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Recent Reactive Incidents and Fundamental Concepts That Can Help Prevent Them

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Introduction

Most chemicals are reactive under the right conditions. Reactivity — tendency of substances to undergo chemical change — is a highly desirable characteristic because it allows a variety of chemical products to be made under relatively moderate process conditions, saving time and money. 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. This paper highlights six reactive incidents that caused widespread impacts. They are representative of reactive incidents identified by United States Chemical Safety and Hazard Investigation Board (CSB) — during its hazard investigation into reactive hazard management — and illustrate the diversity of reactive hazards. These and other incidents across the United States underscore the need to improve the management of reactive hazards. This paper will also discuss some fundamental concepts that aid in preventing reactive incidents.

Napp Technologies

On April 21, 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[1]/OSHA[2], 1997). Additionally, firefighting generated chemically contaminated water that ran off into a river. The property damage exceeded $20 million. Employees were performing 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

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[1] United State's Environmental Protection Agency (USEPA)
[2] Occupational Safety and Health Administration (OSHA)

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).

National Fire Protection Association (NFPA) rates aluminum powder as "1" and sodium hydrosulfite as "2" for reactivity[3]. These chemicals are not included on OSHA's process safety management standard (PSM) list and are not regulated under that standard[4]. The product of the mixture between aluminum powder and sodium hydrosulfite, a Gold Precipitation Agent was 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" for instability. The incident raised questions regarding the use of the NFPA instability rating system as the sole basis for regulating reactive hazards.

The Napp incident, in particular raised concerns about reactive hazards on a national level. After the incident, six labor unions petitioned OSHA for emergency revision of PSM, stating that it failed to cover reactive chemicals. The Chemical Manufacturers Association (now the American Chemistry Council (ACC)) and the American Petroleum Institute (API) disagreed with the unions' petition. They submitted a letter to OSHA, which indicated support of PSM as an effective standard. ACC and API identified several alternatives for regulating reactives, but concluded that each presented significant technical difficulties, significant cost, and minimal benefit. For these reasons, ACC and API opposed any revisions to OSHA PSM.

BPS, Inc.

About two years after NAPP, 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 (EPA/OSHA, 1999). Property damage was extensive. Major roads were closed; and Mississippi River traffic was halted for nearly 12 hours.

This incident occurred on May 8, 1997. BPS–a bulk storage and distribution facility was repackaging an organic pesticide, AZM 50W. The chemical was being offloaded into a warehouse when 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 the explosion occurred. A collapsing cinderblock wall caused the firefighter fatalities.

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 (EPA/OSHA, 1999). The heat caused the material to decompose and release flammable vapors, which resulted in the explosion. This incident illustrates that severe reactive incidents can occur even at companies that are

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[3] NFPA 704, System for the Identification of the Hazards of Materials for Emergency Response, 2001, defines five degrees of hazards on scale of "0" to "4" with "0" representing no special hazard and "4" representing highest degree of hazard.

[4] In 1992, OSHA promulgated its process safety management (PSM) standard. The standard covers processes containing 137 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 NFPA because of their instability rating of "3" or "4".

engaged in the simple storage and handling of chemicals[5]. The facility was not covered by OSHA PSM, and AZM50W does not have an instability rating published by NFPA.

Morton International

Nearly a year after the BPS incident (April 8, 1998), a reactive incident occurred at Morton International, Inc., in Paterson, New Jersey, resulting 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 (CSB, 1999).

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 (*o*-NCB) and 2-ethylhexylamine (2-EHA) were being reacted. This material subsequently ignited and caused the explosion and fire.

Morton's safety programs for managing reactive hazards did not cover the potential for a catastrophic runaway reaction in the production of Yellow 96. The Patterson plant files contained information discovered by Morton's United Kingdom research facility that indicated that the desired reaction to form Yellow 96 from *o*-NCB and 2-EHA was exothermic, and that Yellow 96 would begin to decompose rapidly (runaway) at temperatures close to the upper operating temperature. However, operators and supervisors were unaware that a dangerous decomposition reaction was possible. This lack of understanding of the reactive hazards resulted in design flaws in the kettle and the omission of safe operating instructions for producing the dye.

