Safety in the Chemical and Refining Industry

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Report Abstract
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Safety in the Chemical and Refining Industry

INTRODUCTION

Process safety refers to:

- The replacement and maintenance of equipment
- Having systems in place to insure that industrial installations are in top condition
- Conducting adequate training for employees
- Assuring adequate staffing to avoid fatigue and ensuing mistakes
- Maintaining adequate records and information on possible hazards to workers
- Making sure that changes to a process are recorded and shared with workers

During the 1980-1990 timeframe, the United States had several refinery and chemical plant catastrophic type incidents which triggered the enactment of safety standards by government regulatory bodies such as the United States Department of Labor’s Agency, Occupational Safety and Health Administration (OSHA). These incidents promulgated the Process Safety Management (PSM) and Risk Management Planning (RMP) regulations in the early 1990s.

Investigations done by other United States government bodies such as the Chemical Safety Board (CSB), specifically after the BP Texas City 2005 refinery explosion, were the most important driver in moving regulatory bodies to enact stricter safety standards. After this explosion (resulting in 15 fatalities, 180 injuries and substantial damage compensation which was estimated at $700 million), subsequent investigations resulted in recommendations for greater enforcement of regulations and changes in inspection procedures. Other active U.S. Federal Government Entities and Agencies entrusted with enhancing safety include the Environmental Protection Agency (EPA) and the Department of Energy (DOE).

Nexant presents a summary of relevant hazard and safety analysis methodologies as exists in the U.S., coupled with high level summaries of safety regulations in Canada, the European Union (EU), and the United Kingdom in order to provide global context. A survey of major industry accidents involving process plants is presented and pertinent conclusions drawn from these accidents.

METHODOLOGIES FOR DETERMINING RISKS IN THE PROCESS INDUSTRY

Hazard evaluation methodologies and techniques are an integral part of a process safety management program. These techniques permit plant operators, maintenance planners, and refinery managers to know what they can obtain from a hazard evaluation and which one could fit their needs. Frequently, these techniques are only deemed necessary or receive managerial attention prior to the design of a new plant, a major revamp or when an accident or serious incident occurs. Nexant recommends that these techniques be used on an on-going recurrent
basis. Both operators and management should become familiar and apply them recurrently and consistently, not only leaving them to the specialists.

The use of these techniques provides safeguards that prevent and protect against process upsets and contribute towards devising solutions for the minimization of possible catastrophic or non-catastrophic outcomes.

Limitations exist regarding these techniques. The more familiar workers and management become with them, the more they can be realistic about expected results from their application. HAZOP, FMEA, FTA, and RBI are examples of methodologies available to assess hazardous situations in hydrocarbon and chemical processes, materials handling, disposal etc.

- **HAZOP**

HAZOP is a well-proven, structured team-based method for hazard identification. It is applicable at the project process design completion stage or for planned modifications (i.e., a revamp or a project.). The technique performs a detailed examination of the process and engineering intention of new or existing facilities to assess the hazard potential of operation outside the design scope, or malfunction of individual items of equipment and their consequential effects on the facility as a whole.

Generally, HAZOP is led by an experienced facilitator. For an oil and gas project, a core team would typically include personnel from a refinery or chemical plant in various areas. The acronyms come from: **HAZ**ard and **OP**erating problems since HAZOP is a systematic technique to identify potential hazards and operating problems. It consists of a formal systematic rigorous examination to the process and engineering facets of a production facility. In this scope, it would be done in a refinery process plant or a chemical plant. It is also a qualitative technique based on “guide-words” to help gain insights about the way HAZOP applies to the process industry.

Typically, HAZOP is carried out by a multi-disciplinary team (HAZOP team) during a series of meetings.

**Benefits from HAZOP**

A thorough HAZOP analysis delivers a comprehensive design review from a safety and environmental perspective. This analysis should impact refinery and plant operations, maintenance (preventive and extraordinary if required), and budgeting if it is determined that a project is warranted as a result of the analysis.

**HAZOP Objectives**

HAZOP at a minimum should ensure the following objectives:

- Identification of potential equipment deviations from intended design function
- That HSE process and equipment hazards are revealed;
- Provide an action plan for necessary process or instrumentation improvements that can be planned;
- Enable action responses be collected in a systematic manner so that they are made auditable
Potential operational problems are identified. These problems could degrade plant performance (product quality, production rate) and eventually impact the return and profit in a process plant and extend to the whole refinery or chemical complex.

