An Introduction to Assessing Process Hazards[1]

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Abstract

A surprising number of process incidents occur due to a lack of general understanding of process hazards and lack of basic hazards assessment, subsequently resulting in the absence of or inadequate Process Hazards Analysis (PHA) to provide appropriate safeguards for minimizing process risks. Comprehensive assessment of intrinsic hazards that are present in a chemical process or facility is one of the first steps necessary in documenting process safety information and technology prior to conducting PHAs and requires much more than, for example, just a review of the Material Safety Data Sheets (MSDSs) of materials used in the process. This paper reviews practical approaches for conducting and documenting intrinsic hazards assessments (IHAs).

1. Introduction

A process hazard is like a wild animal trapped in a cage, where the consequences of inadvertent release can be devastating. The hazard may be because of a toxic chemical/mixture, a flammable chemical/mixture, a combustible dust, a reactive mixture, and/or energy (from a pressure buildup, chemical reaction, deflagration, etc.) which must be well understood even when contained. The consequences of release (loss of containment) of these hazards can be serious injuries, business losses, and environmental harm. Therefore, it is always important to understand the ***nature*** of the process hazard (i.e., **what kind of an animal**) and the ***level*** of hazard (i.e., **how dangerous is the animal**) as an essential part of any process safety management (PSM) program.

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A detailed understanding of process hazards must be developed, since a lack of or insufficient understanding is an important factor in many serious process incidents and injuries [1]. Process hazards are almost always present in petrochemical manufacturing processes, unless eliminated or minimized through proper design, including application of inherently safer technology or other approaches. A process hazard can be defined as a physical or chemical condition that has the potential for causing harm to people, property, or the environment [2]. An intrinsic hazards assessment (IHA) is used to understand and document process hazards and is different from consequence analysis, where the impacts of failure events are determined. It is also different from hazards identification and hazards evaluation conducted in Process Hazards Analysis (PHA), where the focus is on identifying relevant hazards, conducting a risk analysis, and ensuring that sufficient layers of protection exist to minimize process risk. Process risks, therefore, are different from process hazards. A process hazard may be very high, but the process risk can still be minimized so that the actual risk of an undesirable release or other event can be quite low. Understanding of the process hazards and related release events is required so that appropriate safeguards can be implemented to minimize process risk.

The key point to remember is that IHA must come before PHA. IHA is part of the process technology or process safety information element of PSM. If this basic work is not done, or is not done well, then the PHA will be missing potentially essential information that can lead to or contribute to ineffective risk evaluation and management. The result can be like the accidental release of a wild animal from it's cage, maybe not dangerous, but in most cases, most likely so. A systematic approach to IHA is introduced in this paper for assessing process hazards, so that the nature of the beast can be well known and understood by the PHA team, allowing appropriate safeguards to be provided to keep the animal caged at a tolerable level of risk and to prevent the potential consequences of release.

2. Intrinsic Hazards Assessment (IHA)

A systematic assessment of intrinsic process hazards is one of the first steps necessary before conducting any consequence and/or risk analyses. Many of the governmental regulations (e.g. SEVESO II in Europe, COMAH in the U.K., OSHA1910.119 in the U.S.A.) require a thorough assessment of hazards. A complete understanding of process hazards is necessary for identification of potential incident scenarios, which provide a pathway for exposure to the hazardous effects of the materials and processing conditions involved.

In the U.S., DuPont global PSM standards and the OSHA1910.119 regulation require that a complete assessment of process hazards be conducted as part of the Process Technology or Process Safety Information (PT/PSI) element of the overall PSM program. Such an assessment must be completed and documented prior to conducting a Process Hazards Analysis (PHA).

In the PT/PSI compilation, complete and accurate written documentation regarding hazards of the process, process design basis, and equipment design basis is considered essential for effective implementation of the overall PSM program and for conducting comprehensive PHAs for managing risk. The compilation of PT/PSI provides necessary information to a variety of users including the PHA team as well as those developing the operating procedures and training programs, contract administrators and contractors who will be working in a process area, those conducting pre-startup reviews, emergency response/preparedness planners, and where appropriate enforcement and insurance officials.

