PROCESS RISK ANALYSIS

W. Witt and N. Ramzan

Brandenburgische Technical University of Cottbus, Cottbus, Germany

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Summary

The development of process and design of chemical plant for the conversion of raw material into final products come under chemical engineering. Process risk analysis is an important activity, which is to be performed at different life stages of process not only to meet the standards/regulations but also for the improvement of the process and/or plant. Process risk analyst may or may not be a chemical engineer but it is better for him/her to have a sound background of chemical engineering. This chapter covers fundamental concepts and important techniques to carry out process risk analysis and references are provided for further details. The terminology and application of risk analysis is presented first. Next, techniques used most commonly for hazard identification, frequency and consequence estimation/modeling are presented. Then, application of these techniques to carry out safety concept design, process safety/risk analysis and safety/risk management is discussed.

1. Introduction

Incidents and accidents especially the well known catastrophic accidents in Flixborough (UK), Serveso (Italy) and Bhopal (India) have shown that effects of process/plant malfunction may not only be hazardous to operators but also catastrophic to human life (including members of public), environment and/or capital. Therefore, removing process/plant malfunctions for reduction of risk and prevention of such accidents in future is of interest for community and company and an emerging subject of chemical engineering as well [1].

Several directives in the European community, e.g. EC Directive of Major Accident Hazards [2] and ATEX Directives 137 (1999/92/EC) and 100A (94/9/EC /3/ for safety and health protection of workers from explosive atmospheres, are based on safety/risk analysis techniques.
However, basic factors determining the magnitude of hazard (1-3) and risk (1-9) are:

1. inventory and properties of hazardous materials (volatility, toxicity, reactivity)
2. type of operation; process conditions
3. complexity of operations
4. design and operation relative to standards and codes
5. layout of equipment
6. plant layout (distance of equipment)
7. preventive and protective measures
8. plant site (distance to population centers, vulnerability of the surrounding)
9. effectiveness of plant management (operator training, production vs. risk)

To come from hazardous process (idea) to safe operation (safe operation means the risk is small enough to be tolerated by community and company) safety/risk analysis work is relevant during process development, plant design and plant operation as well. In addition to safety/risk analysis techniques, inherent safety design practices are also used in order to improve the process, technology and management.

Safety/risk analysis is integrated in management and quality systems e.g. the ESH – program [4]. Investment in safety/risk analysis, safety related process and plant design and safety technique may not only reduce risk but also plant design and/or operation costs.

Safety/risk analysis procedure is presented in a lot of chemical and process engineering publications and books e.g. in Chemical Process Quantitative Risk Analysis (CPQRA) Guidelines [5].

Several fundamental aspects of risk assessment in industry and legislation are presented and discussed e.g. by Shortreed and Steward [14].

2. Terminology Used in This Chapter

**Hazard** is a physical situation with a potential for human injury, damage to property, damage to the environment or some combination of these [6] or we can say a hazard is a combination of a hazardous material, an operating environment, and certain unplanned events that could result in an accident. The degree of hazard depends on inventory and properties of hazardous materials (volatility, toxicity, reactivity), type of operation and process conditions.

**Risk** describes the frequency and magnitude of damage e.g. financial risk may be expressed as a product of frequency and damage costs (\( Risk = frequency \times consequence \)).

**Risk calculation** has to consider the objective, which may be focused on an individual (operator or public at fence), society or company. Individual risk may be related to financial, injury or death. Societal risk may include number of injuries or deaths, contamination of the environment and/or property damage. Company interests may be related to economical aspects and/or loss of production/market.

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Inherent safety measures may be classified in material/chemical, process or construction effects. Reducing inventories of hazardous materials, or - if possible - replacing them by less hazardous chemicals is the preferred inherent safety measure. Next, a less hazardous process, reduction of process parameters (temperature, pressure) will increase inherent safety as well. A simplified construction and design related to maximum pressure possible, e.g. as a result of run away reactions, characterize the third class (e.g. [25] pp.474-482, 484, 542).

Storage of hazardous intermediates should as far as possible be avoided and inherent safety is the best way of ensuring safety, because it does not have to rely on the correct functioning of safety devices [6].

Hazard assessment ends with evaluating various amounts of emissions of hazardous (flammable, toxic) chemicals.

Safety/risk analysis is a qualitative/quantitative estimate of risk based on damage and frequency analysis of relevant harmful events.

Risk assessment underlines the point that the study ends with the assessment of resulting consequences in terms of fatalities and/or damage losses.

Frequency is the number that event (failure or damage) occurs per time.

Probability describes the likelihood that event will succeed or not. The probability number is between 1 and 0 and has no unit.