- **FMEA**
  
  Failure Modes, Effects Analysis (FMEA) consists of a manual analysis to determine the consequences of component, module or subsystem failures. It is considered to be a bottom-up analysis from the particular modes and possibilities that could occur in a system and the concept can be extended to a process plant. Among its modalities for carrying out the analysis is to generate a listing, generally on a spreadsheet, where each failure mode, possible causes, probability of occurrence, consequences, and proposed safeguards for a system, process unit, vessel etc. are noted. FMEA can help identify and eliminate concerns early in the development of a process or new service delivery eliminating the possibility of failure.

- **FTA**
  
  The Fault Tree Analysis (FTA) methodology based on deductive techniques provides a traceable, logical, quantitative representation of causes, consequences and event combinations. It is amenable to the use of software and is particularly useful for comprehensive systems that require such use of software.

  Generally, FTA is centered on a system occurrence or a particular incident and provides a causal type method for analysis.

  The methodology is not intuitive, and reaches a certain level of complexity so it requires training.

  FTA was used after the accident at the Tosco, Avon refinery in Martinez, CA (U.S.) in 1997. In this incident, there was a pipe rupture and related explosion and fire. The team members for the investigation were from six government agencies and used FTA to analyze each major equipment failure.

  The fault trees described all of the possibilities in which a particular failure could have occurred. Afterwards, the work teams gather the necessary information from the documentation to identify how the failure occurred for the accident, thereby identifying the critical path to each equipment failure during the occurrence. The critical paths are then included on the updated E&CF (Events and Causal Factors Charting) in order to show an overall perspective. Industry and researchers have estimated times needed to perform a hazard evaluation using the FTA technique even with an experienced team. For a large process this can take from six to fourteen or more weeks.

- **RBI**
  
  The American Petroleum Institute (API) offers its Risk Based Inspection (RBI) methodology which may be used to manage the overall risk of a plant by focusing inspection efforts on the equipment with the highest risk. In most processing plants, a large percent of the total unit risk will be concentrated in a relatively small percent of the equipment items. These potential high-risk components may require greater attention at some point/s in time, perhaps through a revised inspection plan.
SAFETY IN CHEMICAL PLANTS TODAY

Recent Safety Regulations

Mandates which have an effect on the chemical industry from the application of the National Emphasis Program (NEP) going forward are discussed by Nexant, shown here is the strategy to conduct Chemical NEPs by OSHA and the latest developments.

Strategy for Chemical NEP’s (OSHA)

OSHA’s strategy for conducting Chemical NEP evaluations will focus on three main avenues:

- Preparing the facility
- Corporate compliance strategy
- Verify chemical facility PSM program

Most information available refers to preparing the facility/prior preparation through questions and later verification of the program on OSHA’s part. This verification will entail the following

- Ensure basic programs are operational
- Outside audits focused on chemical NEPs

Chemical Plants Overview: Areas of Concern (OSHA)

Areas of concern for OSHA regarding chemical plants are very similar to those that are being emphasized in the Refinery PSM NEP program. These can be summarized in Table 1.1.

Table 1.1 OSHA Refinery NEP Focus Areas

<table>
<thead>
<tr>
<th>OSHA Refinery NEP Focus Areas</th>
<th>Normal and Emergency Operating Procedures</th>
<th>PSM Elements Recommendations Status&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Employee Participation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Management of Change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-Startup Safety Reviews (PSSR)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relief Systems&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Facility Siting&lt;sup&gt;1&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blowdown Drums and Vent Stacks (Blowdowns)&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Human Factors&lt;sup&gt;1&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vessels&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Hot Work Permits</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piping&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Incident Investigation Reports</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>1</sup> These aspects of a PSM program were examined with respect to mechanical integrity and process safety. Information elements and citations were written against both elements.

<sup>2</sup> Covering the PHA, incident investigation, and compliance audit elements and cited against those elements.

<sup>3</sup> These aspects of a PSM program were examined with respect to the PHA element and cited against the element.

Source: Chemical Processing - "Prepare for More Safety Inspections"

Review of Safety Related Experience. Incident Examples

A survey of industry accidents involving chemical plants was conducted by Nexant highlighting:

- Location
- Date
- Process Equipment Involved
- Causes (Leak/ Release, Fire, Explosion, Operator error or other)
Injuries or Fatalities
Brief description with relevant details

Table 1.2 summarizes selected incidents occurring in chemical plants.