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 (CSB, 1999). This investigation validated 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.

Concept Sciences, Inc. (CSI)

On February 19, 1999, an explosion at Concept Sciences, Inc. (CSI), in Allentown, Pennsylvania, killed five persons, including one worker at an adjacent business (CSB 1, 2002). Fourteen persons, including six firefighters, were injured. The facility was completely destroyed, and several other businesses in the vicinity suffered significant property damage. The blast also shattered windows of homes in a nearby residential area.

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

CSI was aware of HA's hazards, but did not adequately evaluate these hazards during process development to prevent the incident. The explosive decomposition hazard of HA was not adequately translated into CSI's process design, operating procedures, mitigation measures, or precautionary instructions for operators. The offsite fatality dramatically illustrates that reactive incidents can affect the public.

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[5] A reactive incident can occur virtually anywhere chemicals are manufactured or used.

Furthermore, this incident demonstrates that reactive hazard management requires careful and comprehensive application of current engineering codes, guidelines, and good practices throughout all phases of the process life cycle[6]. Based on many years of research and experience, these tools are well established and represent the fundamental principles of chemical process safety. The incident also shows that reactive incidents can cause severe public impacts[7].

HA is not a listed chemical under EPA's Chemical Accident Prevention Regulations (40 CFR Part 68). HA is an OSHA PSM-listed chemical, and has an NFPA instability rating of "3."

Whitehall Leather Company

About three months after the CSI incident, on June 4, 1999, the inadvertent mixing of two incompatible chemicals caused a toxic gas release at Whitehall Leather Company in Whitehall, Michigan. 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." He assumed that sodium hydrosulfide was pickle acid and directed the truck driver to the pickle acid tank. (The material commonly known as pickle acid onsite was actually ferrous sulfate.) Hydrogen sulfide gas was produced when the hydrosulfide solution was unloaded into the ferrous sulfate tank (unintended reaction of incompatible materials). The truck driver was exposed to the gas and died; one Whitehall Leather employee was injured (National Transportation Safety Board, NTSB, 2000).

The Whitehall Leather incident illustrates that reactive hazards other than thermal runaways in reactors[8]—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.

BP Amoco Polymers

On March 13, 2001, three people were killed from a vessel failure and fire at the BP Amoco Polymers plant in Augusta, Georgia. The facility produces plastics. Start-up operations in a process make 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 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 a period of several hours, the vessel became pressurized. The incident occurred as workers attempted to open a cover on the pressurized vessel (CSB 2, 2002).

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[6] All phases of a process from its conception, through chemical and process research and development, engineering design, construction, commissioning, commercial operation, major modification, to decommissioning.

[7] The definition of public impact is based on the criteria for reporting offsite incidents in EPA's RMP regulation (40 CFR 68.42a). "Public" includes anyone except employees or contractors at the facility.

[8] A common misconception within industry is that a majority of reactive incidents involve chemical reactor vessels and these incidents are primarily the result of runaway reactions. In reality, reactive incidents occur in a variety of chemical processing and storage equipment–including reactors, storage tanks, and bulk storage drums from various types of reactive hazards–chemical incompatibility, runaway reaction, and impact or thermally sensitive materials.

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. The incident also involved an endothermic (or heat consuming) reaction rather than the more traditional highly exothermic (or heat producing) runaway chemical reaction. The BP Amoco incident demonstrates the need for a systematic procedure that specifically identifies and controls hazards from unintended or uncontrolled chemical reactions throughout a process life cycle.

