Probabilistic risk assessment of fertilizer plants†
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The paper relates to the application of some advanced operation research techniques to probabilistic risk assessment (PRA) studies of selected plants in fertilizer complex. Hazard prone sections of ammonia plant are identified using Fire & Explosion Index, Toxicity Index and Mond Index. Past accident data analysis with emphasis on failure mode and critical evaluation of Urea plant accident have been discussed. Though probability of occurrence of hazardous event for vulnerable units is studied through fault trees analysis, the uncertainty with respect to top event in fault tree analysis is mitigated with recourse to Fuzzy sets theory. The process hazard for the total system is assessed using failure logic diagrams which simplifies the process by determining minimum cut sets. The reliability of various units is studied as a function of time through construction of pathway reliability block diagram. In order to maintain the desired minimum reliability the procedure for estimation for each path, preventive maintenance scheduling is explained.

Industrial growth is of prime concern in order to achieve self sufficiency as it plays an important role in society. However, these industrial activities have caused growing public awareness that is the outcome of major industrial disasters such as Flixborough disaster (1974), Mexico LPG disaster (1984), Bhopal gas tragedy (1984) and Chernobyl nuclear accident (1986).

In a typical ammonia plant of a fertilizer industry both flammable chemicals such as methane and hydrogen and toxic chemicals such as ammonia and carbon monoxide are handled at a pressure range of over 200 kg/cm² to atmospheric pressure and temperature range of over 850 to −33°C. On the other hand, in Urea plant, ammonia is handled at high temperature (180°C) and pressure (160 kg/cm²). Any small leak may either lead to fire hazard or release of large quantities of toxic substances. It is, therefore, necessary to identify and quantify the effect of any hazardous release in order to arrive at risk mitigation measures which would help in reducing the level of risk in and around the facility.

Need and Relevance

It is obligatory on the part of engineers to design the safest possible system with very low probability of its failure and minimal consequences if system does fail within the given set of engineering constraints. However, accidents in the industrial installation do occur though rarely. It is, therefore, desirable to compute the extent of damage, probability of the occurrence of hazardous event in quantitative terms with recourse to probabilistic risk assessment (PRA) studies for a chemical plant. Such studies also help in obtaining useful information about the system to re-design it with lower probability of its failure and mitigate the ensuing consequences.

A step by step risk assessment, therefore, helps in identification of vulnerable process unit and quantification of risk associated in terms of probability of occurrence of hazardous event and magnitude of its consequence. Formalized approaches for PRA studies are summarised and the application of some of the recent advancements in PRA studies are presented in this paper.

Hazard Identification

Hazard indices computation helps in ranking the most vulnerable units by assigning the penalties based on the properties of the chemical used and the type of installation. Table 1 shows the fire and explosion, toxicity and Mond indices computations for ammonia plant. The toxicity index is arrived at from fire and explosion index. The toxicity index (TI) is computed using the health factor (Nh), maximum allowable concentration (MAC), general process hazard (GPH) and special process hazard (SPH). A factor Tₚ is assigned for MAC value ranging between 5, 5-50, > 50 respectively. Similarly, for Nh range from 0-4, a corresponding factor, Th is assigned. The TI can be calculated using the following formula.

\[ TI = \frac{(Th + Tₚ) \times (1 + GPH + SPH)}{100} \]

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The degree of hazard is identified based on FEI and TI range according to the following criteria:

<table>
<thead>
<tr>
<th>FEI range</th>
<th>Degree of hazard</th>
<th>TI range</th>
<th>Degree of hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-60</td>
<td>Light</td>
<td>0-5</td>
<td>Light</td>
</tr>
<tr>
<td>61-96</td>
<td>Moderate</td>
<td>5-10</td>
<td>Moderate</td>
</tr>
<tr>
<td>97-127</td>
<td>Intermediate</td>
<td>&gt; 10</td>
<td>Severe</td>
</tr>
<tr>
<td>128-158</td>
<td>Heavy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>159 &amp; above</td>
<td>Severe</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The rankings of most vulnerable units are shown in Fig. 1.

**Accident Analysis**
Past accident data analysis of events arising out of unsafe conditions helps in correlating the caus-

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**Fig. 1**—Identification of vulnerable sections of New Ammonia plant

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**Table 1**—Hazard rating using various hazard indices

<table>
<thead>
<tr>
<th>Unit</th>
<th>M.F.</th>
<th>FEI Index</th>
<th>Mond Index (MI)*</th>
<th>Toxicity of hazard</th>
<th>Degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary reformer</td>
<td>21</td>
<td>130.4</td>
<td>2531</td>
<td>—</td>
<td>Heavy</td>
</tr>
<tr>
<td>Secondary reformer</td>
<td>21</td>
<td>128</td>
<td>2579</td>
<td>—</td>
<td>Heavy</td>
</tr>
<tr>
<td>Converter</td>
<td>21</td>
<td>128.2</td>
<td>2568</td>
<td>—</td>
<td>Heavy</td>
</tr>
<tr>
<td>Converter</td>
<td>21</td>
<td>135.4</td>
<td>2562</td>
<td>—</td>
<td>Heavy</td>
</tr>
<tr>
<td>Methanator</td>
<td>21</td>
<td>252</td>
<td>2109</td>
<td>—</td>
<td>Severe</td>
</tr>
<tr>
<td>Converter</td>
<td>21</td>
<td>166</td>
<td>2553</td>
<td>24.12</td>
<td>Severe</td>
</tr>
<tr>
<td>Separator</td>
<td>4</td>
<td>22.4</td>
<td>2075</td>
<td>21.2</td>
<td>Light</td>
</tr>
<tr>
<td>Ammonia storage</td>
<td>4</td>
<td>23.8</td>
<td>412</td>
<td>13.3</td>
<td>Light</td>
</tr>
<tr>
<td>Ammonia tank car</td>
<td>4</td>
<td>34.2</td>
<td>460</td>
<td>14.2</td>
<td>Light</td>
</tr>
</tbody>
</table>