<table>
<thead>
<tr>
<th>Process Equipment</th>
<th>Location</th>
<th>Date</th>
<th>Leak / Release</th>
<th>Fire</th>
<th>Explosion</th>
<th>Operator Error</th>
<th>Other</th>
<th>Injuries</th>
<th>Fatalities, Number</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage Tank/Associated Piping</td>
<td>INDSPEC Chemical Corporation, Petrolia PA</td>
<td>10/11/2008</td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>During an oleum transfer operation, two pumps were being used - one pump was powered by the emergency power supply that can only be controlled locally by a start/stop switch. The operator failed to stop this pump and left the storage building before the high-level alarm was triggered on the tank. This led to a sulfuric acid release that forced 2,500 residents to be evacuated.</td>
</tr>
<tr>
<td>Reactor</td>
<td>Bayer CropScience, Institute, WV</td>
<td>8/28/2008</td>
<td>x x x x x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>A large explosion and fire occurred from a runaway reaction during the production of an insecticide that killed 2 workers. The runaway reaction caused very high temperatures and pressures in the residue treater that caused it to rupture and launch 50 feet in the air, wrecking nearby process equipment, piping, and conduits. This accident was a direct result of poor process safety management, where the operators were not fully trained, procedures were not up to date, and necessary safety systems were overridden.</td>
</tr>
<tr>
<td>Heat Exchanger</td>
<td>Goodyear Synthetic Rubber Facility, Houston, TX</td>
<td>6/11/2008</td>
<td>x x x x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7</td>
<td>During a maintenance operation on an ammonia heat exchanger, steam was being used to clean process piping. The heat from the steam flashed off the ammonia that was in the exchanger, but because the isolation valve on the exchanger was mistakenly closed, the ammonia vapor overpressurized the exchanger and caused an explosion.</td>
</tr>
<tr>
<td>Distillation Column</td>
<td>First Chemical Corp., Pascagoula, MS</td>
<td>10/13/2002</td>
<td>x x x x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Although thought to have been isolated, steam flowed through leaky valves into a distillation column filled with a chemical related to TNT. The steam heated the column contents to a critical temperature and initiated a violent decomposition reaction. The tower exploded sending heavy debris over the area. Three workers were injured and a storage tank on site was punctured that ignited a fire.</td>
</tr>
<tr>
<td>Pump/Associated Piping</td>
<td>Union Carbide, Wilton, Cleveland</td>
<td>7/10/1999</td>
<td>x x x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A pump bearing had failed due to lack of lubrication. This led to excessive vibration which fractured a section of nearby piping. Liquid isododecane (that was above its boiling point) began leaking and ignited from the hot pump. Two firefighters were injured while trying to extinguish the fire.</td>
</tr>
</tbody>
</table>

Descriptions and comments on selected accidents are provided by Nexant.

**SAFETY IN THE REFINING INDUSTRY**

Nexant conducted a survey of refinery process units including an overview of each process that contains a summary with relevant aspects in order to understand safety aspects. A safety profile
for each unit was also developed where it is intended to determine causality for the majority of safety incidents in main process plants.

As part of the safety profile, a survey of incidents/upsets particularly related to each unit was conducted. The following information is included in each survey:

- Location
- Date
- Causes (leak/release, fire, explosion, operator error or other)
- Injuries or fatalities (not applicable in this listing)
- Brief description with relevant details

The following units have been profiled:

- FCC Unit
- Hydrocracker
- Distillation (Atmospheric and Vacuum)
- Catalytic Reformer
- Delayed Coker
- Hydrogen Plant
- Sulfur Recovery Unit
- Amine and Sour Water Treatment Units
- Flares

An example of the analysis is provided for the FCC Unit.

- **FCC Unit**

Fluid catalytic cracking (FCC) is the most common catalytic cracking process. Catalytic cracking is similar to thermal cracking in that both processes’ ultimate goal is the same, but the usage of a catalyst in the reaction increases the yield of lighter products under much less severe operating conditions when compared to thermal cracking. Typical operating conditions include temperatures of 850 to 950 °F and pressures of 10 to 20 psi. Catalysts utilized in most refinery cracking units are typically solid materials such as zeolite, aluminum, hydrosilicate, treated bentonite clay, fuller’s earth, bauxite, and silica-alumina. These generally come in the form of powders, beads, pellets, or extradites.