Failure is when a system is incapable of carrying out its duty. Systems can fail either to a dangerous condition or to a safe condition. Revealed failure will be detected at the time of failure exist. Unrevealed failure will remain undetected until to the time of routinely proof test (standard case).

Fractional Dead Time is the fraction of time a device is in a failed state. The terms probability of failure on demand and unavailability are also used to represent the fractional dead time.

3. Application of safety/risk techniques

Safety/risk analysis work is relevant for operator health, public (health, environment) and company (financial aspects, loss of production, and loss of market). It is an important activity within process development, plant design and plant operation. Most chemical companies have established a step wise procedure, e.g. BASF AG [42] and Bayer Ltd. [7]. The Bayer Ltd. [7] has developed a design stage related safety review/certificate system, see Table 1.

<table>
<thead>
<tr>
<th>Design stage</th>
<th>Review stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preliminary design</td>
<td>Concept certificate</td>
</tr>
<tr>
<td>Basic design</td>
<td>Design certificate</td>
</tr>
</tbody>
</table>
Table 1: Procedure for the design and operation of safe chemical plants (source Bayer Ltd. [7] simplified version

<table>
<thead>
<tr>
<th>Detailed design</th>
<th>Safety certificate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start-up</td>
<td>Acceptance certificate</td>
</tr>
</tbody>
</table>

Process development:
The purpose of a safety/risk study at this stage is related to safe operation of laboratory/pilot plant and/or higher level of inherent safety for the process under development.

Conceptual plant design:
In conceptual plant design stage, safety/risk study should include at least the definition of the safety concept. The study may include topics like accumulation of hazardous chemicals (at normal operation, in case of an incident), increase of inherent safety (reduction of hazardous materials, concentration, temperature, pressure, etc.), application of safety systems (containment, pressure relief, inhibitor, inerting, etc.), operator safety, estimation of magnitude of hazard and/or selection of plant site.

Safety/risk analysis work in plant design and operation:
Safety/risk analysis is a process that includes several steps and carried out at a definite status/time of plant design or plant operation. Within safety/risk analysis, intension/objectives may be the identification of failures/faults that have the potential for hazard (risk), analysis of hazardous events, estimation/quantification of frequencies and consequences, meeting legal or regulatory requirements or standards and calculating employee risk, public risk (health, environmental) and/or financial risk. Besides this, development of proposals for improvement of the process, the plant lay out and/or the safety system is often integrated, especially if a conflict with constraints has been identified [see [5] p. 20].

Plant/process optimization considering risk aspects:
Risk related optimization objectives may include improvement of inherent safety, maximization of profit (long term), minimization of health hazard, environmental and/or financial risk, selection of the best multi objective solution [see [5] p. 20].

Presentation of risk:
The community/companies are sometimes interested in risk profiles (risk contour/F-N curves) outside/inside the plant fence. The motivation may be legislation, off side/on side/emergency response planning and/or management programs. Risk indices (e.g. DOW F&E-Index) or risk figures (e.g. costs) may be of interest as well. Risk presentation may be related to incident scenarios, individuals or society [see [5] p. 395].

4. Hazard identification and safety/risk analysis techniques

A number of hazard identification, weak point analysis and safety/risk analysis techniques have been developed in various fields as well as in chemical engineering. Some of most commonly used methods in process industry are briefly described below.
4.1. Hazard Potential Analysis

The source of a hazard may be hazardous material and/or energy. Hazard potential depends on:

a) material characteristics (toxicity, reactivity and/or flammability),

b) operation/storage conditions (temperature, pressure),

c) amount of material,

d) release mechanism.

Hazard potential analysis is usually carried out at the conceptual design step. It supports safety analyst to separate the plant under study into less/more hazardous sections and selection of safety analysis techniques. Therefore, application of hazard potential analysis may be useful at the beginning of most of safety/risk analysis as well.

4.1.1. Potential Release Estimate

A rough estimate of the size of potential releases is useful for classification of the hazard potentials of the plant facilities. As dominant release potentials are mainly due to the different volumes of vessels, pipes and pump rates, therefore the volume and flow data could be used for rough potential release estimates/potential classification. The releases can be calculated by simplified methods and/or based on rough assumptions e.g. full bore rupture of the barrier.

<table>
<thead>
<tr>
<th>No</th>
<th>Volume</th>
<th>Content</th>
<th>State (p, T)</th>
<th>Discharge</th>
<th>Gas</th>
<th>Liquid</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>main tank</td>
<td>2 x 10^7 L</td>
<td>7, 32°C</td>
<td>rupture of pipe at tank ø 250 mm</td>
<td>10²</td>
<td>3 x 10⁴</td>
<td>10²</td>
</tr>
</tbody>
</table>

Table 2: Example of the potential release estimate

The analysis has to be done for each containment and plant function. For the operation of the isolation valves or pumps a time delay has to be assumed (of e.g. two minutes).

