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MANAGING CHEMICAL REACTIVITY HAZARDS

The Environmental Protection Agency (EPA) is issuing this Alert as part of its ongoing effort to protect human health and the environment. EPA is striving to learn the causes and contributing factors associated with chemical accidents and to prevent their recurrence. Major chemical accidents cannot be prevented solely through regulatory requirements, but by understanding the fundamental root causes, widely disseminating the lessons learned, and integrating these lessons learned into safe operations. EPA publishes Alerts to increase awareness of possible hazards. It is important that facilities, SERCs, LEPCs, emergency responders and others review this information and take appropriate steps to minimize risk.

Chemical Safety ALERT

PROBLEM

Many materials used in industrial facilities can pose chemical reactivity hazards. Conventional management systems frequently do not adequately address the unique behavior of materials that may react to cause excessive temperature or pressure excursions or toxic or corrosive emissions.

Incidents occur not only at chemical manufacturing and processing plants, but also at water treatment plants, swimming pools and spas, metal processing facilities, and mechanical equipment manufacturing facilities.

PURPOSE

The purpose of this alert is to introduce facilities to the methodology for chemical reactivity hazard management as developed by the Center for Chemical Process Safety (CCPS) and made available in a book *Essential Practices for Managing Chemical Reactivity Hazards*. This alert is a follow-on to the recent EPA alert which discusses the CCPS method for screening facilities for chemical reactivity hazards. While the first EPA alert focused on identifying chemical reactivity hazards, this alert focuses on the management of the hazards. This alert does not cover all ten essential management practices, but highlights some common management deficiencies.

This alert assumes that the reader has determined that a chemical reactivity hazard exists at the facility and has:

- Explored opportunities, such as substituting inherently safer chemicals, to reduce or eliminate reactivity hazards;
- Gathered available information from available sources such as MSDS.
- Completed preliminary screening to identify chemical reactivity hazards (see the EPA companion alert *Identifying Chemical Reactivity Hazards: Preliminary Screening Method* for additional information);
- Developed a matrix indicating which chemicals react with each other, including the process or operating area where the chemicals are located;
- Gained management commitment to the safe operation of the facility;
- Ensured resources are available to ensure physical plant is designed or modified as necessary to mitigate chemical reactivity hazard

exposure;
- Implemented a sound training program, operating procedures, and hazard communication program; and
- Implemented an active safety audit program.

INCIDENT EXAMPLES

A number of incidents involving reactive chemicals have resulted in accidental chemical releases, fire, and explosions. The following section describes several recent incidents.

September, 2004 - A transport vessel containing a mixture of recovered monomer was observed to be relieving pressure via the pressure relief valve. The relief valve was lifting (relieving) as a result of the pressure in the vessel exceeding the relief valve setting. The increased pressure was caused by an increase in the temperature within the container. This temperature increase was caused by a polymerization reaction of the monomer mixture. A water deluge was applied to cool the transport vessel and minimize the vapor cloud dispersion. The accident investigation revealed a blockage in the injection feed line which obstructed the addition of inhibitor into the monomer mixture. The immediate term procedure modifications were to manually control the inhibitor injection and, also, to verify inhibitor concentration after loading the transport vessel. The longer term modification includes automatic inhibitor addition with post loading verification of inhibitor concentration.

March, 2004 - Operations personnel were preparing to unload a railcar of methyl chloride when they discovered a product identification label attached to the railcar dome reading “methylene chloride.” Because the label and placards were not in agreement, personnel quarantined the railcar until proper chemical verification could be made with the supplier and the facility quality control laboratory. The verification confirmed that the railcar placarding for methyl chloride was correct. Close attention to material identification used triggered personnel to take steps to verify the contends of the railcar, thereby reducing the likelihood of a serious process safety incident.

March, 1997 - The facility provides an antimony catalyst service. A 1000-pound horizontal cylindrical container was in the process of having a small sample drawn into an open container. However, the handle of the quarter-turn valve leading to the dip-leg had been removed by the customer before returning the container of spent catalyst. The employee opened the valve using a vice-grip tool but was then unable to close the valve. Escaping spent antimony catalyst was believed to have reacted with moisture in the atmosphere, to create hydrogen chloride. The incident investigation led to a management-of-change review, revised sampling procedures and training and a closed sampling system that discharges to a scrubber system. This incident illustrates the need for particular attention to operations that involve removing material from the enclosed system, such as when venting, draining or sampling.

