Reactive Chemical Hazard – an Overview

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The infamous Bhopal incident – is a case of Reactive Chemical Hazard; reactivity of isocyanates in general and Methyl Isocyanate in particular with water. Chemical reactions are the very breath of life of the chemical industry. The capability of chemical substances to undergo reactions, or transformations in their structure, is central to the chemical processing industry. Safely conducting chemical reactions has to be and is the core competency of the chemical manufacturing industry

Definition

Reactivity is the ability, or propensity under certain conditions, of a pure chemical or a mixture of chemicals to undergo chemical change or combine with other chemicals. The nature of some chemicals to be highly reactive can be very beneficial, and this reactivity makes possible a wide variety of synthesized products and a high standard of technology.

United States Chemical Safety Board (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.

Chemical Reactivity

Reactivity is not necessarily an intrinsic property of a chemical substance. The hazards associated with reactivity are related to process-specific factors, such as

1. operating temperatures,
2. pressures,
3. quantities handled,
4. concentrations,
5. presence of other substances,
6. and impurities with catalytic effects.

However, uncontrolled reactivity or lack of knowledge about reactions has led to numerous incidents. While it is generally accepted that reactive chemical incidents pose a significant safety problem, however there is little agreement on how to regulate or implement a reactive hazard management program

Certain incidents have woken up the regulatory authorities and industrial forums in USA and Europe to the problem. The incidents showed up gaps in existing regulations notably those by NFPA, OSHA, EPA - USA and Health & Safety Executive, UK, EU commissioners, *NFPA 491: Guide for Hazardous Chemical Reactions, NFPA 49: Hazardous Chemicals Data,NFPA 491M* Manual of Hazardous Chemical Reactions, OSHA, Process Safety Management (PSM) Standard (29 CFR 1910.119), EPA Accidental Release Prevention Requirements: Risk Management Programs (RMP; 40 CFR 68), Soveso directive II 96/82/EC, amendment 2003/05/EC, 1488/94/EC, 93/67/EEC, COMAH (Control of Major Hazard Regulations) HSE,UK, Chemical Reaction Hazards and the Risk of Thermal Runaway – HSE,UK Some of the incidents are mentioned below in brief.

1.

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. and chlorine releases lasted 3 days. Over 25,000 people were evacuated, and 275 people went to the hospital with skin burns and respiratory problems.

2. Georgia-Pacific

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.

This is for a product that is produced in hundreds of facilities worl wide. Number of such incidents have happened in India and not reported, the author has witnessed one and seen the aftermath of another.

3 NAPP technologies

Five workers were killed when a blender exploded, facility destroyed.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. 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 (MSDS) on the chemical from the company contracting with Napp to produce the material gave it an NFPA rating of “3.”The Napp incident raises questions regarding use of the NFPA rating system as the sole basis for regulating reactive hazards

4. Morton Incident

Morton International, Inc. (now Rohm & Haas) NJ Plant. The explosion and fire were the consequence of a runaway reaction, which over-pressured a 2000 gallon capacity reactor 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 area with a yellow-brown mixture of compounds that included Yellow 96 Dye and *O*-NCB. Yellow 96 Dye was produced by reaction of *ortho*-nitrochlorobenzene (*O*-NCB) and 2-ethylhexylamine (2-EHA). The dye is used to tint petroleum fuel products.The investigation team determined that the reaction accelerated beyond the heat-removal capability of the kettle. The initial runaway reaction was most likely caused by a combination of the following factors:

(1) Reaction was started at a temperature higher than normal,
(2) Steam used to initiate the reaction was left on for too long, and
(3) Cooling water to control the reaction rate was not initiated soon enough.

