FOCUS ARTICLE

Understanding Chemical Reactivity Hazards

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Rapid overpressure events continue to result in large losses in the process industries. These events can occur due to releases of flammable or explosive materials, rapid decomposition of thermally unstable substances, or runaway exothermic chemical processes.

Chemical reactions on an industrial scale are frequently associated with considerable heat exchange. Large amounts of energy can be released when such decomposition reactions are initiated unintentionally through unsuitable operations. The catastrophic effects associated with the release of such energies are well-known.

The actual destructive force originates from the rapid release of pressure contained within the process equipment. Hence, the identification, assessment, and characterization of both intended and – more importantly – unintended exothermic reactions are critical for ensuring the safe scale-up and operation of a chemical process.

Chemical reactivity hazards can be grouped into general categories such as:

- Self-reactive materials (e.g., polymerizing; decomposing; rearranging),
- Reactive with other materials (e.g., oxygen; water) and
- Intentional mixing of two or more chemicals in a chemical process.

The general situations involving chemical reactivity hazards include:

- Mixing or physical processing (e.g., blending; milling; distillation),
- Intentional chemistry (e.g., batch, semi-batch, or continuous processes),
- Transportation, storage, handling, and repackaging (e.g., warehousing or tank storage) and
- Unintentional reaction.

Safety and environmental regulations require systematic risk analysis to be carried out on potentially-hazardous processes in production plants, pilot plants, and auxiliary installations. The risk-assessment strategy would generally include determining heats of reaction/decomposition, exotherm-initiation (onset) temperature, pressure-generation, water reactivity, sensitivity to light and air, and spontaneous combustion. Additional tests regarding compatibility, pyrophoricity, peroxide formation, **thermal stability**, and shock and friction sensitivities could be included as a part of the assessment for chemical reactivity hazards.

"Design of Runaway Scenario" is a powerful method that can be employed for conducting thermal process safety analysis of a batch, semi-batch, or continuous process, taking into account the thermal characteristics of both the desired and unwanted reactions. The method involves determining the maximum temperature of the desired reaction in case of cooling loss and also the maximum temperature of the process due to decomposition reactions. Depending on the energy potential, the severity of the consequences of a runaway reaction can be assessed and then be combined with the likelihoods of various temperature-control failures, to estimate the risks of injury to personnel and property loss. This information would be utilized to develop and implement process improvements and contingency plans that are appropriate and economically feasible. For safe storage of self-reactive materials, the rates of heat production and heat dissipation as determined by the (adiabatic) time-to-maximum-rate and cooling curves should be compared.

The understanding of thermal hazard potential requires various skills and disciplines as listed below.

- **Process Design** - The mode of operation is an important factor; for example, a batch reaction – where all the reactants are charged initially – could be more difficult to control than a semi batch operation in which one of the reactants is charged progressively as the reaction proceeds.

- **Engineering** - Design and layout of the plant/equipment and its built-in controls. The capacities of the heating and cooling systems are important in this context.

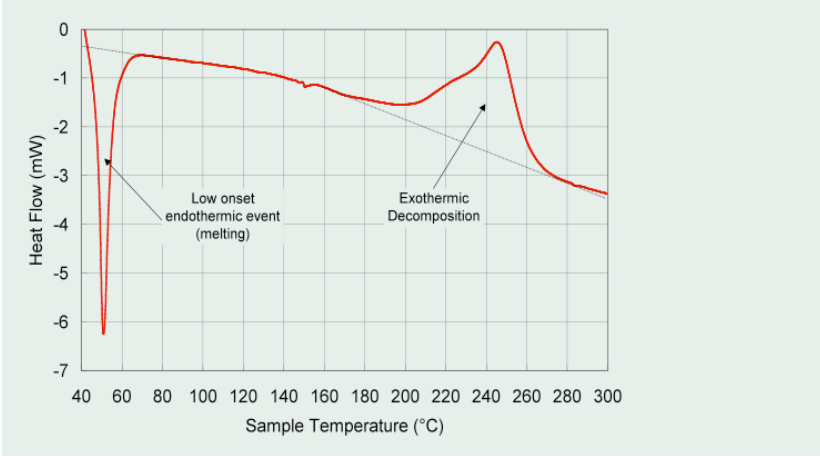
- **Chemistry** - The nature of the process and the behavior of the products must be known, not only under normal reaction conditions, but also in case of unexpected deviations (e.g., side reactions; accumulation and instability of intermediates).

- **Physical Chemistry/Reaction Kinetics** - The thermo-physical properties of the reaction masses and the kinetics of the chemical reaction are of primary importance (e. g., heats of reaction; Arrhenius relationships).