Use of just MSDSs to compile and understand information on hazards within a process boundary is generally inadequate and must be supplemented with additional sources of data. Focusing on specific material properties doesn't provide sufficient information for assessing the hazards intrinsic to a process, especially for chemical reactivity where chemical interactions are important. All the chemicals, materials, chemistry, and operating conditions (temperature, pressure, concentration, etc.) within multiple process boundaries at a typical manufacturing facility must be evaluated to ensure adequate documentation for the PT/PSI compilation.

To systematically assess process hazards, it is necessary first to define process boundaries within a chemical plant. These process boundaries may correspond to those used in PHAs or to other appropriate parts of the facility. Within a process boundary, a complete list of all the raw materials, intermediates, products, utilities, and other materials used should be compiled. In such a listing, it is important to also keep track of amounts, rates, state (vapor/liquid/solid), compositions, etc., as appropriate.

The level and nature of hazard will vary in different process boundaries depending on the quantities of chemicals handled, the intrinsic material properties, and the operating conditions. A tank farm that contains a variety of chemicals stored as liquids under ambient conditions will have a significantly different hazard than a manufacturing building that has a few of the same chemicals in pipes and vessels as vapors in mixtures at high temperature and pressure. Similarly, a tank containing anhydrous ammonia as a liquid under pressure has a much higher level of hazard than piping and columns that contain 20 wt% aqueous ammonia. Consideration should also be given to the potential for chemicals and materials from one process boundary inadvertently entering another process boundary, possibly introducing new hazards or interactions that must be evaluated.

The purpose of IHA is to define the nature/type and levels of all process hazards within each of the process boundaries in a manufacturing plant. A hazard level scoring system should be used based on a general scale identical to the scale used for the NFPA H/F/R Scoring [3] for individual materials: 0 (None), 1 (Low), 2 (Medium), 3 (High), and 4 (Very High). Table 1 shows a simple way to summarize the IHA for a process boundary (e.g. mixing vessels and feed lines) where some toxic & flammable chemicals and small amounts of combustible dusts are handled.

A key part of IHA is taking a broad view of process hazards by looking at a variety of physical & chemical properties and then forming a composite hazard level score. Use of a composite score ensures a comprehensive view of the process hazard using multiple sources and types of data to ensure completeness. Further details are provided in the remaining sections on assessing and documenting individual types of process hazards. An additional discussion is available elsewhere [4].

Type ***Level***	***Toxicity***	***Flammability/ Explosivity***	***Chemical Reactivity***	***Dust***	***Other***
4 – Very High		X			
3 – High	X				
2 – Medium				X	
1 – Low			X		X
0 – None					

Table 1: Example hazards assessment summary table for a specific process boundary.

3. Toxicity

Toxicity is the degree to which a chemical upon exposure can cause harm to any living organism [5]. In assessing toxicity hazards, it is most important to focus on developing an understanding of the acute toxicity effects on people, resulting from short-term exposure from accidental releases, while only noting chronic effects where appropriate. While the MSDS or an International Chemical Safety Card for a chemical might provide some information about toxicity effects, this information is often not complete and generally does not include information on concentrations required to evaluate acute exposure.

Important toxicity parameters include:

- **Acute Toxicity Concentrations.** The Emergency Response Planning and Guideling (ERPG) and similarly Acute Exposure Guideline Level (AEGL) concentrations are developed by toxicologists using a wide range of available toxicological data to conservatively determine the concentration levels that might affect general and susceptible populations for acute exposure. An AEGL-x concentration (like ERPG concentration), is defined as the airborne concentration (in ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience:
    - 1 mild, short-term reversible adverse health effects
    - 2 irreversible or serious, long-lasting adverse health effects or an impaired ability to escape
    - 3 life threatening effects or death

  The concentration values that are most appropriate in terms of assessing toxicity hazards are the AEGL-2/ERPG-2 for injury effects and AEGL-3/ERPG-3 for life threatening effects. In DuPont, concentrations equivalent to ERPGs/AEGLs are developed and made available for use by an internal committee of toxicologists.

- **NFPA Health Scores.** The National Fire Protection Agency (NFPA) in the U.S. publishes the Fire Protection Guide [3] which includes a Health Score that is on a 0 to 4 scale for a variety of chemicals. This score has been very useful from an emergency response perspective and is categorized based on health effects as follows: 0 (None), 1 (Slight), 2 (Moderate), 3 (Severe), and 4 (Extreme).

