Strategy for Managing Reactivity Hazards

An ioMosaic Corporation Whitepaper

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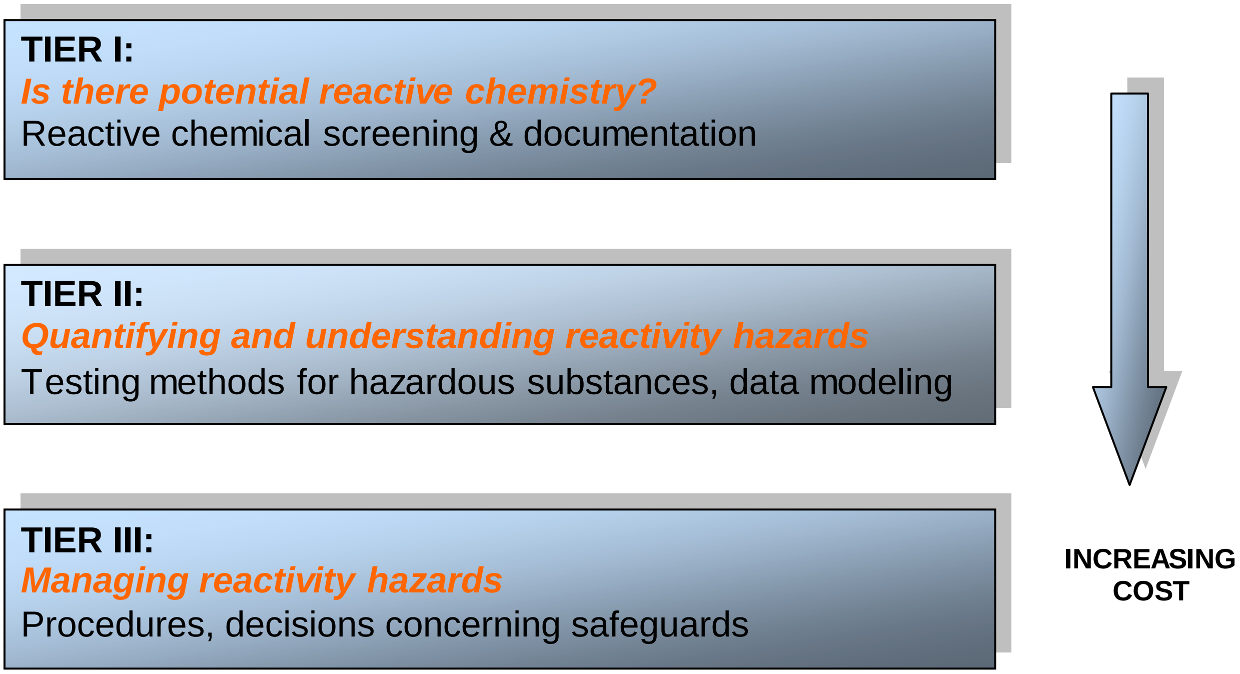
Introduction

Systematic Evaluation of Reactivity Hazards

The last few months have witnessed a high degree of focus on understanding and managing chemical reactivity to improve safety in process plants. These efforts have reinforced an important aspect of chemical reactivity, i.e. it is extremely complicated to try and list properties characterizing reactivity hazards. As an example, commercial explosives contain 2000 cal/g or more of energy; however, most of the chemicals involved in incidents in the process industries have energies between 500 and 1500 cal/g. There are therefore a variety of aspects, besides the energy content, that can pose reactivity hazards and recognizing such scenarios is an area of considerable research. The principle objective of this document is to assist readers in understanding, evaluating, and managing reactivity hazards for a particular situation by directing them to appropriate sources and utilizing a tiered evaluation protocol as shown in Figure 1.

Figure 1: Protocol for Evaluating Reactivity Hazards



TIER I:
Is there potential reactive chemistry?
Reactive chemical screening & documentation

TIER II:
Quantifying and understanding reactivity hazards
Testing methods for hazardous substances, data modeling

TIER III:
Managing reactivity hazards
Procedures, decisions concerning safeguards

INCREASING COST

TIER I: Reactivity Screening and Documentation

This section provides a brief overview of how to screen reactivity hazards through either theoretical[1,2] or experimental[3] techniques. Theoretical screening is advantageous since it is cheaper and less resource intensive. However in cases where adequate information is not available, preliminary testing is recommended.