KEY FINDINGS

a. Morton's initial R & D for the Yellow 96 process identified the existence and described the two exothermic chemical reactions that can occur:
b. The desired exothermic reaction, to form Yellow 96, is initiated at 38°C and begins to proceed rapidly at a temp. of approx. 75°C
c. Undesired, exothermic reaction that results from the thermal decomposition of the Yellow 96 product, is initiated at an onset temperature 195°C (383°F).
d. Neither the preliminary hazard assessment conducted by Morton in the design phase - 1990 nor the process hazard analysis conducted -1995 addressed the reactive hazards of the Yellow 96 process.
e. PSM provided to plant operations personnel and the process hazard analysis team did not warn them of the potential for a dangerous runaway reaction.
f. The hazards of previous operational deviations were not evaluated.
g. Morton did not follow their Management of Change procedures to review changes made in reaction kettle and batch size.

5. MFG Chemicals

This was first attempt to make a production-scale batch of triallyl cyanurate (TAC), a rubber chemical. Accident occurred when a self-accelerating or "runaway" chemical reaction rapidly pressurized a 4000-gallon reactor,emergency vent opens, releasing allyl alcohol and allyl chloride directly into the atmosphere. More than 200 families were evacuated, 154 people decontaminated and treated for chemical exposure to toxic allyl alcohol and allyl chloride

MFG, was producing TAC under contract with GP Chemical, had not fully evaluated the hazards of the TAC-producing reaction, including a review of readily available technical literature. published reports of two previous runaway reactions and fires that occurred during attempts to produce TAC.

6 First Chemical Corporation

The incident caused the rupture of a 145-foot-tall distillation column used to refine mononitrotoluene caused the explosion and fire at the facility. The explosion propelled the top 35 feet of C-501—both the vessel head and approximately 30 feet of the cylindrical shell—offsite**.** A large column sidewall fragment hit a storage tank about 500 ft. away, resulting in a fire in and around the vessel. The tank held more than two million pounds of p-MNT. The cooling tower for the unit was also struck by debris and caught fire. The pressure of the explosion damaged a number of buildings onsite, including the control room.The explosion propelled large fragments from the vicinity of the column. A piece of shrapnel struck a pipe rack directly above a 500,000-pound anhydrous ammonia tank onsite. A 6-ton piece of column sidewall was hurled approximately 1,100 feet onto Chevron property; it landed an estimated 50 feet from a 250,000-barrel crude oil storage tank. A valve and portions of piping were also found on Chevron property as much as 1,700 feet from the column.The column was thought to be isolated and in standby mode at the time of the explosion though it contained 1200 gal.of MNT. It is known that for large batches of [MNT]. .that are exposed to temperatures between 401 F and 419 F, a violent decomposition will occur within 8 to 25 days. The estimated ultimate pressure generated inside due to decomposition could have been as high as 3800 psi.

Key Findings

1. Inadequate understanding of the potential hazard of thermal decomposition in continuous processing equipment.
2. Insufficient instrumentation to allow monitoring and control of the process to prevent a catastrophic release.
3. Lack of a system to ensure isolation of heat sources.
4. Inadequate preventive maintenance, which allowed leaks in isolation valves.

A final year lab. project back in 1961, on direct nitration of benzene without using sulphuric acid as dehydrating agent, was being done at A.C. College of Technology, Chennai, the professor suddenly stopped the project as there had been an explosion in Eastman Kodak facility in USA that was using this process. Later investigations revealed that in a mixture of benzene, nitrobenzene and nitric acid at certain compositions, if water is not present even in very small percentage, the mixture becomes explosive.

7. Bartlo Packaging Inc.

This incident occurred on May 8, 1997 BPS–a bulk storage and distribution facility in West Helena, Arkansas–was repackaging an organic pesticide, AZM50W. As the substance was being offloaded into a warehouse, employees noticed smoke coming from the building. City emergency response personnel were notified. A team of firefighters was attempting to locate the source of the smoke when an explosion occurred. A collapsing cinderblock wall killed three of the firefighters, and one was injured. The most likely causes of the incident were the decomposition of bulk sacks of the pesticide, which had been placed too close to a hot compressor discharge pipe, and the release of flammable vapors (USEPA-OSHA, 1999). This incident 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.

