TATA AIG INSURANCE
WITH YOU ALWAYS

RE-Konnect

Risk Engineering Bulletin

August 2020 Vol. 4 | Issue 1

In Focus

Hazards due to Unintended Chemical Interactions

Preface

Many chemical manufacturing units are designed to produce a wide variety of products. Most of those products are planned during the initial engineering stage of the unit. Continuous change in demand and increased interest in process economics drives the management to optimize the plant infrastructure and add new products to the slate. Thus, the need for a chemical manufacturing unit to have flexibility in terms of production capability (materials handled, process design etc.) is very pronounced. During such changes in plant design, the risk due to chemical reactivity is often poorly managed.

There have been many accidents in the chemical industry caused by unintended mixing of incompatible chemicals. This document will present the hazards involved in Unintended Chemical Interactions, the risk management processes and tools available to evaluate such incompatibilities along with some industry examples of previous losses.

Did You Know?

- Chemical reactivity hazards are posed not only by self-reacting materials such as organic peroxides and polymerizing monomers, but also by uncontrolled chemical interactions

- Many chemicals form flammable / toxic gases when mixed with water. Some examples are given below:
  - Alkali metals with water may form flammable Hydrogen gas
  - Calcium carbide in water produces flammable acetylene gas
  - Triethyl aluminium explodes violently with water
  - Phosphides with water may forms toxic phosphine gas

- Sulphuric Acid is not flammable, but reacts with most metals to form explosive/flammable hydrogen gas

- Sodium Hydroxide (caustic soda) reacts violently with water. When contacted with metals, it liberates flammable hydrogen gas.

- Organic peroxides are relatively unstable compounds which can decompose spontaneously and sometimes explosively. Combustible materials contaminated with most organic peroxides can catch fire very easily and burn very intensely.

- Every packaged organic peroxide has a characteristic temperature at and above which exothermic runaway decomposition takes place, known as the self-accelerating decomposition temperature (SADT). For a peroxide, this generally decreases with increasing packaging size and varies with the stacking arrangement of the packaged product.

Disasters

Explosion due to lack of Process Safety Information

On December 19, 2007, a powerful explosion destroyed T2 Laboratories Inc (T2), a chemical manufacturer in Jacksonville, USA. T2 planned to produce methylcyclopentadienyl manganese tricarbonyl (MCMT) in a 12kL capacity chemical batch reactor. The MCMT process required both heating and cooling. A heating system circulates hot oil through piping installed around the inside of reactor. A cooling jacket covered the lower three quarters of the reactor.

Since Process Hazard Information was not available, T2 performed laboratory testing in a 01L glass reactor to establish the MCMT process chemistry and determine maximum product yield. No exothermic reactions were reported during testing and that temperatures never exceeded 193 Deg C. By not investigating the reaction's behaviour at higher temperatures, T2 did not identify possibility of exothermic runaway potential. The plant scaled up the process to produce commercially.

On the day of accident, there was loss of cooling water to reactor and the reaction temperature continued to rise beyond 180 Deg C, thus initiating a runaway reaction. There was no redundant cooling water supply or other process safety system to control the runaway reaction. The reactor's relief system could no longer control the rapidly increasing temperature and pressure of the runaway reaction. Eyewitnesses from nearby businesses reported seeing venting from the top of the reactor and hearing a loud jet engine like sound immediately before the reactor violently ruptured, its contents exploding. The explosion killed owner/chemical engineer and process operator who were in the control room (50 ft from the reactor) and two outside operators who were leaving the reactor area and left 28 employees injured.

Toxic Gas Release

On October 21, 2016, inadvertent mixing of incompatible chemicals namely, sulfuric acid and sodium hypochlorite at the MGPI Processing, Inc. (MGPI) facility in Atchison, Kansas produced a cloud containing chlorine and other compounds. The cloud impacted workers onsite and members of the public in the surrounding community. The incident occurred during a routine chemical delivery of sulfuric acid from a Harcros Chemicals (Harcros) cargo tank motor vehicle (CTMV) at the MGPI facility tank farm.

Over 140 individuals, including members of the public, MGPI employees, and a Harcros employee, sought medical attention; one MGPI employee and five members of the public required hospitalization as a result of exposure to the cloud produced by the reaction. According to U.S Chemical Safety Board Investigation, Poor design of Unloading facilities, lack of proper pipe marking, and improper communication between Plant Operator and (Truck) delivery operator led to the incident.