Literature Review

Table 1 identifies properties of materials to be considered, and some potential sources, in formulating an opinion on the thermal hazards of particular materials and reactions.

Table 1: Potential Sources of Theoretical Screening Data

Material Properties	Potential Sources
1. Basic chemical data	MSDSs, manufacturer's data, The Merck Index
2. Reactivity data	Bretherick's Handbook, NFPA hazard ratings, Kirk-Othmer Encyclopedia of Chemical Technology or as determined
3. Incident data	Open literature
4. Chemical compatibility matrix	Literature or as determined
5. Chemical structure	Supplied by research scientist
6. Formation energies	Literature or as determined
7. Heats of reaction, decomposition, solution	Literature or as determined

Binary Interaction Matrix

A reactivity interaction matrix is an efficient method of consolidating and documenting reactivity information. The significance of binary interactive matrices is important for safe process plant operations and has led to the establishment of an ASTM standard, E 2012.[4] Although an extremely simple concept in principle, it is not always easy to generate a binary interaction matrix for various reasons, one of them being the availability of relevant information. Due to a lack of standardization of data structure, there is no single reference that integrates this entire body of knowledge. A comprehensive list of hazard codes was created to summarize various available reactivity data and a number of heuristic rules have been added to assist in identifying potential hazards.

A literature search often requires a significant time investment as there is no single/consolidated data source for all the requisite information.

To meet the above-mentioned challenges, ioMosaic has developed ***Reactivity Expert System (RES)*** - a computer algorithm that utilizes a variety of literature sources and databases and displays information as

a compatibility chart. Given a chemical composition, the RES generates compatibility information and displays available toxicity and experimental data on compounds as shown in Figure 2. ioMosaic's industry standard emergency relief system (ERS) design software, SuperChems, currently offers RES as a module.

Figure 2: Incompatibility Matrix Generated Using SuperChems

		DI-t-BUTYL PEROXIDE	ACETONE	METHANE
		A	B	C
DI-t-BUTYL PEROXIDE	A	109	105, 300, 200	300, 200
ACETONE	B	::::::::::::::::::::::::::		
METHANE	C	::::::::::::::::::::::::::	::::::::::::::::::::::::::	

<u>Note</u>:

105	May form explosive peroxides
109	Explosive
200	May cause fire
300	Heat generation by chemical reaction
900	Materials are compatible

DI-t-BUTYL PEROXIDE	DI-t-BUTYL PEROXIDE
	Explosive
DI-t-BUTYL PEROXIDE	ACETONE
	May form explosive peroxides
	Heat generation by chemical reaction
	May cause fire
DI-t-BUTYL PEROXIDE	METHANE
	Heat generation by chemical reaction
	May cause fire

RES also generates a hazard report summarizing all available properties and hazards.

Figure 3: Hazard Report Generated Using SuperChems

Chemical Name >>	DI-t-BUTYL PEROXIDE	ACETONE	METHANE
Chemical Formula >>	C8H18O2	C3H6O	CH4
CAS No >>	110054	67641	74828
Molecular Weight kg/kmol	146.230	58.080	16.043
Melting point K	233.150	178.450	90.670
Normal boiling point. K	384.150	329.440	111.660
Critical temperature K	547.000	508.200	190.580
Critical pressure bar	24.800	47.015	46.043
Liquid density kg/m3	789.91	785.602 @ 298 K	424.056 @ 112 K
Latent heat of vaporization J/kg	229613.619 @ 384 K	512940.691 @ 329 K	508879.141 @ 112 K
Lower flammability limits Vol %	0.900	2.600	5.000
Upper flammability limits Vol %	8.200	12.800	15.000
Flash point temperature K	291.000	255.372	
Auto ignition temperature K		810.927	873.000
Heat of combustion J/kg	-3.3782E+07	-2.8567E+07	-5.0010E+07
Ideal gas Heat of formation. J/kg	-2.3319E+06	-3.7388E+06	-4.6656E+06
Thermodynamic Stability			
Peroxide Former			
Water Reactive			
Pyrophoric			
Explosive	EXPLOSIVE		
Polymerizable			
Heat of decomposition J/kg	-1.6000E+06		
Decomposition onset temperature K	373.15		