8. Whitehall Leather Company

On June 4, 1999, the inadvertent mixing of two incompatible chemicals caused a toxic gas release. One person was killed, and another was injured. A truck driver arrived at the facility to deliver a load of NaHS 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 employee was injured (NTSB, 2000). The case demonstrates that reactive hazards–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.

An incident involving H_2S happened many years back in a pharma unit killing three persons near Chennai.

A factory housing a small scale industry went up in flames in Ambattur in Chennai, when a worker inadvertently added resin to a catalyst container rather then the other way around.

Round Table

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.

3. Over 50 percent of the 167 incidents involved chemicals not covered by existing OSHA or EPA process safety regulations.

4. Approximately 60 percent of the 167 incidents involved chemicals that either are not rated by NFPA or have “no special hazard” (NFPA “0”).

5. Only 10 percent of the 167 incidents involved chemicals with NFPA published ratings of “3” or “4.”

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

CSB sent EPA, OSHA, industry and labor groups a list of recommendations to address reactive chemical hazards. This ended in round table in June 2003, with some 85 experts from industry, regulators, and other stake holders. Some points of consensus were,

1. Reactive chemical incidents are a major national problem that must somehow be addressed;
2. Industry and government must improve their collection of reactive chemical incident and near-miss data, to better understand root causes and prevention strategies;
3. There are major hurdles facing a regulatory approach, such as determining which facilities to cover and what chemicals or chemical processes to include;
4. Because many reactive incidents result from the interaction of two or more agents that by themselves are ordinarily not reactive, to be effective any regulation of reactive chemical hazards must go beyond simply listing individual chemicals;
5. Better education and outreach to plant operators concerning reactive chemical hazards is an essential prevention strategy that can and should be addressed at once.

This should be viewed in the context that here are more than 26,000 chemicals in commercial use, there are more than 150,000 different processes. As an EPA official stated,“If you regulate everything, it's too burdensome, but if you don’t, you’ll miss things.” “The difficulty of defining the universe of chemicals and covered facilities is precisely what is preoccupying govt. regulators” “Dairies, bakeries and swimming pools all handle chemicals with potential reactive hazards.” “There are more than 500,000 sites that handle chemicals – that's our potential universe.” “So our question is how do you pare this down to those who really should look at it? ”

These are genuine concerns of an authority who is interested in the end result. It is difficult to imagine such statements in the Indian context where laws are enacted and remain un-enforceable as there is disconnect between the law and the ground reality.

As a first step after the round table, Center for Chemical Process Safety (CCPS) supported by EPA, OSHA, SOCMA, ACC, has brought out a book **Essential Practices for Managing Chemical Reactivity Hazards** This E-book is freely available now initially for period of 3 years – its original price was $100. It is hoped that every unit that produces, handles or stores chemicals will use the book.

Essentials for Success

Apart from the nitty gritty, the book emphasizes the role of top management and need for its commitment if management of reactive hazards is to be successful. It goes on to state: top management commitment shall be 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 process hazard is clearly established. Line management is committed to managing chemical reactivity hazards, from the chief executive officer to first level supervisor. Develop and formally document clear written statements of what needs to done, when, how, how often, and by whom. 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.

The means and resources should have been permanently allocated. Training shall be conducted at appropriate levels, and verified. (In one accident investigation by HSE. UK the safety manager and supervisor were penalized as they as they had not properly imparted training to the field operator.) It should be understood by every person that following established procedures for managing reactivity hazard is a condition of employment.

Such a system is a major undertaking may require significant changes on “Corporate culture” Attempts to continue without these essentials will not succeed if management commitment and involvement are not obvious or adequate resources are not made available. It is common to have safety policy statement that reflects management’s commitment to safety. However such policy statements are worth very little unless management provides a sustained commitment of resources for carrying out the intent of the policy.

