Chemical Reaction Hazard Identification and Evaluation: Taking the First Steps

David Leggett, PhD, CChem, MRSC

Leggett Technical Consulting
dleggett@leggett-tech.com

Abstract:
The circumstances leading to reactive chemicals accidents are often complex, but most of them could have been foreseen by the use of laboratory tests, hazard analysis and chemical reaction engineering techniques. A hazard evaluation and testing strategy that accomplishes these goals will be comprehensive and probably require significant investment of resources. It typically has the following key steps:

- Initial hazards review of the process chemistry and unit operations
- Identification of potential hazard scenarios
- Assessment of the nature and extent of hazard scenarios
- Development of prevention strategies
- Development of protection strategies
- Implementation of prevention and protection measures.

Once a hazard has been identified and assessed as a credible threat to safe operation, most companies will take measures to mitigate the hazard. However, for small and mid-sized companies, the initial hazard identification and reactive chemicals assessment continues to be troublesome. This paper presents some specific tools to aid in completing these important first steps. They are straightforward to use and provide the information needed to enable a company to reliably determine and justify the need for further reactive chemical hazard testing.

Introduction

This paper advances the proposition that an initial chemical reactivity hazards assessment exists that can be performed by small/medium sized chemical manufacturing companies. Given the limited resources of most small and medium sized companies the scope of a chemical reactivity hazards assessment will be limited. The following limitations are proposed as reasonable for an initial review of the new or changed process:

- First round assessment takes ≤1 day to complete
- Initially no process hazards testing is done
- Assessment can be done by trained chemical engineer
- Most hazards, but not all, will be identified by the assessment
- Conduct hazards testing if need demonstrated by initial assessment

No hazard assessment procedure will catch 100% of all hazards present in a process. The intention of this approach is to identify the maximum number of serious potential hazards

with the minimum of resources. If no serious hazards have been identified it should not assumed that hazards do not exist in the process. However, if by the adoption of this approach four out of five serious hazards are identified then the overall accident and injury rate may be reduced by a significant percentage. This is clearly the preferred option to starting a new process without any chemical reactivity hazards assessment.

The tools discussed in this paper are straightforward and do not take a lot of time to use. However, they are sufficiently informative to provide a realistic assessment of the potential hazards of the process at hand.

Hazard Identification and Risk Assessment

Risk is defined as the product of the frequency (probability, likelihood) of an event occurring and its consequence (severity, impact, injury/fatality rate). Risk assessment is often an iterative process that involves the major steps:

1. Define a worst case scenario (WCS) in terms of its likelihood and consequence
2. Develop line of defense appropriate to the risk
3. Evaluate the risk reduction/elimination afforded by the line(s) of defense
4. Decide if risk reduction is sufficient and complete the project if sufficient
5. Decide if additional risk reduction can be achieved – perform additional risk reduction and return to step 3, or
6. Decide to not perform the process if further risk reduction is not feasible

This iterative process of hazard identification and risk assessment is designed to reduce risk to an acceptable level. Achieving the required level of risk reduction completes the review process. Alternatively, if the risk cannot be reduced using the available resources the process should be terminated.

Chemical Reaction Hazard Identification and Assessment

Chemical process hazard evaluation frequently focuses on the unit operations and operating conditions of the process, i.e., the engineering. A systematic assessment program for the reactive chemicals hazards of a process is less often performed. Large chemical manufacturers (Dow Chemical, Dupont, Ciba to name a few) perform these assessments that involve a significant level of equipment, personnel and time resources.

However, it is possible to obtain a good idea of the nature and degree of hazards that may be encountered in a particular operation involving the storing, handling, or reactions of chemicals from a variety of readily available sources. The information for the review comes from these sources and when viewed as a whole provides more than just clues as to the risk potential of the proposed operation. Important data about the process may be found from many sources:

- MSD Sheets – They may, or may not be fully informative
- Open Literature – Be prepared to look at more than just Perry's Handbook

- Functional Groups – Molecular characteristics provide an important key to reactivity and stability of particular chemicals
- Chemical Compatibility – Consequences of planned and unplanned mixing
- Checklist Tools – A few checklists can be useful
- Assessment Tools – Some specialized hazard ranking tools
- Fundamentals – Chemistry and chemical engineering helps here
- Calculational Tools – A couple of calculations put the reactivity hazards into perspective
- Hazards Testing – If time and resources permits but not necessary at this stage.
- Putting It All Together – How to get the information out of all the data.

The following sections provide more detailed on each of the information sources.

Chemical Process Safety

Chemical products are made from chemical reactions between reactive chemicals. Blending or mixing of chemicals to form a product often involves reactive chemicals even though the components of the chemicals do not, or at least are not intended to, react with each other at the time of blending.