July, 1994 - New steel saddles (internal saddle shaped devices used to promote mixing) were installed in the direct-contact chiller vessel ahead of the chlorine compressor. The saddles should have had no corrosion protection coating, but they did have an undetected coating of mineral oil. When the main stream of chlorine and the chilling material, which was also chlorine, entered the chiller vessel, there was an intense exothermic reaction between the chlorine and the mineral oil which burned through the vessel wall, releasing chlorine to the atmosphere. The subsequent incident investigation, the management-of-change review, and the operating procedure revision focused on verification that mechanical equipment that may come into contact with chlorine is confirmed to be free of any material with which chlorine may react. This incident highlights the need to consider not only process chemicals, but other chemicals and contaminants as well.

MANAGEMENT OF REACTIVE HAZARDS

The consequences of a reactive chemical incident can be severe. In a 2002 study, the U.S. Chemical Safety Board (CSB) collected detailed information on 167 serious incidents that occurred between 1980 and 2001. EPA reviewed CSB's information and identified the most commonly reported management deficiencies. In order of frequency, the reported management deficiencies are:

- Operating Procedures, Safe Operating Limits and Training
- Hazard Identification and Evaluation
- Human Factors
- Management of Change
- Emergency Relief Equipment and Controls
- Process Design
- Process Knowledge
- Incident Investigation
- Process Hazard Analysis
- Safety Auditing
- Equipment Maintenance

In their Reactive Hazard Investigation report, CSB points to the limited availability of accurate reactive chemical incident data. In spite of these limitations, we believe that this data set is useful in identifying areas of management systems that need to be strengthened in order to address the hazards of reactive chemicals.

To assist facilities in managing these risks, the Center for Chemical Process Safety (CCPS) sponsored the concept book *Essential Practices for Managing Chemical Reactivity Hazards* and with the support of its government and industry partners has made this book available free of charge from the Internet. Chapter 4 of this book discusses ten essential practices for managing chemical reactivity hazards. This alert does not cover all ten management practices but highlights some common management deficiencies.

Recommendations for strengthening management systems include:

Communicate and Train on Chemical Reactivity Hazards

Training activities and materials should incorporate the hazards of chemical reactivity and provide information relevant to workers directing and performing process operations. The following are some suggestions for improving communication and training about reactive hazards within a facility:

- State not only the steps required to correctly execute the operation, but also the consequences of deviation. Develop likely scenarios such as incorrect charging, contamination of the process, or operating the process in the wrong range.
- Integrate information about chemical reactivity hazards into the operating procedures and instructions, rather than separately appending it to the instructions.
- Clearly state safe operating limits and the actions to be taken if operating deviations occur.
- Because concepts concerning reactivity hazards may be unfamiliar to some operating staff, these concepts should be clearly and simply worded.
- Chemical reactivity hazards information should be included in the facility's material safety data sheet (MSDS) and, if necessary, described in detail in instructions accompanying the MSDS.
- Share training materials with all operating personnel, including contractors.
- Facility management should ensure that training is understood by employees and contractors.

Identify Process Controls and Risk Management Options

The materials receiving and transfer system should be designed to guard against inadvertent mixing or incorrect handling.

- Material receipt - Is a procedure in place, possibly sampling, to check the material received to ensure that it is the correct material?

- Connection points- Is the connection clearly marked and/or color coded to guard against delivering to the wrong point? Incompatible couplings may also have an application.
- Have piping manifolds, including sampling lines, blow-down and venting or flaring systems been checked to guard against cross connections that can lead to inadvertent mixing?
- If incompatible materials are not handled in dedicated systems, are there positive isolation methods (spectacle blinds, drop-out, double block and bleed valve stations) used to prevent inadvertent mixing?
- Positive Materials Identification (PMI) - Has the material handling equipment been checked to ensure that it is suitable for the material to which it is exposed? In addition to the piping, vessels, pumps and valving, the internal trim, packing, and lubrication and sealant must be considered.

Appropriate safeguards should be considered to minimize hazards related to storage of reactive materials.

- Can the material deteriorate and become unstable because of the ambient temperature being too high, or too low, or because of excessive shelf time?
- If containment is breached, will materials become exposed to air or water to which they are reactive?
- Are incompatible materials stored the proper distance apart, or otherwise isolated?
- Can breached containers allow incompatible chemicals to mix and react?
- Has equipment used in the storage area been evaluated to ensure that it will not act as a heat or ignition source or cause instability (example - fork-lift truck exhaust in a dusty environment)?
- Are sensors and alarms located in the storage to alert personnel in the event of a release or slow leak?

Manage Process Knowledge

Technical information pertaining to fire protection, safety, health and environmental protection should be freely exchanged between organizations within industry and by technical societies.