- **Substance Hazards Index.** In DuPont, a focused PSM approach has been developed for managing the hazards of highly toxic materials. A highly toxic material is one that has a high substance hazard index (SHI) which is determined as follows:

SHI = {Vapor Pressure (in atm @ 20 ºC) x 1E+06 } / {ERPG-3 in ppm}

When assessing overall toxicity level, information about concentration levels of concern (ERPG-3, AEGL-3, or equivalent), NFPA Health Score, and SHI can be used to determine the composite level of toxicity hazard within a process boundary. The overall hazard level uses the same scale developed for the NFPA Health Scoring, based on individual parameter scores, and can be categorized as follows: 0 (None), 1 (Low), 2 (Medium), 3 (High), and 4 (Very High).

4. Flammability & Explosivity

Flammability

Flammability is a property of chemicals that provides an indication of the potential for ignition and burning [6]. The degree of flammability is determined by testing per standard protocols. For chemicals that are flammable, there are a variety of parameters that are useful in assessment of hazards, with a focus on harm to people from 2nd to 3rd degree burn injuries upon exposure. An MSDS or International Chemical Safety Card may contain some of the pertinent data like flash points, flammable limits, auto-ignition temperature, and products of combustion. However, it is important to verify and confirm this data from multiple sources.

Important flammability parameters include:

- **Flash Point.** The NFPA makes a distinction between liquids that are flammable and combustible based on the boiling point and flash point. Liquids below a flash point of 100°F are considered Class I flammable liquids, liquids with flash points between 100 to 140°F are considered Class II combustible liquids, and liquids with flash points above 140°F are considered Class III combustible liquids. The flash point is used as a primary parameter for assessing flammability.

- **NFPA Fire Score.** The NFPA has also published a Fire or Flammability Score that is on a 0 to 4 scale for a variety of chemicals [3]. This score is useful from an emergency response perspective and is categorized based on impacts as follows: 0 (None), 1 (Slight), 2 (Moderate), 3 (Severe), and 4 (Extreme). The NFPA Flammability Score, where available, should be documented for chemicals within a process boundary.

When assessing flammability hazards, information about the flash point, and NFPA Flammability Score are all used to determine the composite level of flammability hazard within a process boundary. Operating conditions (e.g. temperature, pressure) must always be used in the determination of hazard: a liquid that may be regarded as combustible when in storage at ambient conditions could well be flammable in a different process boundary where the operating temperature is above the flash point. The overall hazard level score used is identical to NFPA Flammability Scoring, based on individual parameter scores, and can be categorized as follows: 0 (None), 1 (Low), 2 (Medium), 3 (High), and 4 (Very High).

Explosivity

Explosivity can be viewed as the measure to which a fuel & oxidant mixture is explosive. Explosion hazards can result from the presence of flammable chemicals or combustible dusts in flammable concentrations in a confined and/or congested environment inside or outside equipment [6]. The confinement and congestion causes a flame to accelerate resulting in a deflagration. In some cases, detonation can occur that causes generation of higher overpressure and impulse from the resulting blast wave.

The maximum deflagration pressure and the rate of pressure rise are important parameters that can be measured for a variety of fuels. Once a fuel ignites, the rate of flame acceleration determines the maximum pressure generated in a confined and congested environment. The fundamental burning velocity of a material is a measure of the rate of flame propagation that can occur. Fundamental or laminar burning velocity (LBV) is available for several flammable chemicals [7], and is a measure of how reactive a material might be in terms of generating high deflagration pressures and increased rate of pressure rise.

If flammable chemicals or combustible chemicals above their flash point are handled within equipment in a process boundary then the potential for internal deflagration or detonation is also always present. The explosivity hazard level, in such as situation, should be regarded as 3 (High) or 4 (Very High). Vapor cloud explosions can occur where the release of a flammable chemical/mixture (of a certain flammable mass) is in a confined or congested volume. Information such as the LBV of a chemical and the levels of confinement and congestion can be used to determine what the overall hazard level might be.