Fundamental Concepts in Reactive Incident Prevention

Each of the incidents described above vividly illustrate the tragic potential of reactive hazards. Also the incident descriptions show that these hazards may occur at different stages of the process life cycle; and in a variety of operations, such as chemical manufacturing, waste processing, or bulk storage, handling, and distribution. "What is necessary" is a systematic management approach, which incorporates the following fundamental concepts — hazard identification, hazard evaluation, and hazard control — throughout the process life cycle. The following discussion briefly highlights some practices based on these fundamental concepts that can aid in reactive incident prevention[9] (see table 1).

The identification of reactive hazards requires a well thought out, detailed strategy, beginning with the literature search and proceeding to screening tests and then to more sophisticated tests (CCPS, 1995). Table 2 lists several useful techniques for identifying reactive hazards. The purpose of this table is to illustrate that no one technique or method can fully uncover the reactive hazards of a chemical (s). A variety of techniques and methods need to be considered.

Literature searches provide insights into the general properties of chemicals and the hazardous properties of individual chemicals, either alone or in combination with other substances. They highlight the hazards of common industrial reactions, such as polymerization, decomposition, acid-base, oxidation-reduction, and reactions with water. These searches also provide information on "well-known" reactive incidents, and possible prevention and mitigation measures.

The chemical structure (i.e., the presence of unstable, high-energy functional groups) of a substance may indicate the presence of possible reactive hazards. For example, relative degree of unsaturation, high proportions or high local concentrations of oxygen or nitrogen atoms consecutively bonded, and nitrogen-to-halogen bonds indicate the potential for releasing substantial energy.

In some circumstances, thermochemical calculations can aid in estimating the capability of an intended or unintended reaction to release energy. Heat of reaction, heat of decomposition, adiabatic temperature rise, and oxygen balance are key indicators of possible reactive hazards.

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[9] Fundamental concepts, process safety practices and principles discussed in this paper are taken from various literature sources produced by organizations such as American Institute of Chemical Engineer's Center for Chemical Process Safety (CCPS) and Institution of Chemical Engineers (IChemE), a CSB survey of reactive hazard management practices within industry, and CSB site visits to companies with reactive hazard management programs.

Table 1: Some Practices for Managing Reactive Hazards

Hazard Identification	Hazard Evaluation	Hazard Control
Obtain basic chemical data (e.g., material safety data sheets, manufacturer's data) Identify unstable chemical structures, polymerizable compounds, oxidizing and reducing agents, etc. Identify chemical interaction hazards Obtain experimental chemical reactivity test data through screening tests or literature (e.g., DSC, DTA) Obtain prior incident data associated with chemical (s)/process of concern Obtain thermodynamic data (e.g., max heat of reaction, rate of gas evolution, rate and quantity of heat generated, adiabatic temperature rise) Use computer-aided tools to assist in determining reactive hazards (e.g., NOAA reactivity worksheet, CHETAH) Use expert judgment to go through collected data and identify any potential reactive hazards	Interpretation of reactivity test data and need for more sophisticated follow-up tests Consequence modeling to estimate extent of hazardous effects and impact severity Determine process deviations/hazardous reaction scenarios through formal hazard reviews (e.g., HAZOP, checklists, what-if analysis) Determine worst-case scenarios	Inherently safer process design and process chemistry (e.g., use substitutes, less amount of hazardous substances, use moderate reaction conditions) Documentation of process knowledge (e.g., well defined technical information/ operating procedures) Provide adequate lines of defense (e.g., emergency relief devices, interlocks, detection and suppression systems) Preventive maintenance on equipment, piping, and instrumentation Provide adequate personnel training and communication of hazards Revalidation of formal hazard reviews after changes to process (management of change) Incident follow-up (e.g., ensure that proper changes are made to eliminate hazardous conditions that led to an incident)

Table 2

Reactive Hazard Identification Methods (CCPS, 1995)