Indian Scene

To the authors knowledge, and I stand to be corrected, the vast majority of Indian companies in the +Rs 25 Crore league have little commitment as mentioned here. Below this level whether there is any awareness at all is a point to be considered. A few have a process safety management documentation, but without the commitment of top management in terms of decision and resources in most cases.

India produces a vast number of chemical products by a large number of entities
The reactive intermediates have been highlighted in earlier, Have the entities that use them assessed the reactive chemical hazards? Claims of new products, implying newer processes are being made almost every day. Whether the safety implications have been studied and documented? Most safety reports in India routinely give NFPA ratings

without understanding the limitations and going into other information available in the literature on incompatibilities, etc.

Lessons From The Past

In the western world there is great emphasize on going to the root cause of the accident, defining the key issues and propagating the findings to as wide an audience as possible. In India most incidents are reported in news papers, and that is how knowledge is spread, there is a hardly any voluntary statements from the authorities that be. Investigative reports are not publicly available. Illustrative list of incidents given below is indicative of the malaise. Are there no lessons to be learnt?

1. GNFC – nitro-phosphate plant- 5 deaths – 31 injured- loss estimates Rs 200 cr to 6.3 cr (14/10/2003)
2. Tamilnadu Industrial Explosives Ltd – 25 dead, 3 injured (16/8/2001)
3. IOC,Gujarat refinery – 2 dead, 15 injured (29/10/2004)
4. Orchid Chemicals – 2(3) dead, 3(12) injured (3/11/2005)
5. Chemplast Sanmar – chlorine release more than 50 treated– fire in dowtherm heater (18/7/2004)
6. Everest organics – 5 deaths, (19/12/2002)(30/4/2006)
7. Aurobindo Pharma – two incidents with deaths (28/11/2005)(9/3/2005)
8. Finolex – 3 dead, 7 injured (26/5/2005)
9. Kinjal chemicals – 2 killed- plant destroyed (31/1/2004)
10. Link pharma – plant destroyed (1/12/2005)
11. Ranbaxy – two accidents with deaths(11/6/2003)
12. Alembic Chemicals – 2 dead (16/12/2006)

All the information about these has been gleaned from sources outside the Government organizations and regulatory authorities. In all cases the causes are not publicly available or not known, the statements to the press are vague. In contrast the U.S. Chemical Safety Hazard and Investigation Board (CSB)- all reports are free and publicly available

In this secretive world of Indian Administration and Regulators are there are no lessons to be learnt – and no need to impart knowledge –to the chemical industry operators In USA vast array of information is available free of charge EPA, OSHA, CSB, NOAA, NCI, NIH are few of the organizations that are publicly funded and who give vast amounts of information free of charge.

Brief information on accident investigations is available from the annual reports of Petroleum and Explosives Safety Organization, The Oil Industry Safety Directorate (OISD) keeps its safety standards, regulations, investigations, confidential except a small circle non-other should get the benefit of knowledge. It is informed that the safety standards are available for fee of Rs 500 but nothing is mentioned in the website.

“Better education and outreach to plant operators concerning reactive chemical hazards is an essential prevention strategy”- that is the consensus in USA between the regulators as well as the Industry

EPA Alert

EPA was sufficiently worried and it issued an Alert in 2004 so that the facility operators could make a self-assessment and review the situation. Following are excerpts from the alert. These questions may be answered by one person, but you may be able to do a more thorough screening by setting up a team composed of people with diverse expertise. Whenever possible, include people representing technical, production, health and safety, and the purchasing perspectives. In any case, if you or your team is not certain about the right answer to any question, you should seek expert advice.

You are not likely to have any chemical reactivity hazards at your facility! If the answer is NO to the first four questions

Q1. Is intentional chemistry performed at your facility?

Intentional chemistry means the processing of substances such that an intended chemical reaction takes place.

A—Yes? º Go to Question 5
B—No? º Answer Question 2

Q2. Is there any mixing or combining of different substances?

Consider a wide range of activities, from large scale formulations to individual procedures when answering this question.