Unintended Chemical Interactions

Chemical Reactivity Hazard is a scenario where an uncontrolled chemical reaction could result directly or indirectly in serious harm to people, property, or the environment. These scenarios could lead to hazardous consequences and could be a result of either Self-Reacting Materials or Incompatible Chemical Interactions.

Self-Reacting Materials

Reactive materials that are capable of self reaction by:

- Polymerization or forming more complex molecules by polymerization-type mechanisms.
- Decomposition or breaking down into simpler molecules such as water and nitrogen; (e.g.) shock sensitive, Thermal Decomposition.
- Rearranging to form variants on the same basic chemical structures or formulas. (e.g.) Isomerization, Disproportionation.

Unintended Chemical Interactions

The hazards arising from Intentional process chemistry are assumed to be adequately managed / controlled as part of plant design, procedures and hence not covered in this document.

Unintentional Chemical Interactions refer to those scenarios where incompatible chemical come into contact unintentionally / accidentally. Such scenarios are not only limited to Production facilities but are also possible in Bulk Storage Facilities, Warehouses and repackaging units, where incompatible materials are present.

Chemical Incompatibility reactions could also result due to contact of certain chemicals with impurities, Heat Transfer Fluids, Wrong Material of Construction, Insulation and even Fire-fighting agents to mention a few.

The term “Incompatible” refers to the characteristics of materials to lead to hazardous consequences including Flammable / Toxic gas formation, Rapid pressure increase or Explosion.

Examples of Unintended Chemical Interaction Scenarios

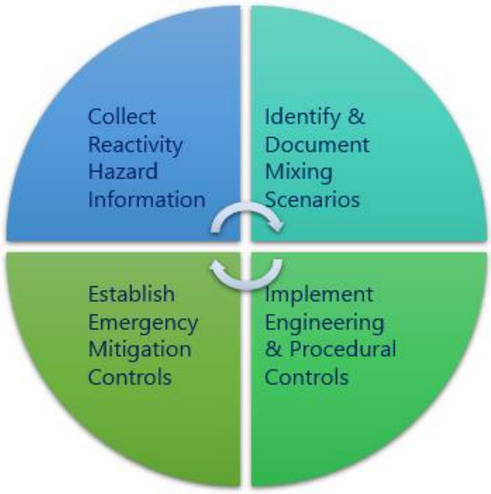
At any facility, there are multiple possible scenarios of unintended chemical interactions. Some of them are listed below:

- Raw material pumped into wrong storage tank
- Material pumped or transferred to wrong process vessel
- Material left in process equipment from previous batch or run
- Product or waste is transferred into container with residual material present
- Leaking liquid contacts adjacent material or container

Any of the above scenarios could initiate the hazard, however the conditions under which the materials are used (pressure, temperature, humidity, concentration, etc.) can also change the reactive behaviour dramatically. Also, it is interesting to note that most of the scenarios involve human error.

Management of Unintended Chemical Interaction Hazards

Unintended Chemical Interaction Hazards can be effectively managed in a facility with proper support and guidance from Site Management Personnel.



Collect Reactivity Hazard Information

The first step is Managing Chemical Reactivity hazards is to identify all chemicals handled at the site. Once identified, the reactivity hazards of the chemicals must be referred and documented. There are multiple sources to identify the reactivity nature of chemicals handled. Some of them are listed below:

Material Safety Data Sheet (MSDS)

According to ISO 11014, Section 10 of any MSDS should contain data related to Stability and Reactivity hazards of the chemicals

Bretherick's Handbook of Reactive Chemical Hazards

This book includes reactivity information on over 5000 materials, plus a like number of secondary entries involving interactions between two or more materials.

CAMEO Chemicals suite provided by NOAA

CAMEO Chemicals is a database of hazardous chemical datasheets that emergency responders and planners can use to get response recommendations and predict hazards—such as explosions or toxic fumes.

Key features of CAMEO program involve:

- **Search** by name, CAS (Chemical Abstracts Service) number, or UN/NA (United Nations/North American) number to find chemicals of interest in the extensive database of thousands of hazardous substances.
- Review **chemical datasheets** for physical properties, health hazards, information about air and water hazards, recommendations for firefighting, first aid, and spill response, and regulatory information.
- Get information from **additional sources** using the U.S. Coast Guard CHRIS (Chemical Hazards Response Information System) manual, the NIOSH (National Institute for Occupational Safety and Health) Pocket Guide, and International Chemical Safety Cards links on many chemical datasheets.
- Access **UN/NA datasheets** for response information from the Emergency Response Guidebook (ERG) and shipping information from the Hazardous Materials Table.
- **Predict potential hazards** that could arise if chemicals were to mix.

