



WHITE PAPER

Testing Guide for Management of Flash Fires, Explosions, and Runaway Reactions

Where flammable (combustible, explosible) gases, liquids/vapours, and powders/dusts, and reactive materials are processed, handled, and/or generated, fire, explosion, and/or runaway chemical reaction hazards exist. These hazards can lead to catastrophic events involving fatalities, injuries, environmental impact, facility damage, and economic losses. In the US alone, each major industrial incident costs an average of \$80 million (Ref 1). Largely as a result of the disastrous incidents in Seveso, Italy in 1976 and Bhopal, India in 1984, a number of systems for the management of process safety have been developed and implemented, including the early CCPS process safety management model (1989), Responsible Care code (late 1980's), OSHA PSM rule (1990), EU's Seveso I, II, and III directives, CCPS 2007 risk-based PSM mode, as well as numerous company-specific approaches. Although most chemical companies have adopted one or more versions of these models, serious and catastrophic process safety incidents continue to occur (Ref 2).

The continuing occurrence of process safety incidents is an indication that the traditional and often disjointed application of **Process Safety Management (PSM)** elements is not proving to be adequately effective. What we believe is regularly missing is

appropriate organisational capability and culture to underpin the effective operation of the process safety management program. Organisational capability means having suitable data, information, tools, expertise, and experience. Organisational culture represents the underlying, unstated, shared beliefs and values that exist within an organisation "what we do when no one else is looking" (Ref 3).

Effective assessment of process safety hazards and management of risks therefore involves creating an organisational capability and culture that focuses on identifying exposures, acting on them before events occur, ensuring that hazards are fully understood, and making consistent execution the rule.

A major concern in many process industries, including the chemical, pharmaceutical, food, petrochemical, metals, wood, and pulp/paper is the risk of flash fires, explosions, or otherwise unplanned loss of containment and release of energy due to the use or presence of flammable gases and liquids (vapours), explosible powders/dusts, and unstable/reactive materials. A flammable atmosphere is typically created when the right amount of a fuel (flammable gas, vapour, dust) is mixed with the right amount of an

oxidant, usually the oxygen in air. Ignition of flammable atmospheres occurs if the ignition source energy exceeds the minimum energy that is required to ignite the flammable atmosphere under the process condition. As one can consequently imagine, a flash fire or an **explosion hazard** can exist during the transfer, handling, processing, and packaging of many flammable gases, liquids, and powders. It is therefore necessary that precautions are taken to prevent their inadvertent ignition or protect the people and facility against the effects of fires and explosions.

Management of flash fires, explosions, and runaway reactions resulting from the use, handling, and processing of flammable liquids, explosible powders, and reactive/unstable materials often involves taking the following steps:

- > Establishing a sound process safety management system and competency within the organisation that is based on appropriate data, information, expertise, and experience in all related process safety areas, including:
 - Having appropriate data for the understanding of the flammability, electrostatic properties, reactivity, and explosion characteristics of the fuel(s)
 - Understanding of all operations and processes, and review of all pertinent information (P&ID's, specifications, process/operation descriptions, material of construction of storage, transfer, and process equipment)
 - Identification of locations where flammable atmospheres (gas, vapour, dust) are, or could be, present during normal and foreseeable abnormal operating conditions
 - Identification of potential ignition sources (including potential electrostatic sources) that could be present under normal and foreseeable abnormal conditions
 - Defining the “Basis of Safety” including proper process and facility design to prevent and/or minimize the occurrence of flash fires, explosions, and uncontrolled reactions and protect people and facilities against their consequences
- > Establishing a safety culture that starts at the top but pervades consistently through the whole organisation
- > Regular review and maintenance of data, information, behaviors, systems, facilities, and equipment to ensure continued safety of people, community, and business

This article focuses on the **process safety data** that is necessary for the effective understanding and management of flash fires, explosions, runaway reactions, and accidental release of energy and toxic materials.