Heat of polymerization J/kg		
Polymerization onset temperature K		
EPA Threshold Quantity kg		4,536
OSHA Threshold Quantity kg	2,268	
NJ TCPA Threshold Quantity Kg	1,134	
SEVESO Threshold Quantity Kg		

Melhem Index

Since RES depends on available reactivity information, it is bound to encounter compositions for which sufficient hazard information is not available and it becomes necessary to predict potential reactive hazards. A lot of information can be understood by a review of certain thermo-physical properties of materials and mixtures. In comparing the values of heats of reaction, heats of decomposition, and CART to values for known hazardous compounds, an estimation of thermal hazard potential can be made. Table 2 outlines thermal hazard ranking values to be used in classifying materials and processes based on heats of reaction and CART determinations. For materials considered to contain zero or low thermal hazard, no additional testing is required beyond a confirmed DSC test. For materials with intermediate hazard ranking, experimental analysis would be necessary to further characterize the thermal hazards of the materials and mixtures. For materials with mixtures in the high hazard ranking, experimental analysis combined with further process definition would be necessary to further identify appropriate processing conditions.

Table 2 Theoretical Hazard Rankings

Hazard Ranking	Rank	Characterization	Heat of Reaction Estimate (cal/gm)	+	CART Estimate (K)
No Hazard	D	Endothermic or low exothermic reaction	≤ 100		
Low Hazard	C	Reactions with low heat release per unit mass such as suspension polymerizations	> 100 and ≤ 287	**AND**	≤ 700
Medium Hazard	B	Moderately exothermic reactions such as bulk polymerizations	> 287 and ≤ 724	**OR**	> 700 and ≤ 1600
High Hazard	A	Very high heat release like oxidation reactions	> 724	**OR**	> 1600

Two standard estimation methods for ΔHr and CART, Chetah 7.2 and NASA CET, are discussed herein.

Chetah™ Version 7.2 is a computer program capable of predicting both thermochemical properties and certain reactive chemical hazards of pure chemicals, mixtures or reactions. Available from ASTM, Chetah 7.2 uses Benson's method of group additivity[5] to estimate ideal gas heat of formation and heat of decomposition. This heat of formation value can be used to calculate a heat of reaction for a known balanced reaction or a worst case thermal decomposition. These ideal gas values are commonly used on a comparative basis to qualitatively characterize reactive systems. This new version is easier to use than earlier versions and contains the most extensive listing of Benson Groups available in a software package. In the event a compound cannot be estimated in Chetah, additional estimation methods and software are available.