- Does the facility management have at least one person designated to explore available information on chemical reactivity hazards that may pertain to their operations?
- Is information gathered from the above sources distilled down into an understandable form and made available to persons that may be involved with or exposed to the hazards of reactive chemicals present at the operating facility?
- Is every opportunity taken to upgrade operating procedures and instructions as new information becomes known?
- Is facility management strongly encouraged to contribute its own new information, including lessons learned and near-misses to others within industry?

Conduct a Process Hazard Analysis (PHA)

Many methods of conducting a PHA are suitable for assessing the hazards associated with operation of facilities involving reactive materials or mixtures. Several methods, such as “hazard and operability” and “what-if,” rely on a base set of questions for identifying risks. These base sets of questions should be expanded to include aspects that may be unique to reactive chemicals. Additionally, any process change that is made should receive a management of change (MOC) review.

Consider Abnormal Situations

The severity of many chemical accidents can be attributed to a reluctance to seriously consider all scenarios and to develop an appropriate action plans. Identifying and evaluating deviations that may occur and developing appropriate responses must be thought out before the fact. Possible abnormal situations must be documented and incorporated into instructions and training for operating personnel and for emergency responders. Otherwise, there is likely to be no response or an inadequate one. Some questions that should be

considered:

- What out-of-control conditions are possible? What remedial steps are authorized and by whom?
- What firefighting actions may be taken? What actions should be avoided?
- Is emergency response equipment appropriately located and accessible in all types of situations?
- Which neutralizing or mitigation initiatives may be taken?
- What secondary hazards may result from pressure relief or blow-down systems?
- What contaminants are likely to be encountered?

Conduct Frequent Audits

Safety, health and environmental (SHE) audits can serve a number of invaluable functions, including verification that the concepts of reactive chemical hazards are understood by operating personnel and have been built into the operation. The SHE audit may be the last line of defense against an accident. In verifying that the management system is reliable, the SHE audits can also serve as an excellent training activity for key personnel and for "guest" audit participants. Audits provide an opportunity for input from individuals in all levels of the organizations. Audit teams must also include at least one person with a good understanding of the methods for identifying chemical reactivity hazards. Team members should be familiar with the different elements of a sound management system and be able to determine if each element is functioning as intended. The effectiveness of the training programs and the operating procedures should be a focal point of the audit program.

RECOMMENDED READING

Essential Practices for Managing Chemical Reactivity Hazards – 2003, 194 pages, – Chemical Center for Process Safety (CCPS).

CCPS has teamed with US OSHA, US EPA, the American Chemistry Council, the Synthetic Chemical Manufacturers Association, and Knovel corporation to make this important new CCPS concept book available for free on the Internet. "Essential Practices" identifies a simple process to determine if your operation may be at risk of a chemical reactivity incident, and then guides you to resources to manage that risk. Persons wishing free online access to this book will need to follow a one-time sign-up procedure through Knovel, CCPS's on-line book distributor, prior to gaining access to the document.
http://info.knovel.com/ccps/

Chemical Safety Alert: Identifying Chemical Reactivity Hazards Preliminary Screening Method – 2004, 5 pages -- US EPA.

The purpose of this alert is to introduce small- and medium-sized facilities to a simple method developed by the Center for Chemical Process Safety (CCPS), published in Essential Practices for Managing Chemical Reactivity Hazards, to screen facilities for chemical reactivity hazards.
http://yosemite.epa.gov/oswer/ceppoweb.nsf/vwResourcesByFilename/flowchart.pdf/$File/flowchart.pdf

A Checklist for Inherently Safer Chemical Reaction Process Design and Operation What You Need to Know – 2004, 8 pages – Chemical Center for Process Safety (CCPS).

CCPS has developed this free pamphlet as a summary of basic principles for safe operation of chemical reaction processes.
http://www.aiche.org/ccps/pdf/CCPSAlertChecklist.pdf

Reactive Material Hazards What You Need to Know – 2001, 11 pages – Chemical Center for

Process Safety (CCPS).

CCPS has developed this free pamphlet to help safety managers, chemists, and engineers determine whether a process could have a chemical reactivity hazard and what they should do to prevent potential hazards.
http://www.aiche.org/ccps/pdf/reactmat.pdf

SOME USEFUL WEBSITES

OSHA Reactives Alliance
http://www.osha.gov/dcsp/alliances/reactives/reactives.html

OSHA Chemical Reactivity Safety
http://www.osha.gov/dep/reactivechemicals/

Mary Kay O'Connor Process Safety Center– Reactive Chemical Research
http://process-safety.tamu.edu/research/reactivechem_lab/RC_home.htm

National Oceanic and Atmospheric Administration (NOAA) Chemical Reactivity Worksheet
http://response.restoration.noaa.gov/chemaids/react.html

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