Tests/Equipments That Provide Process Safety Related Information

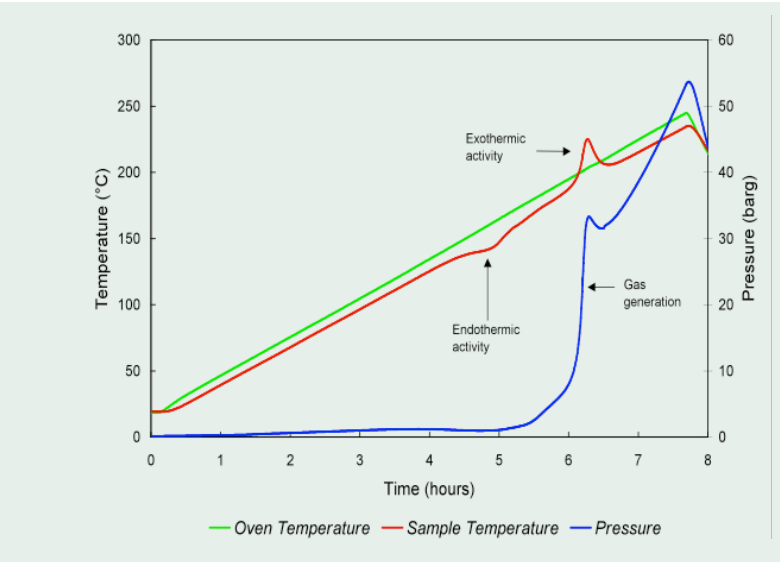
It is critical to obtain chemical reactivity data under the desired and undesired process conditions via **experimental testing**, to ensure the safety of a chemical process. When processing exothermic chemical reactions – including thermally unstable substances and mixtures – it should be remembered that the hazard arises from heat and pressure generation. Below is a list of some of the equipments that can be used to gather process-safety related information.

- **Differential Scanning Calorimetry (DSC)**: This is a contained, ramped-temperature screening test on a small sample of material (normally 2 to 10 mg) which provides an indication of the onset temperature and, more importantly, the magnitude of any heat release (ΔHr).



DSC thermograms, indicating endothermic and exothermic events

- **Carius Tube:** This test is similar to a DSC test; however, it uses slightly higher sample mass (normally 10 to 15 g) and is designed to collect temperature and pressure data. The test provides the reaction-onset temperature, the maximum temperature and pressure that can be attained, the rates of reaction (dT/dt) and (dP/dt), the onset temperature for gas generation, and the quantity of gas generated.



Temperature and pressure traces collected in Carius tube test

- **Accelerating Rate Calorimetry (ARC):** This is a test that is performed in a heat-wait-search mode under pseudo-adiabatic conditions. The test determines the onset temperature of any self-accelerating exothermic reaction activity, the rate of temperature rise (dT/dt), the rate of pressure rise (dP/dt), and the volume of gas generated in a chemical system under conditions normally encountered during large-scale manufacturing and/or transportation. The sample mass is in the range of 2 to 5 grams.

- **Micro-Stirred Reaction Calorimetry (µCal):** This reaction calorimeter can be used to determine the heat of reaction under isothermal conditions and identify the effects of changes in feed rate, temperatures, and concentrations on the instant-by-instant behavior of a reaction system. The heat of reaction (ΔHr) can be used to predict the adiabatic temperature rise in case of loss of cooling.

- **Reaction Calorimetry:** Reaction calorimetry can be used to determine the heat of reaction under isothermal (constant sample temperature) or isoperibolic (constant temperature of the surroundings) conditions and identify the effects of changes in feed rate, temperatures, and concentrations on the instant-by-instant behavior of a reaction system. The extent of reagent accumulation can be quantitatively determined, and the heat of reaction (ΔHr) can be used to predict the adiabatic temperature rise in case of loss of cooling.

- **Vent Size Package (VSP):** The VSP is a pressure-compensated adiabatic calorimeter, and it can be used to determine the onset temperature, thermodynamic (heat of reaction, ΔHr), reaction pressure, and pressure-increase rate (dP/dt) for the reaction associated with the process.

- **Adiabatic Pressure Dewar Calorimetry (ADC II):** This equipment is used to determine the stability of materials under adiabatic conditions. The thermal inertia of this system is very low and the test results are generally directly applicable to large-scale process vessels (e. g., up to 25 m3). The test provides direct measurement of temperature and pressure as a function of time, and time-to-maximum-rate data that can subsequently be used in the specification of maximum allowable handling temperatures, vent sizing for protection against runaway reactions for batch and semi-batch processes. Also, the test results aid in determining whether a reaction is "gassy" or if vaporization of a reaction component can be used to "temper" (control) the reaction. Additionally, blowdown tests can be conducted to determine if the vented materials are single-phase or two-phase (foamy) fluids.

- **BAM Fallhammer and Friction:** The ignition sensitivity of solids, pastes, and gels to impact and frictional forces can be tested by the BAM Fallhammer and BAM Friction Apparatus, respectively. [BAM = German Institute for Materials Testing] The methods yield quantitative results in the form of limiting impact and friction energies. DEKRA Process Safety performs BAM Fallhammer and Friction Testing in accordance with the United Nations (UN) Recommendations on the Transport of Dangerous Goods - Manual of Tests and Criteria (ST/SG/AC.10/11/Rev.2 - 9/95).

