Practical Assessment Resources/ Tools for Reaction Safety Management

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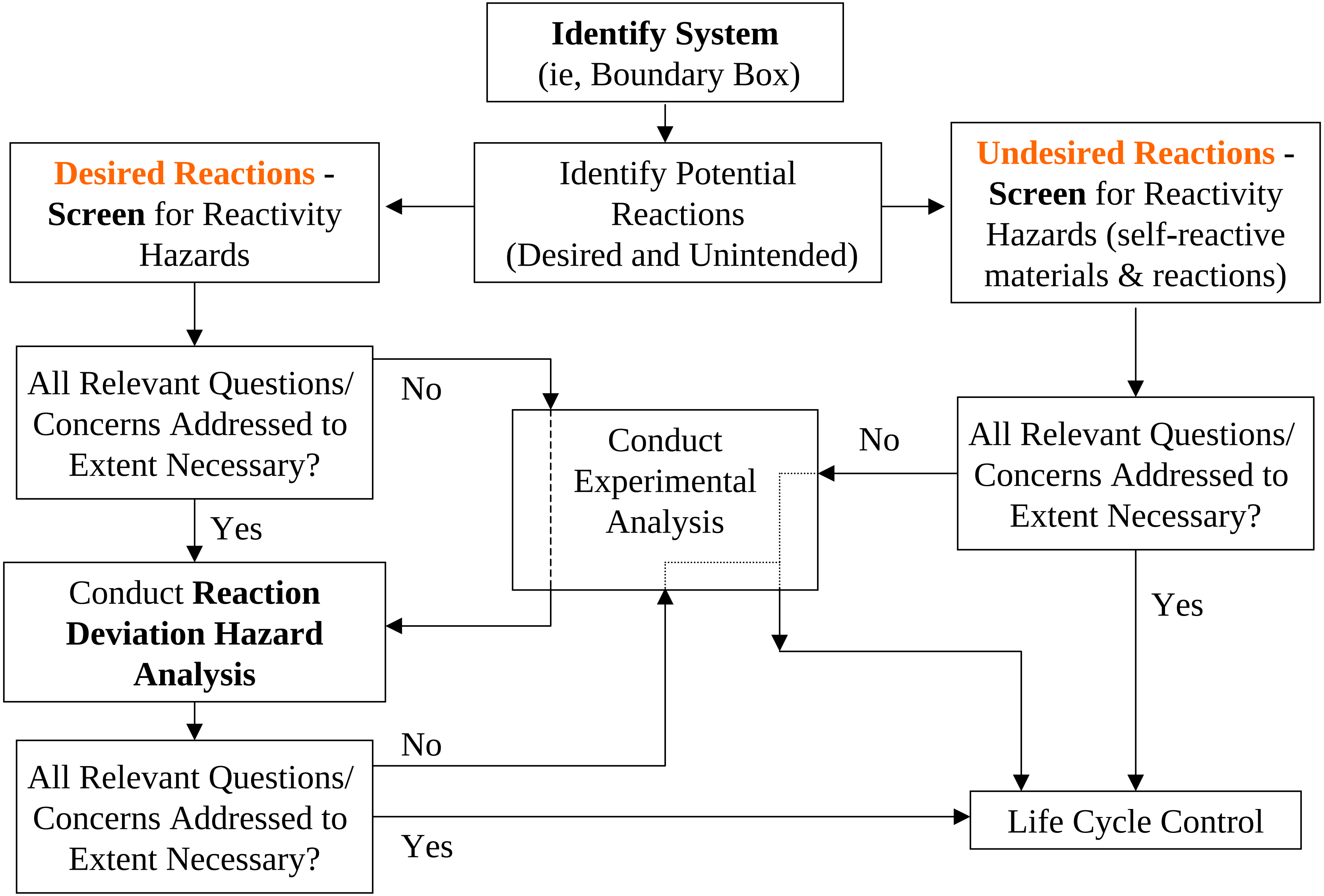
Reactive Hazards Process Safety Management (PSM) Holistic Approach for Determining Reactive Hazards



Definitions

- **Reactive Hazard** – situation that has potential to lead to a reactive incident
- **Reactive Incident** – sudden event involving an uncontrolled chemical reaction with significant increase in temperature, pressure or gas evolution that has caused, or has the potential to cause, serious harm to people, property or the environment. Although the event may be sudden, the reactive incident can, sometimes, be slow in forming.