Explosions can also result from the bursting of a vessel caused by a rapid increase in pressure. Pressure build-up could be the result of uncontrolled vessel heating, an uncontrolled chemical reaction, failure of pressure regulators upstream of equipment, deflagration of combustible dusts, or deflagration of flammable vapors within pipes/equipment. If the pressure inside the vessel exceeds the maximum working pressure, then vessel rupture is possible, resulting in propagation of a blast wave. A rapid increase in temperature and pressure from a fire under a container can also lead to a boiling liquid expanding vapor cloud explosion (BLEVE) if the material in the container is a liquid under pressure at a temperature greater than its boiling point. If a BLEVE occurs, a fireball typically forms leading to potential thermal radiation impacts. The overall explosivity hazard level determination for vessel bursts, vapor cloud explosions and BLEVEs and the corresponding scoring is identical to NFPA Flammability Scoring and can be categorized as follows: 0 (None), 1 (Low), 2 (Medium), 3 (High), and 4 (Very High).

The explosivity hazard in process boundaries where combustible dust is handled is covered in Section 6 below.

5. Chemical Reactivity

Chemical reactivity hazard is a hazard that results from uncontrolled chemical reactions in any equipment within a process boundary [8]. An exothermic chemical reaction leads to release of heat, and an increase in temperature and pressure. An endothermic chemical reaction could lead to generation of products that are unstable and or gases that causes an increase in pressure.

- **Types of Reactions.** Exothermic reactions are usually of greater concern than endothermic reactions. Therefore, the first step in chemical reactivity hazard assessment is to identify the possible uncontrolled chemical reactions that can occur. These are often side reactions that may not be normal within the process boundary and that could occur because of even small changes in operating conditions (i.e., pressure, temperature, composition, etc.) or from inadvertent mixing of materials. Each reaction of concern within a process vessel should be evaluated to determine the potential level of hazard.

  Based on the reaction type, the exothermic nature can be used to determine the level of hazard on a scale of 0 to 4. If any reaction (exothermic or endothermic) can generate a gas the level of hazard is considered 3 (High) to (4) Very High due to the potential for rapid pressure rise.

- **NFPA Instability Score.** The NFPA has also published a Reactivity/Instability Score that is on a 0 to 4 scale for a variety of chemicals [3]. This score is categorized based on impacts as follows: 0 (None), 1 (Slight), 2 (Moderate), 3 (Severe), and 4 (Extreme). For each specific reaction, the NFPA Instability Score, where available, should be documented for all the reactants and products and the highest score should be selected. Where an NFPA score is not available, an equivalent score can usually be determined based on the structure of the chemical molecule.

- **Heat of Reaction.** For any reaction, the heat of reaction is a potential measure of the hazard. In many cases, it can be estimated using the heats of formation of each of the reactants and products. If the exothermic heat of reaction, expressed (as a positive number) usually as calories per gram of reaction mass, is greater than 300 cal/g of reaction mass then the hazard level is regarded as 4 (Very High) and if it is less than 20 cal/g the hazard level is 1 (Low). If a reaction (exothermic or even endothermic) can generate a gas the level of hazard is considered 3 (High) to 4 (Very High).

- **Adiabatic Temperature Rise and Self Heat Rate.** Once the heat of reaction is available through estimation or measurement using calorimetric methods, it can be used to estimate the adiabatic temperature rise. Adiabatic temperature rise can be calculated using the overall heat generated in a reaction, the reaction mass, and the heat capacity of the mixture. In addition to the adiabatic temperature rise, the self heat rate is another important parameter that can be used to determine the level of hazard, which has to be measured or can be estimated based on the type of reaction. The rate of reaction, which is a kinetic measure, is also important in addition to the heat of reaction which is a thermodynamic measure.

- **Onset Temperature.** For exothermic reactions, the temperature at which the onset of an exotherm occurs is another important parameter. This is a value that has to be measured using calorimetric methods. The ratio of the onset temperature to typical process temperature can also be used to estimate the level of hazard.

The overall hazard level score is on a scale identical to the NFPA Instability Score, based on individual parameter scores, and can be categorized as follows: 0 (None), 1 (Low), 2 (Medium), 3 (High), and 4 (Very High). It should also be noted that high temperature and pressure from uncontrolled chemical reactions could lead to a vessel burst (an explosivity hazard) and subsequent loss of containment of contents, resulting in injuries from additional toxic exposure, fire, and/or explosions.