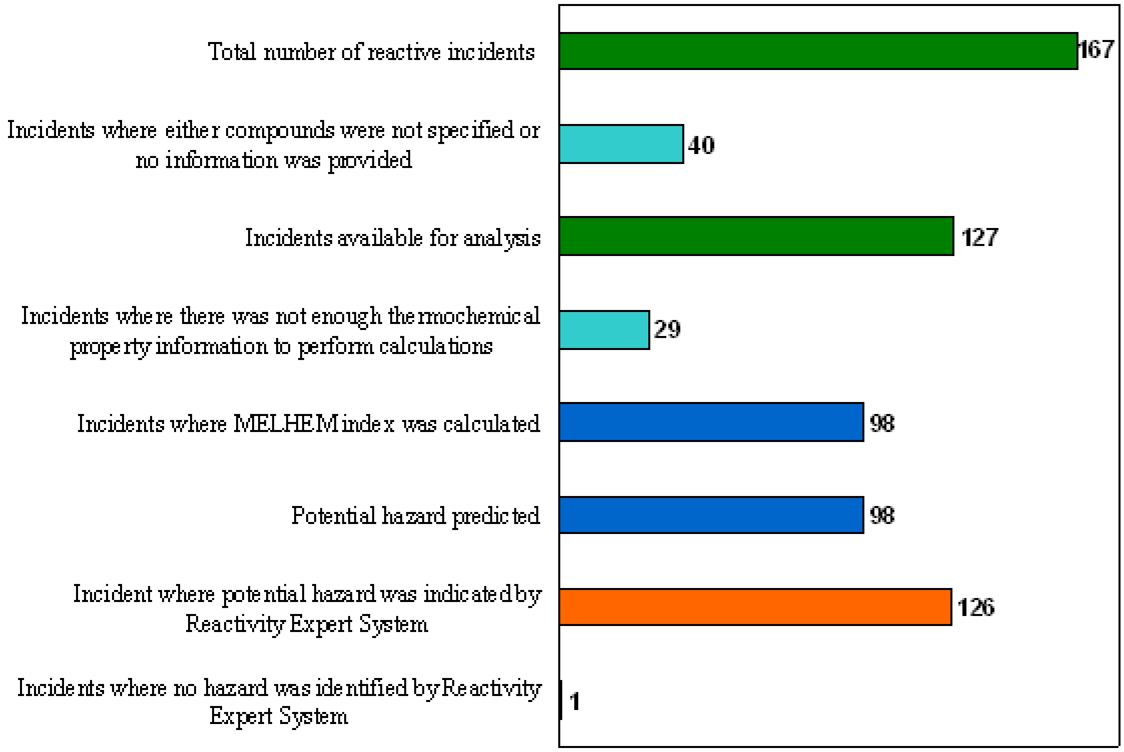
NASA CET is a computer program that calculates both the adiabatic decomposition temperature (maximum attainable temperature in a chemical system) and the equilibrium decomposition products formed at that temperature. Extremely cumbersome to use, but highly useful in evaluating reactive hazards, it is capable of calculating CART values for any combination of materials, including reactants, products, solvents, etc. The equilibrium code is available in SuperChems and can be used to calculate the hazard index for various compositions.[1]

How Good Are Theoretical Screening Techniques?

The Chemical Safety Board has published a report summarizing reactive chemical incidents from 1981 – 2001.[6] To test the applicability of the interaction matrix for recognizing chemical hazards, we generated chemical interaction matrices for chemicals involved in these incidents. Out of 167 total incidents, 127 have adequate chemical information available for analysis.

Out of the 127 cases we analyzed by generating binary interaction matrices, a reactive hazard was indicated for 126 incidents. The one incident where no reactive hazard was indicated involved Freon TF – a Chloro-fluorocarbon. The Melhem Index was successful in recognizing reactive hazard potential in 98 incident mixtures. There was not enough thermochemical data for the remainder of the incidents to calculate the Melhem Index. Details of the analysis are attached as Appendix A and a summary is displayed in Figure 4.

Figure 4: Summary of ioMosaic's Screening Techniques Applied to CSB Incidents



Experimental Screening

As implied, experimental screening involves experimental testing to gauge the thermal hazard of materials and processes. The object of these tests is to verify previously identified theoretical values and provide additional information by which the materials and processes may be characterized. Experimental screening can be divided into four different areas of concern, self-reactivity, mechanical sensitivity, thermal sensitivity, and dust explosibility and ignitability.[7,8] These are summarized in Table 3.

Table 3: Different Experimental Screening Methods

Nature of Hazard	*Experimental approach*	*Information gleaned*
Self-reactivity	DSC, DTA, TGA	Heats of reaction, onset temperature, approx. kinetics
Mechanical sensitivity	Drop weight test, blasting cap test	relative mechanical shock susceptibility of the composition
Thermal sensitivity	Konen	potential for a material to explode under a thermal stimulus
Dust explosibility and ignitability	ASTM recommended tests	potential for a combustible material, in dust form, to explode or ignite

TIER II: Detailed Experimental Analysis

Experimental analysis involves the conduct of thermal hazard analysis tests (summarized in Table 4) to verify previous results as well as identify reaction rates and kinetics. This level of testing is geared towards verifying calculated and experimental results and providing additional information by which materials and processes may be characterized. A detailed discussion of the experimental technique is provided in Appendix B.