> **Isothermal Basket Test:** While screening tests are useful for identifying a potential thermal stability hazard, more exacting isothermal tests are necessary to establish safe operating temperatures. Isothermal Basket Tests can be used to identify the minimum onset temperature of exothermic activity for a powder or dust sample.

These tests are performed according to European Standard EN 15188:2007 (Determination of the spontaneous ignition behavior of dust accumulations) to measure the dependence of self-ignition temperature upon powder volume. The method requires that the sample be held in a wire-mesh basket, thus it is only suitable for solids. Each individual test run is made at a fixed oven temperature. A powder specimen is prepared by packing it into a wire gauze basket, usually in the form of a cube. The basket is placed in an oven where the temperature can be controlled accurately to better than ±1°C. Experiments are conducted on a number of different-sized cubes. Further, since tests are conducted using at least three (3) sizes of basket, extrapolation techniques can be used to determine the maximum safe operating or storage temperature for virtually any vessel size or geometry.

Summary of some of the equipment used to understand the thermal runaway reaction hazards:

Equipment	Scale	Data recorded
Differential Scanning Calorimetry (DSC)	2 - 10mg	Thermal activity, onset temperature, magnitude of any heat release (ΔHr)
Accelerating Rate Calorimetry (ARC)	2 - 5 grams	Onset temperature, rate of temperature rise (dT/dt), rate of pressure rise (dP/dt) and volume of gas generated, magnitude of any heat release (ΔHr)
Carius Tube	10 – 15g	Onset temperature, rate of temperature rise (dT/dt), rate of pressure rise (dP/dt) and volume of gas generated
Reaction Calorimetry	70mL - 1.5L	Heat of reaction (ΔHr) and adiabatic temperature rise
Micro-Stirred Reaction Calorimetry	1 - 100mg, µL	Heat of reaction (ΔHr) and adiabatic temperature rise
Adiabatic Pressure Dewar Calorimetry (ADC II)	800mL	Onset temperature, rate of temperature rise (dT/dt), rate of pressure rise (dP/dt), volume of gas generated and vent sizing information for runaway reactions.
Vent Size Package (VSP II)	100mL	Onset temperature, rate of temperature rise (dT/dt), rate of pressure rise (dP/dt), volume of gas generated and vent sizing information for runaway reactions.
Isothermal Basket Test	5 gallon pail	Minimum onset temperature of exothermic activity for a powder or dust sample. Tests are conducted using at least three (3) sizes of basket, extrapolation techniques can be used to determine the maximum safe operating or storage temperature for virtually any vessel size or geometry.

ABOUT THE AUTHOR:

Dr. Swati Umbrajkar, Ph.D. is the Manager of the Chemical Process Evaluation Group. Dr. Umbrajkar received her Doctorate from the New Jersey Institute of Technology. Her research interests include the synthesis of metal/metal oxide nanocomposites; analysis of highly energetic materials using X-ray diffraction, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and a number of post analysis techniques to characterize the thermodynamic and kinetic parameters of a test system.

Dr. Umbrajkar consults with clients on a variety of process safety issues including but not limited to high-pressure DSC cell tests, adiabatic calorimetry (ARC and ADC), reaction calorimetry (RC-1), all of which allow for the safe scale-up of batch and semi-batch processes. She has expertise in determining self-acceleration decomposition temperature (SADT) and time to maximum rate (TMR), which are critical issues associated with the storage of bulk materials. As the Manager and Consultant in the Chemical Process Evaluations Laboratory, she is proficient in the interpretation of data for a wide variety of process safety scenarios. She has authored several articles in the fields of, 'Synthesis and Analysis of Highly Energetic Materials' and 'Chemical Process Safety'.

For further information regarding testing for Chemical Reaction Hazard Assessments and Chemical Reactivity Hazard Analysis of chemicals at elevated temperatures and pressures, please contact Swati Umbrajkar, Ph.D., Manager – Chemical Process Evaluation Group at Tel: 609-799-4449, Fax: 609-799-5559, Email: ***swati.umbrajkar@dekra.com****, or you may also visit our website at:* ***www.dekra-process-safety.com****.*

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> Support the implementation, monitoring, and sustainability of PSM programs
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> Correct and improve deficient programs

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> Chemical reaction hazards and chemical process optimization (reaction and adiabatic calorimetry RC1, ARC, VSP, Dewar)
> Thermal instability (DSC, DTA, and powder specific tests)
> Energetic materials, explosives, propellants, pyrotechnics to DOT, UN, etc. protocols
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> Electrostatic testing for powders, liquids, process equipment, liners, shoes, FIBCs

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> Hazardous area classification
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