Process Safety Data - Flash Fires & Explosions

Formation of a Flammable/Explosible Atmosphere

A flammable atmosphere is formed when a sufficient amount of a fuel (gas, vapour, or/and dust) is mixed (suspended) with an oxidant. As is highlighted above, in order to assess flash fire and explosion hazards in a facility and to select the most appropriate basis of safety, fire and explosion characteristics of the fuel(s) that could be present must be determined for handling and processing conditions. The first step in the assessment of flash fire and explosion hazards is to establish whether a gas, vapour, and/or dust cloud atmosphere, if formed, is flammable/explosible under the process/operating conditions. For some common materials, particularly liquids, this information may be available in the accompanying Safety Data Sheet, manufacturers' technical bulletins, or other publically available sources. Otherwise, some well-established tests such as Flash Point and Limits of Flammability tests for liquid vapours and Explosion Classification (Screening), Fire Train, and Minimum Explosible Concentration tests for powders/dusts can be considered as outlined in Table 1 as shown on page 3. The methods used for conducting the tests listed in Table 1 can be found in the Annual Book of ASTM Standards, Volume 14.05 (Ref 4), International Electrotechnical Commission (IEC) (Ref 5), and the European Committee for Electrotechnical Standardisation (CENELEC) (Ref 6).

The data obtained from the test(s) in Table 1 will provide the information that is necessary for determining whether or not a flammable atmosphere exists in a vessel or a building under optimum or actual operating/process conditions. Importantly, the data obtained from these test(s) will also be used for evaluating the options of avoidance of the fuel or oxidant (Limiting Oxidant Concentration) as a basis for ensuring safety from flash fires and explosions.

Determining Ignition Sensitivity

Once the flammability/explosibility of a material or an atmosphere is confirmed, then testing normally falls into two groups, “Ignition Sensitivity” and “Explosion Severity”.

Ignition Sensitivity - There are a number of tests that are designed to determine the sensitivity of a flammable atmosphere to ignition by the type of ignition source(s) that could be present during normal and also foreseeable abnormal operating conditions. So, the selection of appropriate “ignition sensitivity” test(s) requires a good understanding of the type of ignition source(s) that could be associated with specific unit operations and activities in a facility.

Flammable Atmosphere	Examples	Initial Test(s)	Follow up Tests
Flammable Gas or Vapour	<ul style="list-style-type: none"> > Headspaces of storage vessels and equipment containing flammable liquids > Buildings where flammable liquids are handled/processed in open vessels, containers 	One or a number of the following tests: <ul style="list-style-type: none"> > Flash Point Temperature (Flammable Liquids) > Lower Temperature Limit of Flammability (Flammable Liquids) > Lower Flammable Limit (LFL) > Upper Flammable Limit (UFL) > Limiting Oxygen Concentration (LOC) * 	<ul style="list-style-type: none"> > Simulation of actual process / operating conditions
Explosible Dust Cloud	<ul style="list-style-type: none"> > Headspaces of storage vessels and equipment during powder transfer, blending, mixing, fluidisation, etc. > Buildings where combustible powders are handled/processed in open vessels, containers > Poor housekeeping resulting in accumulation of unsafe levels of dust on various building and equipment surfaces 	One or a number of the following tests: <ul style="list-style-type: none"> > Explosibility Screening > Fire Train > Minimum Explosible Concentration (MEC) > Limiting Oxygen Concentration (LOC) * 	<ul style="list-style-type: none"> > Simulation of actual process / operating conditions
Explosible Dust Cloud Hybrid (gas/vapour coexisting with dust cloud even when individually below their respective LFL and MEC levels)	<ul style="list-style-type: none"> > At open manways during transfer of powder to vessels containing > Fluidised bed drying of solvent-wet powders 	One or both tests: <ul style="list-style-type: none"> > Minimum Explosible Concentration > Limiting Oxygen Concentration (LOC) * 	<ul style="list-style-type: none"> > Simulation of actual process / operating conditions
Flammable Mist (fine liquid droplets) Cloud	<ul style="list-style-type: none"> > Mist cloud can be flammable even if formed/present at a temperature below its Flash Point > High-pressure cleaning of process and storage vessels using flammable/combustible liquids > Leakage of liquids from pipes and vessels under high pressure 	One or both tests: <ul style="list-style-type: none"> > Minimum Explosible Concentration > Limiting Oxygen Concentration (LOC) * 	<ul style="list-style-type: none"> > Simulation of actual process / operating conditions

Table 1. Flammability/Explosibility Tests

*LOC testing is usually only considered when basis of safety is decided to be inert gas blanketing

For example, simple gravity transfer of a powder or liquid from a container into another vessel may only give rise to electrostatic discharges if conductive components are not grounded or non-conductive components are utilised. In this example, and under the said conditions, the only “Ignition Sensitivity” test to consider would be Minimum Ignition Energy (MIE). MIE test is used primarily to assess the susceptibility of flammable atmospheres to ignition by electrostatic discharges and is defined as the smallest electrostatic spark energy that is capable of igniting a flammable atmosphere at its optimum concentration for ignition.