Source	Method
Literature surveys	Reactivity data Common incompatibilities Unstable structures within chemicals Known reactive hazards (i.e., unsafe process conditions or deviations) Incidents Recognized prevention or mitigation measures
Thermo-chemical calculations	Oxygen balance Heat of reaction Maximum pressure/rate of pressure rise Adiabatic temperature rise Reaction rate constant
Computer programs	CHETAH
Incompatibility analysis	Chemical Interaction Matrices
Screening tests	Differential scanning calorimetry (DSC) Differential thermal analysis (DTA) Thermo-gravimetric analysis (TGA) Mixing calorimetry
Sophisticated tests	Adiabatic calorimetry Reaction calorimetry

Theoretical evaluations generally consider only thermodynamic potential, not the kinetics (or rate) of a hazardous reaction. Establishing the rate of reaction often requires chemical testing; additionally, rates are influenced by process abnormalities, such as overcharging or undercharging, variations in concentration, or abnormal heating or cooling. These site-specific factors are critical to understanding the reactive hazard.

Chemical testing–including screening tests and sophisticated calorimetry–can be used either to identify or to evaluate hazards. Testing can precisely measure thermal stability characteristics, establish a safe operating envelope for reaction systems, evaluate consequences of a runaway reaction, and determine reaction kinetic (or rate) effects. It allows for the possible impact of a wide range of process-specific conditions to be directly evaluated in the lab, before scaling up to commercial production. These conditions include variations in temperature, pressure, reaction time, catalysts, concentrations, or contaminants; effects of mischarging; variations in cooling, stirring and possibilities for inadvertent mixing of incompatible materials.

Hazards that have been identified must be evaluated to understand what can go wrong and the potential consequences. A hazard evaluation is a study of how hazards would affect process development and operation and how these hazards can be eliminated or controlled through good science, sound technology, and recognized professional practices. A prerequisite for any process hazard evaluation is full knowledge of the chemistry of the process. A variety of approaches are used to evaluate reactivity hazards. The following are key aspects of any reactive hazard evaluation (CCPS, 1992):

- Interpretation of the thermal decomposition characteristics of the raw materials, products, and by-products
- Use of expert knowledge to understand chemical test data (evaluate screening test data and need for further sophisticated calorimetry)
- Use of past process development and operation experience
- Defining the process and operating conditions
- Analysis of normal process conditions
- Assessing the consequences from deviations and failures, in terms of their severity and likelihood
- Knowledge of boundary process conditions and engineering parameters
- Establishing appropriate layers of protection
- Use of industry guidelines and good practices
- Determining worst case scenarios.

Reactive hazards should continually be evaluated throughout the process life cycle.

Once hazards are identified and evaluated, they can be eliminated or controlled. The following measures are typically used to eliminate or control hazards (ICHEME, 1997):

- Inherently safer design
    - Modify process chemistry to avoid high concentrations of hazardous materials
    - Use less hazardous raw materials or intermediates
    - Minimize hazardous inventories of raw materials, intermediates, and products
    - Isolate storage of highly hazardous materials
    - Transport combustible powder as slurry or replace with granules or flakes
    - Change from batch to semi-batch processing
    - Use hazardous substances under less hazardous conditions (reduced pressure, temperature, etc.)
    - Design the plant to contain maximum pressure
    - Simplify parts of complex plant design
    - Revise confusing operating procedures (also have translations into other commonly spoken languages by operators)
    - Replace active safeguards with passive ones
    - Use buddy system for hazardous operations such as cleaning of spills, enclosed spaces.
- Protective and preventive measures
    - Adequate cooling systems
    - Proper emergency relief systems
    - Adequate safety interlocks, detection and suppression systems (e.g., reaction inhibition capabilities)

    - Secondary containment/blast protection
    - Safe distance siting for buildings
- Organizational procedures
    - Proper personnel training (operations and emergency situations)
    - Adequate supervision of operators
    - Proper preventive maintenance and management of change
    - Prompt investigation and communication of incidents

The key to improving reactive hazard management is to establish a flexible, systematic, performance-based approach that effectively incorporates fundamental process safety principles. Such an approach would allow safety systems to be developed that reduce the overall risk (to workers, public, environment) to a level, which is as low as reasonably practicable and ultimately lead to prevention of reactive incidents.

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