For Example, a basic compatibility search for Organic Peroxide and Nitric Acid returns the following:

	NITRIC ACID, RED FUMING
ORGANIC PEROXIDE TYPE B	**Incompatible** Flammable Generates gas Generates heat Intense or explosive reaction Toxic

Laboratory Tests

This includes calorimetric testing, Self-Accelerating Decomposition Temperature, Isoperibolic Calorimetry, Assessment of Maximum Pressure and Temperature etc.

Identify and Document Mixing Scenarios, Hazards

Once the information related to chemical reactivity is available, assemble a team of Operations, Maintenance, Projects and Safety personnel to identify all routine and non-routine activities, Plant Layout and piping arrangement, which could lead to unintended chemical interactions. It is also important to identify the volumes of chemicals involved and the process parameters during time of mixing. Some of these unintended interactions would also be covered as part of the plant HAZOP.

Create a Table with the List of chemicals involved, Consequences. Sa sample table is presented below:

Scenario	Process Conditions	Reactive / Non-Reactive	Consequence

Implement Engineering & Procedural Controls

Best approach to process safety is achieved by having Inherently safer design. In addition to safe design, more safety barriers need to be included. Some of them are included below:

- Designing and maintaining a high-integrity primary containment system
- Testing, and conducting preventive maintenance on reliable equipment and instrumentation
- Clear labelling of lines and connections
- Avoiding impurities by having quality control of incoming materials through sampling and analysis procedures.
- Detailed safety review of plant layout and piping arrangement
- Review of material compatibility with material of construction
- Reliable manual or automatic control systems, adequate redundancy, and operator training to compensate for abnormal conditions.
- Establish detailed procedures for all routine and non-routine operations
- Displaying detailed Chemical compatibility chart in various plant areas
- Operator training to minimize operational errors
- Provide detailed training to contractors on hazards involved in their operational area/process
- Conduct competency assessment on process hazards for Employees and Contractors
- By having Alarms, Interlocks and Emergency Relief Systems.
- Review other Industrial losses and determine proactive measures needed to avoid similar scenarios
- Periodic review of Chemical Reactivity Hazards MGPI Processing, Inc incident

Establish Emergency Mitigation Controls

Despite having detailed understanding of reactivity hazards and controls required to prevent them, unintentional chemical interactions hazards are still possible. Hence detailed Emergency Mitigation controls including Emergency Containment, Relief and Quench systems, Flaring, Spill handling etc. needs to be analysed and designed.

Guidelines

Following codes and standards can be referred for further reading:

- UK HSE Chemical reaction hazards and the risk of thermal runaway, 2014
- OSHA 29 CFR Part 1910 Subpart H - Hazardous Materials
- NFPA 400 Hazardous Materials Code
- CCPS Essential Practice for Managing Chemical Reactivity Hazards
- CAMEO Chemicals Suite: https://cameochemicals.noaa.gov/
- Bretherick's Handbook of Reactive Chemical Hazards

Engage

Answer the following questions and win **amazon** coupons worth INR 500.

Send in your answers to editor.bulletin@tataaig.com. Five winners for this quiz will be announced in next issue.

Q1. Sodium Hydroxide reacts violently with which of the following?

a) Nitrogen
b) Air
c) Carbon di Oxide
d) Water

Q2. Where can an unintentional chemical reaction occur?

a) Chemical Production plant
b) Bulk storage terminal
c) Warehouse
d) All of the above

Q3. Select the tools where data about chemical reactivity can be obtained?

a) MSDS
b) CAMEO Chemicals
c) Laboratory tests
d) All the above

For feedback or comments related to this bulletin, please write to editor.bulletin@tataaig.com

Editor
Nanda Kishore Danduprolu
AVP and National Head - VAS and Risk Engineering
nandakishore.d@tataaig.com

Contributed by
Ganesh Kumar
Senior Risk Engineer
ganesh.kumar@tataaig.com

To download previous issues of the bulletin, please visit the following link:
https://www.tataaig.com/PropertyEnergyLossPrevention

Chemical Plant Explosion in Beijing, China in March 2019

Tata-AIG General Insurance Company Limited
Peninsula Business Park, Tower A, 15th Floor
G. K. Marg, Lower Parel, Mumbai 400013
www.tataaig.com