Table 2 below summarises the initial and perhaps the follow-up “ignition sensitivity” tests that are normally considered for the common ignition sources that might exist in a facility.

The methods used for conducting the tests listed in Table 2 can be found in the Annual Book of ASTM Standards, Volume 14.05 (Ref 4), International Electrotechnical Commission (IEC) (Ref 5), and the European Committee for Electrotechnical Standardisation (CENELEC) (Ref 6).

Ignition Source / Hazard	Examples	Initial Test(s)		Follow up Test(s)	
		Liquids/Vapours/ Gases	Solids/Powders	Liquids/Vapours/ Gases	Solids/Powders
Electrostatic Discharges	Discharges from ungrounded conductive (e.g. metal) objects and people, insulating objects such as plastic containers, liners, hoses, etc., non-conductive liquids, Insulating Powders	One or a number of the following tests: <ul style="list-style-type: none"> > Conductivity > Capacitive) Minimum Ignition Energy 	> (Capacitive) Minimum Ignition Energy	If Conductivity <100pS: <ul style="list-style-type: none"> > Electrostatic Chargeability > Simulation of actual process / operating conditions 	If MIE < 25 mJ: <ul style="list-style-type: none"> > Volume Resistivity > Surface Resistivity > Electrostatic Chargeability
Electrical Arcs and Sparks	Arcs/sparks from electric appliances (motors, switches, etc.) during normal operation or by accidentally cutting the connecting circuit	<ul style="list-style-type: none"> > Minimum Ignition Current (Ratio) > Maximum Experimental Safe Gap (MESG) 	> Minimum Ignition Current (Ratio)	> Simulation of actual process / operating conditions	> Simulation of actual process / operating conditions
Self-Heating/ Auto Ignition	Unintentional heating (e.g. during mechanical milling) of powders, various powder drying operations, bulk storage of powders after heating Intentional or unintentional heating of liquids to elevated temperatures	<ul style="list-style-type: none"> > Auto-Ignition Temperature 	One or a number of the following tests: <ul style="list-style-type: none"> > Differential Scanning Calorimeter > Accelerating Rate Calorimeter (ARC) > Screening Bulk Powder > Screening Aerated Powder > Screening Air-Over-Layer > Minimum Ignition Temperature - Dust Cloud 	> Simulation of actual process / operating conditions	One or a number of the following tests: <ul style="list-style-type: none"> > Isothermal Bulk Powder > Isothermal Aerated Powder > Isothermal Air-Over-Layer > Basket > Adiabatic Dewar
Hot Surfaces	Liquid (vapours), dust clouds, and/or dust deposits in contact or in close very close proximity to hot surfaces for example uninsulated steam pipes, lighting fixtures, and hot process equipment (exterior surfaces of process equipment, electric motors, etc.)	<ul style="list-style-type: none"> > Auto-Ignition Temperature > Liquid Vapour Pressure at elevated temperature 	<ul style="list-style-type: none"> > Minimum Ignition Temperature - Powder Layer > Minimum Ignition Temperature - Dust Cloud 	> Simulation of actual process / operating conditions	> Simulation of actual process / operating conditions
Friction / Grinding Sparks and heating	Breakdown of bearings, misalignment of screw conveyers, entrainment of foreign objects causing sparks and hot surfaces (hot particles, spots)	<ul style="list-style-type: none"> > Auto-Ignition Temperature > Hot Particles Ignition test 	One or a number of the following tests: <ul style="list-style-type: none"> > Friction Sensitivity > Minimum Ignition Temperature - Dust Cloud > Inductive Minimum Ignition Energy 	> Simulation of actual process / operating conditions	> Simulation of actual process / operating conditions
Impact Energy	Energy release resulting from the (accidental) impact between two hard objects in the presence of a flammable vapour or a combustible solid/powder	> Impact Sensitivity	> Impact Sensitivity	> Simulation of actual process / operating conditions	> Simulation of actual process / operating conditions
Adiabatic Compression	Some chemical & physical processes occur so rapidly that no transfer of heat or matter takes place between the thermodynamic system and its surroundings. This can be referred to as an "adiabatic process". Planned or unplanned adiabatic compression processes can lead to heating and subsequent auto-ignition of flammable atmospheres that are under elevated pressures. Ignition of pressurised flammable atmospheres can cause very high maximum explosion pressures and even detonations.	> Adiabatic Compression	N/A	> Adiabatic Compression Evaluation under Simulated of actual process / operating conditions	N/A

Table 2. Ignition Sensitivity Testing Guide

Appropriate information on the sensitivity of a flammable atmosphere(s) to ignition by source(s) that might likely be present in the same location and at the same time (fire triangle) would be a powerful tool in the hands of process safety practitioners for deciding on the applicability and practicality of the elimination of ignition source(s) as the primary basis for safe operation. It should be noted that avoidance of ignition sources(s) as a primary basis of safety not only requires a proper understanding of the atmospheres' ignition sensitivity, but it also requires rigid management of all credible ignition sources under normal and abnormal operating conditions. Finally, even if all foreseeable ignition sources cannot be reliably controlled at all times, avoidance of ignition sources should still be considered as a secondary basis of safety (i.e. to reduce the frequency of undesirable ignitions).