Types of Reactive Hazards

- Self-Reacting
  - Involves one chemical but is sometimes promoted by catalysts or contaminants
  - Examples:
    - **Runaways or uncontrolled reactions (35% of reactive incidents)**
      - **Polymerization, Decomposition**
    - **Impact sensitive (copper acetylide)**
    - **Thermal sensitive (organic peroxides)**
- Chemical Incompatibility (36% of reactive incidents)
  - Requires two or more (known) substances coming into contact (inadvertently or intentionally)
  - Examples
    - **Acids and Bases**
    - **Water Reactions**
    - **Pyrophoric Reactions (when contacting air)**

Identifying the System

- "Interaction Matrix"

	Chemicals	**Materials of Construction**	**Utilities**	**Energy**
Chemicals	Rxn?			
Materials of Construction	Rxn?	Rxn?		
Utilities	Rxn?	Rxn?		
Energy	Rxn?	Rxn?	Rxn?	
Atmosphere (Air, Water)	Rxn?	Rxn?		
People	Haz?	Haz?	Haz?	Haz?

Reactivity Screening Tools

Chemical Compatibility Matrices and Their Sources

- **Internet: Example E.P.A.-600/2-80-076 – A Method for Determining Compatibility of Chemical Mixtures**
  - **Chart uses reactivity groups (eg, acids, alcohols, aldehydes, esters, ethers, etc)**
  - **Intersecting cell identifies consequences (eg, fire, explosion, violent polymerization, toxic gas formation, heat generation, etc)**
  - **Caution: Not possible to make any chart definitive and all inclusive**
- **Books: Example "Chemical Risk Analysis – A Practical Handbook", Bernard Martel, Penton Press**
  - **Using a matrix format identifies dangerous reactions for specific chemicals and their derivatives when in contact with select chemicals, chemical types, and groups**
  - **Also identifies material instability and polymerization potential**
- **Software: Example U.S. N.O.A.A. Reactivity Worksheet**
  - **Identifies general hazards of substances**
  - **Identifies interaction hazards for mixtures**
  - **Identifies hazardous interaction with air or water**

Reactivity Screening Tools (Continued)

Databases & Reports

- **Bretherick's Reactive Chemical Hazards Database**
- **"Accident Database" from U.K. Institution of Chemical Engineers (IChemE)**
- **"Process Safety Incident Database" from American Institute of Chemical Engineers**
- **Reports from U.S. Chemical Safety & Hazard Investigation Board (a.k.a Chemical Safety Board)**
- **User-Developed Database**

Reactivity Screening Tools (Continued)

Calculated Adiabatic Reaction Temperature (CART) + Heat of Reaction ΔH_{RXN}

- **New concept – Feb 2003**
  - **“Reactivity Screening Made Easy” by George Melhem of ioMosaic**
  - **“Computationally Evaluate Self-Reactivity Hazards” by Michelle Murphy, Surendra Singh, Edward Shanley. Chemical Engineering Progress**

Reactivity Screening Tools (Continued)

CART + Heat of Reaction ΔH_{RXN} (Continued)

- For most stable reaction products – usually decomposition products
- Based on potential for rapid release of stored chemical energy
- No lab data needed
- Basic information needed - ΔH_f° of compound's composition and its decomposition products
  - **Literature:** Pedley, J.B., et al, "Thermodynamic Data of Organic Compounds", 2nd ed., Chapman and Hall, New York (1986)
  - **Computer Calculated:** ASTM's CHETAH (Chemical Thermodynamic and Energy Release Program)
    - User can specify functional groups for a chemical(s), select a chemical from the database or can select reactants & products from the database
    - Functional group method - uses Benson's method of group additivity
- $\Delta H_{RXN} = \Sigma\ \Delta H_f^\circ$(decomposition products) - ΔH_f°(Substance)
- CART determined using NASA-Lewis CET89 computer program. Updated version called Chemical Equilibrium and Applications (CEA)