6. Dusts

Fire and explosion hazards can exist in handling of fine combustible powders in equipment or releases of a combustible dust cloud into a confined and/or congested environment [6]. The confinement and/or congestion causes a flame to accelerate resulting in a deflagration. According to NFPA-654, combustible dust is defined as "A combustible particulate solid that presents a fire or deflagration hazard when suspended in air or some other oxidizing medium over a range of concentrations, regardless of particle size or shape."

The maximum deflagration pressure and the rate of pressure rise are important parameters that can be measured for dusts. Once a fuel ignites the rate of acceleration of a flame determines the maximum pressure generated in a confined and congested environment. The rates of pressure rise and expansion volume are combined to provide a measure of the extent of explosion. This measure is called the deflagration index (K_{st}).

Some K_{st} values for dusts are available [7] but it is usually best to measure them. K_{st} values are typically used to classify dusts into different hazard classes, sometimes referred to as St-1, St-2, and St-3 corresponding to low, medium and high. For dusts, the particle size can have a significant impact on K_{st} and the other parameters such as Minimum Ignition Energy (MIE), Minimum Explosible Concentration (MEC), etc., and must be well understood to accurately assess dust hazards.

For assessing dust explosivity hazards, it is important to know the amount of powders handled, the smallest particle size (or the particle size distribution), MEC, K_{st}, and process conditions. Secondary dust explosions, where dusts are distributed in air from an initiating process event, are often more devastating than primary dust explosions. The confinement and congestion inside buildings where dust can accumulate on surfaces, therefore, must be also be evaluated. In addition, if fine combustible dusts are handled within equipment (e.g. dust collectors) in a process boundary, above MEC, the potential for internal deflagration is always present.

For any process boundary where combustible dusts are handled, inside or outside buildings and equipment, the available information mentioned above should be used to determine the overall hazard level. The overall dust hazard level score is determined using the scale for NFPA Flammability Scoring and can be categorized as follows: 0 (None), 1 (Low), 2 (Medium), 3 (High), and 4 (Very High).

7. Other Process Hazards

Other process hazards are those that cannot be easily classified into toxicity, flammability, explosivity, chemical reactivity, and dust hazards. They include hazards of high energy rotating equipment (like compressors, turbines, large pumps, centrifuges, etc.), hazards of extreme hot or cold temperature materials that are otherwise not hazardous (e.g. steam), hazards of low oxygen environments, hazards of high pressure or vacuum, etc. Many other hazards, such as mechanical hazards associated with lower energy moving equipment, infrastructure forces (e.g. collapsing equipment), electrical energy hazards, ionizing radiation hazards, noise hazards, and environmental hazards are usually considered "general hazards" rather than "process hazards." For a process boundary, once the types of other process hazards have been identified a combination of the relevant levels of concern, and any other available information should be used to determine the overall hazard levels that are present. The overall hazard level score would be on a scale identical to the scale used for the NFPA Scoring and can be categorized as follows: 0 (None), 1(Low), 2 (Medium), 3 (High), and 4 (Very High). See Table 1.

8. Summary

A process hazard is a physical or chemical condition that has the potential for causing harm to people, property, or the environment. ***A Process Hazard is like a wild animal trapped in a cage, where the consequences of a release event can be devastating. We must always understand all the types and levels of hazards in each part of a manufacturing process.***

All the different types of process hazards in each process boundary, such as acute toxicity, flammability, explosivity, chemical reactivity, dust, and others, must be assessed and documented. It is important to account for all the chemicals, materials, chemistry, and operating conditions (temperature, pressure, concentration, etc.) within multiple process boundaries at a typical manufacturing facility. A complete intrinsic hazards assessment of process hazards using methods introduced in this paper must be conducted as part of the Process Technology or Process Safety Information (PT/PSI) element of the overall PSM program and should not be relegated to the PHA team. The purpose of an intrinsic hazards assessment is to define the nature/type and levels of all process hazards within each of the process boundaries in a manufacturing plant. A hazard level scoring system should be used based on the scale used for the NFPA Health/Fire/Instability Scoring for individual materials. The levels of process hazards in a process boundary can then be categorized as follows: 0 (None), 1 (Low), 2 (Medium), 3 (High), and 4 (Very High).

There are also two other Process Safety Progress (PSP) articles that cover this process hazards topic [9,10].

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