A—Yes? º Go to Question 6
B—No? º Answer Question 3

Q3. Does any other physical processing of substances occur at your facility?
Physical processing means any modification that result in a product that is physically, but not chemically, different from the original material.

A—Yes? º Go to Question 6
B— No? º Answer Question 4

Q4. Are there any hazardous substances stored or handled at your facility?

Hazardous substances include materials for which material safety data sheets are required as well as chemical intermediates and by-products.

A—Yes? º Go to Question 7
B—No? º

With the exception of question 5, a positive answer to any of the following questions means that chemical reactivity hazards do exist at your facility and you have to address them.

Q5. Is combustion with air the only chemistry intended at your facility?

Burning of ordinary flammable and combustible material is not considered a chemical reactivity hazard.

A—Yes? ᵒ Go back to Question 2
B— No? ᵒ Chemical Reactivity is expected to occur

Q6. Is any heat generated during the mixing or physical processing of substances?

Heat can be generated by heat of solution, heat of\ absorption, mechanical energy, or other physical heat effects.

A—Yes? ᵒ **Address Reactive Chemical Hazard!**
B— No? ᵒ Go to next Question

If your facility stores, handles, repackages, produces or uses any hazardous materials, you should give special consideration to the following set of questions.

Q7. Is any substance identified as spontaneously combustible?

"Spontaneously combustible" refers to substances that will readily react with the oxygen in the atmosphere, igniting and burning even without an ignition source.

A—Yes? ᵒ **Address Reactive Chemical Hazard!**
B— No? ᵒ Go to next Question

Q8. Is any substance identified as peroxide forming?

"Peroxide forming" refers to substances that will react with the oxygen in the atmosphere to form unstable peroxides, which might decompose and explode if concentrated.

A—Yes? ᵒ **Address Reactive Chemical Hazard!**
B— No? ᵒ Go to next Question

Q9. Is any substance identified as water reactive?

"Water reactive" refers to substances that will chemically react with water, particularly at normal ambient conditions.

A—Yes? ᵒ **Address Reactive Chemical Hazard!**
B— No? ᵒ Go to next Question

Q10. Is any substance identified as an oxidizer?

'Oxidizers' are materials that readily react to promote or initiate combustion of combustible material.

A—Yes? ° **Address Reactive Chemical Hazard!**
B— No? ° Go to next Question

Q11. Is any substance identified as self-reactive?

“Self-reactive” refers to substances that self react (e.g., polymerize, decompose, or rearrange), often with accelerated or explosive rapidity.

A—Yes? ° **Address Reactive Chemical Hazard!**
B— No? ° Go to next Question

Q12. Can incompatible materials coming into contact with each other cause undesired consequences?

'Incompatible materials' are materials that when accidentally mixed or brought into contact with each other will result in an uncontrolled chemical reaction.

A—Yes? ° **Address Reactive Chemical Hazard!**
B— No? ° Chemical reactivity hazards are unlikely to be present.

You have completed the Preliminary screening method.

Some of the resources required to answer or proceed further are *Guidelines for Safe Storage and Handling of Reactive Materials* (CCPS 1995b), “International Chemical Safety Cards” (ICSC’s),(EC), *NIOSH Pocket Guide to Chemical Hazards* (NIOSH 2001), NFPA 325, *Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids, Bretherick’s Handbook of Reactive Chemical Hazards* (Urben 1999), *Chemical Hazards Response Information System* (CHRIS) Manual (USCG), U.S. National Oceanic and Atmospheric Administration provides a *Chemical Reactivity Worksheet program* (NOAA 2002), . *Sax’s Dangerous Properties of Industrial Materials, BNL Chemical Compatibility Table* - Issue Date 12-17-02

In conclusion it is hoped that the industry will see that another Bhopal in waiting does not happen. This article extensively quotes sources from EPA, USCSB, OSHA, CCPS, HSE. Those interested in getting “Essential Practices for Managing Chemical Reactivity Hazards" please contact Chemical Industries Association, Chennai, chemindassn@sify.com

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