Reactivity Screening Tools (Continued)

CART + Heat of Reaction ΔH_{RXN} (Continued)

- Interpretations
  - ΔH_{RXN} – represents stored chemical energy
  - CART – relates to attainable reaction rate
- "Hazard Indexing"
  - Two approaches
- Murphy, Singh, Shanley Approach
  - **Place substance of interest into one of 5 groupings of similar composition: General Hydrocarbons, CHO, Nitro Compounds & Nitrates, Other Nitrogen Compounds, Organic Peroxides**
  - **Compare ΔH_{RXN} & CART of substance with corresponding values for other substances in same group. By looking at substances with well-defined hazard potential, the hazard for the substance can then be predicted**
  - **Hazard Index:**
    - **N = Non-Explosive Even With Intense Initiation**
    - **NX = Non-Explosive When Unconfined**
    - **E = Explosive**
    - **E^* = Assumed to be Explosive (no experimental information available)**

Reactivity Screening Tools (Continued)

- **CART + Heat of Reaction ΔH_{RXN}** (Continued)
- ioMosaic Hazard Index
  - "No Reactivity Hazard" or "D" means
    - ΔH_{RXN} no more negative than –0.42 kJ/g
  - "Low Reactivity Hazard" or "C" means
    - ΔH_{RXN} between –0.42 and –1.2 kJ/g, and
    - **CART** ≤ 700 K
  - "Intermediate Reactivity Hazard" or "B" means
    - ΔH_{RXN} between –1.2 and –3.0 kJ/g, or
    - 700 < **CART** ≤ 1600 K
  - "High Reactivity Hazard" or "A" means
    - ΔH_{RXN} more negative than –3.0 kJ/g, or
    - **CART** >1600 K

Reaction Deviation Hazard Analysis

- Parallels “Hazard & Operability” (HAZOP) Analysis used in Process Industries
- Assumes chemistry is safe if done as intended (to be confirmed by chemist)
- Combination of guideword and chemistry parameter = chemistry deviation
- Guidewords: No, More, Less, Part Of, Reverse, As Well As, Other
- Focus on potential consequences and not on causes
- Reference: Mosley, D.W., A. Ness and D.C. Hendershot. “*Tools for Understanding Reactive Chemical Hazards Early in Process Development*”. Rohm and Hass Company

Reaction Deviation Hazard Analysis

- **Reaction Example**
- **A(liq) + B(liq) -> X(solid) + Y(gas) + Heat**
- **Conditions: Temp = T,   Pressure = P, Catalyst = C, Solvent = S**
- **Activities: Reacting, Mixing, Cooling, Reagent Addition**

- **Example of Reaction Deviations (Not Complete)**

Guideword	Examples of Possible Deviations To Consider or Ask in a Review
No	NO – Reactant A, Reactant B, Solvent S, Catalyst C NO – Reaction, Mixing, Cooling Etc
More	More – Reactant A, Reactant B, Solvent S, Catalyst C More (Higher) Conditions: Higher Temp, Higher Press More Activities: Higher reaction rate, Faster rate of addition of material, Higher Cooling, Higher Mixing Etc

Reaction Deviation Hazard Analysis – The Results

Partial Sample

Guide-word	Deviation	Consequence	Recommendation
Reverse	Catalyst added after reagents are added	Violent and explosive reaction	Have checklist. Have two people involved.
As Well As	Rust	Unknown	Investigate

Residual Reactivity Questions/ Concerns

- Hazard Laboratory Evaluation
- In-House or External
- Develop thermo-chemical, kinetic or reactivity data needed to complete screening and assessment

Conclusion

- Although these resources/ references will allow for a more focused and efficient effort to screen and evaluate reactivity hazards without the need for lab-generated data, users must always satisfy for themselves that they have adequately identified and evaluated reactive hazards to the extent that they require. Controlled experimental testing is the ultimate approach to answer any theoretical question… but at the expense of efficiency and cost.

THANK - YOU