept of a safety case comes from the requirements of 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 that directive. 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.[64] The requirement for a safety case is initiated by a list of chemicals and a class of flammables. Like the hazard analysis 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.

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."

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[63] 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.

[64] 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 Improved Coverage Under 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, coverage under the OSHA PSM Standard and the EPA RMP regulation should be more compatible. EPA should seek the authority needed to allow it to address reactive hazard coverage in a manner compatible with any revised OSHA approach.

8.3 Regulatory Relief Absent Catastrophic Consequences

Physical processing conditions and even small amounts of extraneous materials (contaminants) that may have catalytic properties 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 Improved 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; 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, Sax’s Dangerous Properties of Industrial Materials*, and computerized tools (e.g., CHETAH, The Chemical Reactivity Work Sheet).

8.4.2 Improved 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 Improved Reporting Requirements

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 (40 CFR 68) 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 focus 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 performing a process hazard analysis. Given that reactive incidents are often caused by inadequate recognition and evaluation of

reactive hazards, improving reactive hazard management involves defining and requiring relevant factors (e.g., rate and quantity of heat and gas generated) to be examined within a process hazard analysis.

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

11. Publicly available resources[65] 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[66] 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.

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

[66] " 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., ASTM's CHETAH, NOAA's The Chemical Reactivity Worksheet).

  - 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 Firefighters

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

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

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)

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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 that is used 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 similar data to DSC. DTA uses temperature differences to generate test results; DSC has largely replaced the DTA technique as a screening tool for obtaining 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): A 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 chemical process safety: Systematic identification, evaluation, and control of reactive hazards at all phases of the production life cycle–from R&D to pilot plant, change management, and decommissioning; and for all types of operations–from storage or manufacturing to packaging or waste processing.

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 http://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 industry 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 site 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 correspondingly recognize that the conclusions are also 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. The site also has an extensive 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 Analysis of Practices for Reactive Chemical Hazard Management

C.2.1 Company A (Major Pharmaceutical Manfacturer)

C.2.1.1 Program Philosophy

- Reactive chemical hazard management is one element of an overall process safety program, but 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 Program

- 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 play a key role on the PHA team.
- The thermal hazards laboratory, in consultation with pilot-plant engineering, typically assess 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

- PHA 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 for review.

- 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 Program

- 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 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 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 Programs

- 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 only 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°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 good practices that are nonmandatory and 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 current 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 the topic of 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 for thermal hazard assessment and prevention.
- Prepare guidelines for thermal hazard assessment and prevention.
- Disseminate knowledge and methodologies to small- and medium-sized enterprises.
- 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.[67] 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.

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[67] 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 Abstract 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	Evaluation of reactive hazards and	Elsevier (Yoshida, Wada, and

Title	Contents	Source
Pyrotechnics	case histories	Foster)
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	Correlates the chemical structure of compounds to their 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 43 B 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	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

Title	Source	CSB Action
The Community Documentation Centre on Industrial Risk (CDCIR)	MAHB	Reviewed only
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 (CFOI)	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 1	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.[68] Table F-1 summarizes this information.

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 substances (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.

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[68] It is important to note that 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 is conservative in that it does not include fatalities that occurred to contractors or to personnel in other industries, such as petroleum refining, rubber products, paper products. Contractor fatalities are documented within BLS according to the services the contract company provides. For example, in the ARCO incidents there were 17 fatalities, 5 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 rather they were grouped under the construction SIC. Thus, these 12 contractor fatalities would not have been included in our analysis of BLS data.

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.

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 also 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 (^{o}C) above the maximum operating temperature of a process event under upset conditions (CCPS; 1995b; p. 93).

CCPS (1995b; p. 94) recommends more sensitive and sophisticated methods if screening calorimetry shows thermal instability at or near the temperature range of large-scale storage or processing. The next logical choice is adiabatic calorimetry,[69] which uses a larger sample and more advanced technology. This technique is more sensitive to detecting the onset temperature[70] for exothermic reactions, adiabatic temperature rise, and rate of reaction; it also can 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. CCPS (1995a; p. 13) suggests that when designing processes for conducting chemical reactions, all materials should 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

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[69] 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.

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

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 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.