Determining Explosion Severity

The severity of an explosion that is caused by the ignition of a flammable gas, vapour, and/or dust cloud atmosphere in a confined space/enclosure is defined by the (maximum) rate of pressure rise resulting from the expanding fire ball and the maximum explosion pressure. The maximum explosion pressure and maximum rate of pressure rise are typically measured in a 20-liter or a 1m³ spherical vessel. These values are used to calculate the Deflagration Index for a gas/vapour atmosphere (Kg) or a dust cloud atmosphere (Kst) to classify the atmosphere's explosion severity. These data can be used for the purposes of designing explosion protection measures as summarised in Table 3.

Basis of Safe Operation	Purpose	Required Test	Discussion
Explosion Resistant Equipment	Enclosure is designed to withstand the maximum pressure resulting from the ignition and deflagration of the flammable atmosphere	> Maximum Explosion Pressure (Pmax) (Ref. 7, 8)	Although possible, explosion containment is generally not feasible for large vessels/equipment due to the high costs associated with ensuring that they are strong enough to withstand the maximum explosion pressure (typically 8- 10 bar). Smaller items such as transfer lines, screw conveyors and rotary valves can often be more easily designed for containment. Operating enclosures/equipment built for containment can be cumbersome as all openings have to be sealed to the correct pressure resistance before the process can start.
Explosion Relief Venting	One section/area of the enclosure is designed to be weaker than the rest of the enclosure so that in case of an explosion the weaker section would rupture/open and relieve the explosion products (pressure, flame, gases, unburnt fuel) to a safe location	> Maximum Explosion Pressure (Pmax) (Ref 7, 8) > Maximum rate of pressure rise (dp/dt) _{max} (Ref 7, 8)	Explosion venting is the most commonly used protection measure, particularly for dust handling/processing equipment such as dust collectors, large bins, and dryers. The explosion relief vent must be located to direct any products of an explosion (i.e. fireball, pressure, combustion gases and particulates) to a safe area outside of the building.
Explosion Suppression	Explosion is detected (by infrared or pressure sensors) at the early stages of the explosion and a suitable suppressant is injected into the enclosure to quench the developing fireball	> Maximum rate of pressure rise (dp/dt) _{max} (Ref 7, 8)	Explosion suppression is commonly used when, for example, the location of the vessel / equipment prevents the use of relief venting or if the material is hazardous to health and/or the environment. Explosion suppression is generally more expensive than relief venting and requires regular maintenance.
Explosion Isolation	Propagation of an explosion from a protected enclosure to any interconnected equipment or the work area is prevented by the provision of mechanical or chemical isolation systems	> Maximum Explosion Pressure (Pmax) (Ref 7, 8) > Maximum rate of pressure rise (dp/dt) _{max} (Ref 7, 8)	Explosion isolation is usually considered in conjunction with explosion protection measures (containment, relief venting, and suppression).

Table 3. Application of Maximum Explosion Pressure and Explosion Severity Data

It is important to note that the provision of any type of explosion protection implies that a deflagration is expected to occur within the protected enclosure. However, if the explosion protection and isolation systems are correctly specified, installed, and maintained, there will be no harm to people in the vicinity and no unforeseen damage to the equipment and the facility.

Process Safety Data – Chemical Reactivity

Chemical reactions are frequently associated with considerable heat exchange. Large amounts of energy can be released when decomposition reactions are initiated unintentionally through inappropriate operations such as loss of power, loss of cooling, loss of agitation, and/or unintentional mixing (e.g. waste/ disposal) of incompatible chemicals. This can cause a destructive force resulting in the rapid release of the reaction products, including toxic gases and vapours. Hence, the identification, assessment, and characterisation of both intended and, more importantly, unintended exothermic reactions are critical for ensuring the safe scale-up and operation of a chemical process (Ref 9, 10, 11, & 12).