Table 4: Experimental Methods

Test	**Typical Application**	**Data**
autoMate™	Process development	T_o $^{dT}/_{dt}$ and $^{dP}/_{dt}$ Composition
Isothermal storage test (IST)	Operating/storage temperature development	Shelf-life
Accelerating rate calorimeter (ARC)	Calorimetry	ΔH_d ΔH_r T_o Vapor pressure P_{max} Global kinetic data $^{dP}/_{dt}$ and $^{dT}/_{dt}$ T_{nr} TMR Gas generated
Vent sizing package (VSP™)	Emergency Relief Vent Design	T_o $^{dT}/_{dt}$ and $^{dP}/_{dt}$ Vapor pressure
Reaction calorimeter (RC-1™)	Process development	ΔH_r C_p q_r $^{dT}/_{dt}$ $^{dm}/_{dt}$ % Conversion Composition
Automatic pressure tracking adiabatic calorimeter (APTAC™)	Process development, Calorimetry	ΔH_r T_o Vapor pressure P_{max} Kinetic data $^{dP}/_{dt}$ and $^{dT}/_{dt}$
LabMax	Process development	T_o $^{dT}/_{dt}$ and $^{dP}/_{dt}$ pH Composition
Dewar Flask	Calorimetry	ΔH_r C_p Q

The decision on the type of experimental analysis that should be undertaken is dependent on a number of factors, including perceived hazard, planned pilot plant scale, sample availability, regulatory drivers, equipment availability, time pressures and financial resources. Most of these factors will be specific to a given project or dependent on the timing of the work to be completed. Additionally, it is relatively simple to factor these into the testing regime being developed for a particular process. Two of these factors, perceived hazard and planned pilot plant scale, are more involved and will be discussed in more detail here.

One of these, the perceived hazard, is understood from the theoretical and experimental screenings completed previously. Screening results in the intermediate or high hazard ranking require experimental analysis. Processes operating within a 100°C range of a DSC detected onset temperature also need to undergo this more detailed experimental analysis. In some cases, all that would be required is a verification of the DSC detected onset temperature using a more accurate instrument, such as an ARC® or APTAC for energetic systems or an RC-1 for less energetic systems. In other cases, for example, operations very close to the onset of a runaway reaction, more detailed process design information is required. This may be achieved by completing one or more adiabatic calorimetry experiments followed by development of a kinetic model. Many of the tests listed in Table 4 can be used to generate data for input into the development of a kinetic model.

Coupled with the physical description of the reactor system, accurate scale-up can be achieved. The final scale of the process under review is critical in deciding the particular test to be completed. It should be noted that reaction heat generation rate shows an exponential increase with temperature while the reactor cooling rate shows a more linear relationship. Therefore, the heat rate due to internal reaction must be coupled with the linear increase in cooling to arrive at an operating temperature within the margin of safety. Once the point of no return is reached (TNR), the system can not remove heat fast enough to prevent a runaway reaction.

The data shown in Table 5 [9] gives extrapolated experimental heat generation data for various test methods currently in general use. This data show how various test methods have sensitivities characteristic of the natural cooling losses of specific size industrial reactors. For example, SEDEX$^{\text{TM}}$ and ARC® systems have detection sensitivities in line with the natural cooling losses expected in a 2,600 gal industrial reactor. That is, the SEDEX$^{\text{TM}}$ and ARC® systems would be expected to identify any exotherms that occur at a rate higher than that expected to dissipate due to natural heat losses (heat accumulation in the reactor).