Hazards arising from the storing, handling, or reacting of reactive chemicals may be classified into three groups:

- Thermal Stability Hazards
  - Self Reactivity
  - Inappropriate storage conditions
  - Runaway Reactions and Thermal Explosions
  - Loss of utilities leading to loss of cooling, loss of agitation
- Reactivity Hazards
  - Water and Air reactivity
  - Materials of Construction
  - Wrong Chemicals, Addition Rates, Order
  - Hypergolic and Pyrophoricity
- Operational Hazards
  - Flammability Dusts, Vapors and Gases
  - Mechanically induced hazards
  - Static induced hazards

By referring to the process block diagram, process chemistries, and the piping and instrumentation diagrams (P&IDs) the hazards that may be encountered can be determined and the need for a particular type of chemical reactivity data established.

It is always good practice to ask questions about how the process can change from a successful campaign into a situation in need of emergency actions. During the process evaluation is the time to ask the following questions:

- How can my process go wrong?

- Are the thermodynamics and kinetics of desired and upset situations known?
- What are the failure points and weaknesses?
- What are the consequences of a process upset?
- Will there be a major loss of containment?
- Are there any process material incompatibilities?
- Did I ask the *right* questions?
- Did I ask *all* the questions?

A systematic approach to answering these questions involves breaking the review process into separate reviews of the chemistry and the unit operations. The chemistry and unit operations that are performing as intended and the chemistry and unit operations that are in upset conditions are both carefully reviewed. Preparations for the analysis include defining all the reactions for the chemicals involved. That involves not just the desired reactions but also the side reactions that lead to yield loss, the reactions between reactants and process chemicals and materials, and reactions than can occur in storage.

This exercise should be done even if the operation is only blending or mixing. Several serious accidents, some including fatalities, have occurred because the consequence of reactions between chemicals involved in a blend reacted violently with inadvertently added process chemicals. Water and air can be particularly treacherous process materials with often unexpected results of reaction.

Material Safety Data Sheets

Material Safety Data (MSD) sheets should not be used as the sole source of process safety information. This was not their intended purpose and they do not supply the level of information that is required to perform an information-based hazard analysis. MSD sheets do provide guidance on:

- Toxicity, health and first aid
- Physical properties – flash points, UFL/LFL
- Stability & reactivity; temperature effects
- Fire fighting and spill management
- Storage conditions required and to avoid
- Specific chemical interactions to avoid

Specifically, MSD sheets ***do not*** provide:

- Quantitative thermodynamic / kinetic information
- Relevant / specific process safety information
- Consistent information coverage

The following is an example of the use of MSD sheets to assist in a preliminary hazard evaluation. The process involving blending three ingredients, aluminum powder, sodium dithionite ($Na_2S_2O_4$) and potassium carbonate. Superficially, there appears to be no reaction between any of the ingredients. However, after reviewing the MSD sheets for Al

and $Na_2S_2O_4$ water appears to present problems for both materials for different reasons. If $Na_2S_2O_4$ began to overheat large quantities of water are recommended as extinguishing agent. However, addition of small quantities of water to $Na_2S_2O_4$ can lead to overheating and ignition of combustibles. Large quantities of water added to aluminum powder may lead to the generation of hydrogen that is explosively flammable. With just this information it immediately becomes apparent that control of water within the processing area will require special precautions. Further review of additional publicly available chemical information regarding the chemistry of $Na_2S_2O_4$ led to the following conclusions regarding the initial assumptions:

Initial Assumption: No Chemical Reaction When Blending Al, $Na_2S_2O_4$ & K_2CO_3
After Hazard Assessment: The assumptions are not true:

All reactions between ingredients are not known
Role of moisture not known, but appears to be significant
Impact of water not known, but could be serious
Individual Ingredients must be kept dry
Control or removal of sources of water in blending area is the Basis of Safety of the blending process.

Initial Assumption: Spill management and cleanup
After Hazard Assessment: The assumptions are not true:

Overheating is noted as a possible scenario for $Na_2S_2O_4$
Control or removal of sources of water in blending area is the Basis of Safety of the blending process.

Initial Assumption: No Obvious Processing Hazards
After Hazard Assessment: The assumptions are not true:

Severity (nature and extent) of plausible process upsets are not known
Probability of process upsets not considered

Open Literature

There are many excellent source of information that can provide assistance at all stages of hazard assessments. In particular, the first six references to resources are frequently used for the initial assessment.