Chemical reactivity hazards can be grouped into a number of general categories including:

- > Self-reactive materials (e.g., polymerising; decomposing; rearranging),
- > Self-heating materials (smoldering, burning)
- > 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; 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 sensitivity could be included as a part of the assessment for chemical reactivity hazards. Table 4 highlights a number of laboratory tests for the study of runaway scenarios.

“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.

Ignition Source / Hazard	Examples	Initial Test(s)		Follow up Test(s)	
		Liquids/Vapours/ Gases	Solids/Powders	Liquids/Vapours/ Gases	Solids/Powders
Chemical Reactivity	Runaway reaction causing loss of containment and release of hazardous chemicals, fires, and/or explosion due to: <ul style="list-style-type: none"> > Loss of power > Loss of cooling > Loss of agitation > Unintentional mixing (e.g. waste/disposal) of chemicals 	<ul style="list-style-type: none"> > CHETAH > Differential Scanning Calorimeter (DSC) > Accelerating Rate Calorimeter (ARC) > Reaction Calorimeter > Carius Tube Test > Adiabatic Dewar Calorimeter (ADC) 	<ul style="list-style-type: none"> > CHETAH > Differential Scanning Calorimeter (DSC) > Accelerating Rate Calorimeter (ARC) > Carius Tube > Adiabatic Dewar Calorimeter (ADC) 	<ul style="list-style-type: none"> > Simulation of actual process / operating conditions as well as potential process deviations 	<ul style="list-style-type: none"> > If MIE < 25 mJ: Volume Resistivity Surface Resistivity Electrostatic Chargeability

Table 4. Laboratory Testing for the Study of Runaway Scenario

Concluding Remarks

Fire and explosion risk management could include taking measures to avoid an explosion (explosion prevention) or designing facilities and equipment so that in the event of an explosion, people and facilities are protected (explosion protection). Selection of explosion prevention and/or protection measures is usually based on:

- > Availability of applicable and appropriately obtained data and information on the flammability, electrostatic properties, reactivity, and explosion characteristics of the materials (gases, liquids, powders),
- > Nature of the process and operation,
- > Level of personnel's knowledge and appreciation regarding the consequences of potential process safety upset conditions and adherence to safety measures,
- > Consequences of a flash fire or an explosion on personnel safety, community, and business.

Effectiveness of measures for ensuring safety is dependent on availability of appropriate data, information, process safety management systems, organisational capability, and organisational culture.

Flash fire and explosion prevention measures typically include:

- > Avoidance of Ignition Sources - All ignition sources capable of igniting the foreseeable flammable atmosphere are identified and eliminated or effectively controlled,
- > Avoidance of flammable (gas, vapour, dust cloud) atmospheres – A flammable atmosphere is never allowed to form by proper plant design, maintenance, application of exhaust ventilation, and housekeeping,
- > Inert Gas Blanketing - The atmosphere is sufficiently depleted of oxidant (normally the oxygen in air) so that it cannot support combustion.

If all sources of ignition cannot be reasonably excluded and/or flammable atmosphere(s) cannot be prevented, then the possibility

of a flash fire or explosion persists. Under such conditions “explosion protection” measures should be taken to protect people and minimize damage to facilities. It should be noted that explosion protection measures should be considered in addition to taking all reasonable steps to reduce the possibility of formation/spread of flammable atmospheres and exclude ignition sources. Explosion Protection measures include:

- > Explosion Containment - Equipment is constructed to withstand the maximum explosion pressure resulting from the deflagration of the fuel that is present within the process,
- > Explosion Relief Venting - Relieving the explosion products from the equipment to a safe location,
- > Explosion Suppression - Detecting an explosion at an early stage and suppressing it with a suitable suppressant,
- > Explosion Isolation - Explosions can propagate through pipes, chutes, conveyors, etc. Regardless of what type of explosion protection measure is considered, the explosion should be prevented from propagating from the location where it originates to other locations in the plant. The first step in isolating an explosion is to avoid unnecessary connections. If this is not possible, barriers should be created in the path of the explosion to protect personnel.

Management of runaway reaction hazards typically involves an understanding of the thermochemistry of reactions and the thermal stability limits of process materials (raw materials, intermediates, products, by-products, and waste streams). As with flash fire and explosion risks, control strategies typically fall into categories of “avoidance” (inherently safer process design or process control) or “protection” (**relief venting**, containment, reaction inhibition, or emergency cooling).

The key to success is in having a robust assessment strategy, specific to the materials involved and the process/operation, combined with competency in correct application of the data and information to ensure that an effective basis of safe operation is specified, designed, and operated.

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