An estimate of the size of potential releases is used in barrier analyses [9] and release scenario analyses [8] to find out the most significant consequences and/or contributions to risk.

4.2. Matrices

4.2.1. Reaction Matrices

A systematic investigation of the behavior of chemicals in mutual contact or in contact with construction materials is performed by the use of reaction matrices. If nature and
quality of chemicals and construction materials involved are known then the matrices should lead to a documentation of the complete set of binary reaction possibilities. The investigation on construction materials can also be expanded to some other materials typically used for plant construction and instrumentation. These matrices are of two types:

**Chemical/Chemical matrix:**
A systematic listing of all chemical/chemical reaction possibilities is very useful for further hazard investigations. Because unwanted simultaneous contact of more than two streams is unlikely, the matrix should cover most of the significant reaction possibilities that could lead to a hazard. However, this kind of matrix does not cover reactions between three or more substances.

![Chemical/Chemical matrix](image)

Figure 1: Chemical/Chemical matrix integrated in the plant design tool ComosPT-RMO [11]

The matrix should include that all chemicals used in a plant which might come into contact due to erroneous handling or switching, leaks or other abnormal circumstances. All possible combinations are systematically checked in the chemical/chemical-reaction matrix. The kind of reaction is indicated by symbols. For the judgment normal and abnormal conditions in temperature (and pressure) should be considered. This matrix is used to describe the potential of reactions like fires, explosions, other exothermic / hazardous reactions and solutions [9, 10]. Figure 1 represents the integration of that matrix in a commercial plant design tool.

**Chemical/construction material matrix:**
The reaction possibilities between all chemicals and materials of construction used in the plant can also be investigated systematically based on this method. The main results are documented in a matrix using a small number of symbols [10, 11]. The investigation is based on experience, literature research, expert opinion and if necessary special experiments. All chemicals used during operation, maintenance or cleaning should be considered with regard to their reactivity with construction materials as pure substances only. The reaction may depend on process parameter (temperature, concentration of
oxygen, impurities) and/or construction parameters (stress, welding materials).

4.2.2. Process Control/Shut Down and Automation Matrices

**Process control/shut down system matrix (PC matrix):**
The PC-matrix may not only be used in safety/risk analysis. It is also of value for plant design, plant management and operators. For the safety study it is important to know, which signals causes alarms and control the active plant components. These interactions can be described with the help of a matrix, correlating the measuring devices and controller/switches with field components. The matrix comprises information contained in several sources like: P and I-diagrams, trip list, operation manual, and operator instructions.

**Remark:** Normally only the correlation between the automatic shut down and safety system is shown in a simplified matrix [12, 13].

**Process automation matrix (PA matrix):**
The PA-matrix describes the time related interaction between the process control system and field components. It is an aid not only for safety/risk analysis but also for plant design, plant management and operators [13].

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Biographical Sketches

Werner Witt was born in Gehrhof, Germany; he obtained his first degree in Process Engineering (Dipl.-Ing., FH - applied science -, 1972) and his second degree in Process Engineering (Dipl.-Ing., 1976) at the TFH-Berlin and the TU-Berlin. In 1982, he obtained his doctor degree (Dr.-Ing.) in Process Engineering. Werner Witt has been professor at the BTU-Cottbus since 1995 and also has practical and research experience of working in industry. He did work for the apparatus design company, Klöpper, in Dortmund from 1977-1978. Next, he did work with the Battelle Institut in Frankfurt from 1983-1985 in the safety research department. Further he was also responsible for the safety laboratory and the leader of the safety group in the process development department Henkel Company in Düsseldorf (1985-1995). Presently, Prof. Witt is a member of the DECHEMA expert group for "Safety related plant design" and guest of several DECHEMA/VDI expert groups in process engineering and plant design. His research focus is mainly on multi-objective process optimization, development of safety risk methodologies and development of safety related operation limits for process plant apparatus. He has been coordinator of diverse national research projects within the mentioned areas. Prof. Witt is also author of several scientific publications.

Naveed Ramzan was born in Lahore, Pakistan. He did his bachelor degree in chemical engineering (1994-1998) and master degree in chemical engineering (2001-2003) from Department of Chemical Engineering, University of Engineering and Technology Lahore, Pakistan. He has been the faculty member in Department of Chemical Engineering, UET Lahore. Presently, he is pursuing his doctorate degree in engineering at chair of plant design and safety technology in BTU-Cottbus. He is also author of several research papers in well known journals and has experience of supervising research work of undergraduate and graduate students at Btu-Cottbus and UET, Lahore. His research focus is on multiobjective optimization, safety and risk analysis in chemical process plants.