1. Urben, P.G.; *Bretherick's Handbook of Reactive Chemical Hazards, Volume 1 & 2, Sixth Edition*, 1999.
2. Sax, N. I., *Dangerous Properties of Industrial Materials*.
3. Crowl, D. A. and Louvar, J. F.; *Chemical Process Safety: Fundamentals with Applications,* 1990.
4. National Fire Protection Association, *Fire Protection Guide to Hazardous Materials, 10th Edition*, NFPA (1991). (Complete text of NPFA 49, 325M, 491M, and 704).
5. Center for Chemical Process Safety; *Guidelines for Safe Storage and Handling of Reactive Materials,* American Institute of Chemical Engineers, New York, 1995.
6. Center for Chemical Process Safety; *Guidelines for Design Solutions for Process Equipment Failures,* American Institute of Chemical Engineers, New York, 1997.
7. Bartknecht, W., *Dust Explosions Cause Prevention Protection*, Springer-Verlag, 1989.
8. Fisher, H.G. *et al*; *Emergency Relief System Design Using DIERS Technology, The*

Design Institute For Emergency Relief Systems (DIERS) Project Manual, American Institute of Chemical Engineers, 1992.
9. Center for Chemical Process Safety; *International Symposium on Runaway Reactions and Pressure Relief Design*, American Institute of Chemical Engineers, New York, 1995.
10. Bowes, P. C.; *Self-heating: Evaluating and Controlling the Hazards*, 1984
11. Center for Chemical Process Safety; *Guidelines for ……*, American Institute of Chemical Engineers, New York, 1990 - 2001.

As the process hazard evaluation proceeds increasingly specialized sources, such as those referred to in references 7 through 11, become important. Reference 11 refers to at least 40 specialist monographs on a wide range of process safety subjects – an invaluable resource to anyone involved with recommending or implementing process safety solutions.

Functional Groups and Chemical Identity

The structural factors within the chemical molecule (bond groupings) are indicative, often strongly, of instability or high reactivity within the molecule. These relationships have been reduced to a practical list of bond groupings and are presented in Bretherick's Handbook, reference 1 above.

The list of molecular fragments may be daunting to those who are not organic chemists by training. Inspection of the bond groupings reveals a few simple themes that are derived from the constituent atoms of these molecular groupings. The trends show that groups of the same atom (except carbon) or multiply bonded carbon atoms may be hazardous. In particular, the presence of the following groupings in a molecule should be viewed with caution:

- C-C and C-N triple bonds & metal salts
- Adjacent N-O atoms (many combinations with or without C)
- Adjacent and consecutive N atom pairs, triplets and higher
- Adjacent O-O pairs
- Adjacent C atoms bridged by O or N
- Many ring combinations of 4 or less atoms
- O-X atomic Pairs
- Many N-Metal atomic pairs

While there are more complex and sophisticated schemes for estimated molecular (in)stability the above list is straightforward and requires only that the molecular structure is known. It is also true that if the structure of the molecules involved in the reaction are not known, then the quality of the hazard assessment will be seriously degraded.

Chemical Compatibility

Chemical compatibility is frequently concerned with the consequence of inadvertent mixing of chemicals present on-site or that can be introduced unexpectedly into the processing area. The information is usually presented in the form of a compatibility chart. The charts provide a quick reference guide to the consequences of inadvertent

mixing and provide an excellent training tool for operators, focusing on the areas of the operation that have a potentially high hazard. Setting up the compatibility chart is also a valuable way of providing an initial view of the potential hazards due to inadvertent mixing that could arise by the introduction of new chemistry or a major process change.

When developing the compatibility chart for process materials, reactants and products the hazards involved in process upsets caused by ingress of these materials into the reactor, and upsets within storage areas begin to become apparent. A typical list of chemical and process materials, for inclusion in a compatibility chart is shown below.

- Reactants and product
- Air / oxygen
- Water
- Heat / light
- Solvents
- Heat transfer media
- Previous batch chemicals
- Next batch chemicals

At this stage in the assessment it often sufficient to simply setup the compatibility chart to indicate how much is known about the undesired reactions between all combinations of reactants, products and process materials. It may be quite a surprise to discover how little is known about undesired chemistry that could arise as a result of a process upset.

Checklist Tools

Checklists are a straightforward way of reviewing the potential hazards of a particular aspect of chemical manufacturing. They provide the inexperienced reviewer with a wealth of questions to ask about the intended process, or unit operations, as well as the causes, consequences, and probability of an upset condition arising. When used at the beginning of the review they will often stimulate questions unique to the process in hand. In either situation they can be a powerful and easy-to-use assessment tool. There are many checklists that are available for use assessing; for example, the potential hazard scenarios for unit operations, equipment failure scenarios, preliminary hazard evaluation issues, human factors, facility siting, etc. The downside of this approach is that the checklist may reflect an emphasis of one area of hazard analysis over another; for example process engineering vs. reactive chemistry.