In catalytic cracking, there are three main parts of the process:

- Reaction
- Regeneration
- Fractionation

The reaction section is where the feedstocks react with the catalysts to form shorter-chained hydrocarbons. The regeneration section is where the catalysts are treated and reactivated in order to rid them of coke that is formed as a byproduct. Finally, the fractionation section is where the newly formed hydrocarbons are separated into various products.
Safety Profile

The majority of safety incidents in FCC units are due to hydrocarbon leaks that find ignition sources. Leaks in FCCs generally occur from undetected corrosion that eats away enough at a piece of piping or equipment over time to lead to a loss of containment. The presence of heaters in these units creates a strong possibility that a leak will lead to a fire. Nexant suggests that for the safe operation of any catalytic cracker unit, particular emphasis should be put on:

- **Minimizing leaks** – Corrosion via sour crude, erosion, catalyst buildup on expanders, and the formation of coke can all lead to leaks in piping and equipment
- **Having adequate fire prevention and protection systems** – Fires can always follow hydrocarbon leaks, so adequate fire systems are a necessity
- **Avoiding exposure to hazardous materials present in the unit** - During sampling or if a leak or release does occur, there is always the possibility of an operator being exposed to extremely hot (~700 °F) hydrocarbon liquids or vapors as well as hydrogen sulfide and/or carbon monoxide gas

Nexant concludes that a great number of the accidents that occur in FCC units are a result of releases and losses of containment that lead to catastrophic fires due to the contents of the unit and the presence of heaters. Accident potential can be greatly diminished by complying with OSHA’s recommendations above to prevent or minimize leaks and fires. Additionally, prevailing international norms and regulations regarding frequent and thorough maintenance and inspections should be followed, up to date safety devices should be installed, and adequate safety practices and other applicable safeguards (including the use of appropriate personal protective equipment) should be utilized.
Table 1.3 provides summaries of selected incidents occurring in refinery process units worldwide.

### Table 1.3  Refinery Catastrophic Incidents

<table>
<thead>
<tr>
<th>Process Unit</th>
<th>Location</th>
<th>Date</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
<td>Total La Mede, France</td>
<td>10/9/1992</td>
<td>Hole in bypass line from corrosion led to release of 15 tonnes of hydrocarbons. This created a vapor cloud which engulfed other process units. The cloud then ignited, and a massive fire was started. Total cost estimated ~$600 million - 64% attributed to repairs, 34% loss of production, and 2% civil liability.</td>
</tr>
<tr>
<td>Hydrocracker</td>
<td>Grangemouth Refinery (Scotland)</td>
<td>3/21/1987</td>
<td>Explosion due to gas blow through completely destroyed LP Separator. When control valves were placed in manual mode during startup, they opened fully and overpressured the low pressure separator. Plant built prior to HAZOP analysis. Heard up to 30 km away. Rebuilding took over 18 months, total cost of the accident ~$107 million. BP prosecuted under the UK Health and Safety at Work Act, fined £500,000 (c. $750,000).</td>
</tr>
<tr>
<td>Distillation</td>
<td>Tosco Avon, Martinez, CA</td>
<td>2/23/1999</td>
<td>Workers were attempting to replace piping attached to a 150-foot-tall fractionator tower while the process unit was in operation. During removal of the piping, naphtha was released onto the hot fractionator and ignited.</td>
</tr>
<tr>
<td>Catalytic Reformer</td>
<td>Sakai, Osaka, Japan</td>
<td>10/4/1987</td>
<td>The reaction control valve flange bolts loosened gradually because of constant pipe vibration. High-temperature gas leaked, mixed with air, self-ignited, and a fire occurred.</td>
</tr>
<tr>
<td>Delayed Coker</td>
<td>Digboi Refinery, Assam, India</td>
<td>5/13/2009</td>
<td>Failure of bend on discharge side of fractionator column bottom pump of delayed coker unit due to loss of thickness and metallurgical mismatch led to leakage of high temperature hydrocarbon which ignited killing two people.</td>
</tr>
<tr>
<td>Sulfur Plant</td>
<td>New Orleans, LA</td>
<td>10/24/2003</td>
<td>Sulfur Recovery Unit went down - Vent system overpressurized leading to leak of H2S and SO2 - 78 people injured</td>
</tr>
<tr>
<td>Amine/SWS</td>
<td>Union Oil Company of California Refinery, Romeoville, Illinois</td>
<td>7/23/1984</td>
<td>An amine absorber pressure vessel ruptured and released large quantities of flammable gases and vapors resulting in a devastating explosion and fire. The Union Oil absorber had a lengthy history of in-service defects and appeared to have been inadequately maintained. 17 lives were lost, 17 people were injured and more than $100 million in damages resulted.</td>
</tr>
<tr>
<td>Fuel Gas/Flares</td>
<td>BP Grangemouth Refinery (Scotland)</td>
<td>3/13/1987</td>
<td>During maintenance on a flare main valve, hydrocarbon liquid was released when the valve flanged joints were being broken. The liquid vaporized and then ignited resulting in two deaths and two serious injuries. BP were prosecuted under the UK Health and Safety at Work Act and fined £250,000 (c. $375,000).</td>
</tr>
</tbody>
</table>
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