Table 5: Detection Sensitivity of Various Test Methods

Test Method	Experimental Parameters	Sample Mass	Detected Onset (C)
DTA	10 C/min	8.1 mg	125
DSC	10 C/min 5 C/min 1 C/min	3.4 mg 4.4 mg 6.4 mg	122 101 93
ARC	Start: 50C Heat Step: 10 Wait: 15min PHI = 2.38	3.5 g	82
SEDEX	0.5 C/min “Scanning” Experiment	5.8 g 2.0 g	84 88
SIKAREX	0.125 C/min Scanning	5.0 g	72

TIER III: Implementing Reactivity Management Systems

Upon completion of the testing phase, the following information needs to be compiled:

- Enthalpy of desired/undesired reactions
- Specific heat of process mixture
- Rate of desired/undesired reactions as a function of temperature
- Kinetic data
- Rate and quantity of gas evolved

Table 6 from *Guidelines for Chemical Reactivity Evaluation and Application to Process Design* (updated to include the recently available APTAC™ instrument), shows questions which need to be asked regarding the safety of the proposed reaction, the data required to answer those questions, and some selected methods of investigation.

Table 6: Essential Questions on Safety Aspects of Reactions[10]

Question	Data Required	Selected Methods of Investigation
1. What is the potential temperature rise by the desired reaction? What is the rate of the temperature rise? What are the consequences? What is the maximum pressure?	• Enthalpy of desired reaction • Specific heat • Vapor pressure of solvent as a *f*(T) • Gas evolution	• Table of data • Thermodynamic data • Calculations; estimations • DTA/DSC • Dewar flask experiments • Reaction calorimetry with pressure vessel • Thermometry/manometry • APTAC/ARC/RSST/VSP
2. What is the potential temperature rise by undesired reactions, such as from contaminants, impurities, etc.? What are the consequences? What is the maximum pressure?	• Data from No.1 • Enthalpy of undesired reaction • Specific heat • Rate of undesired reaction as a *f*(T)	• See No. 1 • DTA/DSC • Dewar flask experiments • APTAC/ARC/RSST/VSP
3. Is reactant accumulation possible? What are the consequences?	• Steady state concentrations • Kinetic data • Data from 1 and 2	• Reaction calorimetry combined with analysis • Potential energy by DSC/DTA • VSP/APTAC
4. What is the temperature rise due to physical aspects of the system?	• Heat transfer data • Agitation (power input) • Pumps (power input) • Radiation	• Design data

In order to enable pilot plant designers to take into account thermal hazards during the design phase, specific data needs to be available. This data should include sufficient information for the development of quantity and rate of heat generation and quantity and rate of gas evolved. As the design needs to incorporate desired reactions and worst-case decompositions, data must be provided for both situations.

A summary of information that should typically be made available is provided in Table 7 below.

Table 7: Thermal Hazard Analysis Summary Information

Information	Suggested Experimental Source
Process materials	R&D
Desired chemistry	R&D
Heat capacity	DSC/RC-1
Onset temperature of desired and undesired exotherms	DSC/ARC/APTAC/RC-1
Adiabatic temperature rise of desired and undesired exotherms	ARC
Quantity of heat generated during desired and undesired exotherms	DSC/ARC/APTAC/RC-1
Adiabatic self heating rate vs. temperature	ARC/APTAC
Time to maximum rate	ARC
Pressure generated vs. temperature	ARC/APTAC/RC-1
Pressure rise rate vs. temperature	ARC
Kinetic data	Calculated from ARC data

The tools and methodologies discussed so far are critical for understanding and quantifying reactivity hazards. However it is equally important to translate this knowledge into developing management systems to prevent reactive incidents. Although appropriate strategies would depend on specific situations, industry personnel can use the following guidelines to develop policies for managing reactive systems.

Procedures

For reactive systems, suitable procedures should be developed to avoid initiation of hazardous reactions. Such procedures may be directed to prevent inadvertent mixing or a set of actions if the system temperature reaches a particular value.

Training

Plant personnel must be provided adequate training in understanding potential reactive hazards and their trigger factors. Case studies and incident investigations can be effectively utilized as part of this training.

Protective Measures

Reactive systems can be protected by pressure relief valves or by using safety instrumented systems. The sizing of valves for reactive systems is a complicated task that requires an understanding the modeling of reaction kinetics.[11]

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APPENDIX A

ioMosaic’s Screening Techniques Applied to Compositions in CSB’s Reactive Chemical Incident Report