Assessment Tools

Assessment tools are specific calculation packages or database resources that may be used to determine the potential hazard resulting from reaction between two or more chemicals. Pre-prepared chemical (inter-reactivity) charts are useful to quickly evaluate hazards of mixing members of chemical classes (amines, ketones, etc.) together. The US Coast Guard has a widely used chart that provides information for about 40 chemical classes or mixtures. CAMEO is a reactivity worksheet and compatibility database produced by NOAH. The Fire and Explosion Index (F&EI, by Dow Chemical) provides

an assessment of the hazards of storage and handling of many flammable and reactive materials. CHETAH (originally by Dow Chemical, currently available from ATSM) enables formation and reaction heats to estimated using Benson's group contribution methods. Numerical reactivity hazard indicators are also provided by CHETAH.

Calculational Tools

It is important to remember that a hazard analysis based on fundamental parameters requires quantitative information about both the thermodynamics and kinetics of the key reactions. These data may not be available during this limited hazard evaluation. However, there are some straightforward calculational tools that can provide estimates that are reasonably good for hazard assessment purposes.

CHETAH allows estimates to be made of formation heats of molecules in the gas phase. These calculations also lead to reaction heats, estimates of the plosive characteristics of molecules and reactions, and adiabatic temperature rises for reacting mixtures.

It has been noted that many good explosives have an oxygen balance (OB) $\cong 0$. Therefore, this tool provides a numerical indication of molecular stability. The OB is calculated from the balanced combustion reaction of the molecule.

If differential scanning calorimetry (DSC) data have been obtained for a pure material or a reaction mixture several thermal stability indicators (ASTM E1231-96) may be estimated from the data. These are adiabatic temperature rise, explosion potential, instantaneous power density, time to maximum rate, and NFPA instability index.

Hazards Testing of Process Chemistry

This presentation focuses on obtaining a hazard assessment without gathering new experimental hazard test data. However, the assessment may highlight a potentially hazardous situation but without any indication of the severity of the upset. This section provides a brief overview of hazards testing. The purpose of the testing is to quantify the nature and extent of the energy and power output resulting from the upset condition or the desired reaction. The three types of hazards detailed earlier are thermal stability hazards, reactivity hazards, and operational hazards.

The testing appropriate for each of these types of hazards is as follows:

- Thermal Stability Hazards
  - Differential Screening Calorimetry
  - Adiabatic Calorimetry
  - Dewar Calorimetry
- Reactivity Hazards
  - 2 Drop Isothermal Calorimetry
  - Heat Flow Reaction Calorimetry
  - Iso-Peribolic Calorimetry
- Operational Hazards

20-Liter Sphere Dust Explosion Severity
MIE, MIT, AIT, COC, LFL, UFL, Layer Ignition
Bulk Resistivity / Charge Relaxation
Impact and Friction Sensitivity

The table below provides an overview to the types of testing that could be employed to quantify the consequences of thermal and reactive events.

Table 1. Summary of Reaction Hazard Testing Methods

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 150C • No mixing • Cannot test multi-phase liquids
	DSC / DTA	• Reaction enthalpy, ΔH • Reaction 'onset' temp, T_{ONSET}	• Very quick (~2 hours), needs little sample • No mixing, no pressure data, no multi-phase • 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 (~1/2 day) • Poor/moderate sample agitation • Not reliable for scale-up (high-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}, • Vent sizing data	• Sample size ~ 100 ml • 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 – 50ml, μW/g sensitivity • Shelf life studies by accelerated aging • Combine with low adiabatic to confirm solids low self-heating rate studies

Putting It All Together

Of the tools introduced in this paper not all are needed to perform an adequate initial reactivity hazards assessment. The typical time required to obtain important information from some of the sources described is shown below. If only the underlined italicized items are considered the task can be completed in a single day. Hazards testing is not included in the first day of assessment. It can take from 1 to 4 days to complete depending on the type of data required.

Written Information - (*1* + 1.5) hrs

MSD Sheets, Bretherick's, Sax, CCPS Guidelines, NFPA Standards

Chemical information - (*3* + 4) hrs

Functional Groups in Molecules, Compatibility Review

Compatibility Chart, CAMEO Reactivity Worksheet

Calculation Tools - (*1.5* + 1) hrs

CHETAH, Oxygen Balance, Thermal Stability Indicators

Hazard Assessments - (*3* + 4) hrs

Checklists for Hazard Scenarios, Equipment Failures, Facility Siting F&EI and CEI

Summary and Conclusions

This presentation has introduced straightforward reactivity assessment tools that can be performed by small/medium sized chemical manufacturing companies. In particular it has been shown that:

- First round assessment may be completed in about one day
- Initially no process hazards testing is done
- Assessment can be done by trained chemical engineer
- Conduct hazards testing if need demonstrated by initial assessment.