*Reported as equivalent DOW Index
Accident in Urea Plant

The analysis of an accident that occurred in urea plant in one of the large fertilizer industry and resulted in the release of 2.85 tones of ammonia leading to nine casualties. Fig. 4 shows the process flow diagram of the section where accident occurred. The booster pumps were pumping liquid ammonia from ammonia receiver to 4 High Pressure (H.P.) reciprocating ammonia pumps through a parallel feed arrangement. Out of the four H.P. pumps, one was standby and the other three were on line. At the time of accident both the booster pumps were working with discharge pressure of 21.5 kg/cm². One of the H.P. pump was under maintenance after closing suction (globe) valve. The delivery valve of pump leading to reactor was closed and the lines were flushed with water for eliminating ammonia. At the time of accident the pump was isolated, drained and flushed to replace relief valve (PSV) on the standby H.P. pump by a new one HOV suddenly failed open. The cause of the incident was the failure of the yoke bush, which had permitted opening of spindle and the disc of the globe valve and escape of ammonia through the pump and piping. The instant failure and the presence of highly toxic liquid ammonia in large volume led to formation of heavy clouds preventing visibility and contributed to the helplessness of the people on the platform. The booster pumps were running as it was not possible to trip it from control room and access to substation and local control was prevented due to the presence of ammonia. Booster pump was stopped after a period of 10-15 min by cutting off the power supply to the Urea plant from main receiving station. Subsequently, all the pump valves were closed using safety equipments. The cause of accident being the failure of element, i.e., yoke bush of suction valve of H.P. ammonia pump that would occur rarely. The possible solutions to prevent such accidents could be to either provide a slip disk or valve in series with H.O.V. This rare incident gives the mode of failure and help in suggesting preventive measures. The collection of such data also helps in suggesting the corrective actions.

Hazard Quantification

Consequence analysis gives the damage for various release scenarios of toxic and flammable
Toxic Releases
1. Ammonia from main plant (8" line)
2. Unloading of ammonia from 32T Rail Tanker
3. Catastrophic rupture of 32T Rail Tanker
4. Suction of liquid ammonia to pump, P-3301 (14" line)
5. Dispatch of liquid ammonia to Urea Plant (8" line)
6. Emergency line (6" line) to Flare
7. Preheated ammonia to dispatch through unloading line (8" line)
8. Catastrophic rupture of storage (T-3301) with 50% inventory
9. Line from tank to header before preheater inlet (8" line)
10. Line to GB 101 (16" line)
11. Line from economiser (6" line)
12. Ammonia from unloading station (12" line)
13. Ammonia from plant (20" line)
14. Catastrophic rupture of storage tank (FA-101)

Flammable Releases
15. Rupture of associated gas pipe line (6" leak) — VCE*
16. Rupture of associated gas pipe line (10" leak) — VCE
17. Inlet to Secondary Reformer (6" leak) — VCE
18. Inlet to Secondary Reformer (10" leak) — VCE
19. Catastrophic Rupture of Secondary Reformer — VCE
20. Outlet of Methanator (6" leak) — VCE
21. Outlet of Methanator (10" leak) — VCE
22. Hydrogen release from CO₂ system (6" leak) — VCE
23. Hydrogen release from CO₂ system (10" leak) — VCE
24. Gas from top of Ammonia Separator (B-501) — VCE
25. Inset to Secondary Reformer (6" leak) — Flare
26. Inlet to Secondary Reformer (10" leak) — Flare
27. Outlet of Methanator (6" leak) — Flare
28. Outlet of Methanator (10" leak) — Flare

Flammable Releases
15. Rupture of associated gas pipe line (6" leak) — VCE*
16. Rupture of associated gas pipe line (10" leak) — VCE
17. Inlet to Secondary Reformer (6" leak) — VCE
18. Inlet to Secondary Reformer (10" leak) — VCE
19. Catastrophic Rupture of Secondary Reformer — VCE
20. Outlet of Methanator (6" leak) — VCE
21. Outlet of Methanator (10" leak) — VCE
22. Hydrogen release from CO₂ system (6" leak) — VCE
23. Hydrogen release from CO₂ system (10" leak) — VCE
24. Gas from top of Ammonia Separator (B-501) — VCE
25. Inset to Secondary Reformer (6" leak) — Flare
26. Inlet to Secondary Reformer (10" leak) — Flare
27. Outlet of Methanator (6" leak) — Flare
28. Outlet of Methanator (10" leak) — Flare

*Vapour Cloud Explosion

Fuzzy Fault Tree Analysis (FFTA)\(^{(3,9,10)}\)

The fault tree constructed for ammonia storage tank (Fig. 6) gives the maximum damage consequences (Fig. 5). Failure of ammonia storage tank is the most vulnerable unit in the fertilizer complex. Average failure probability data was used for the computation of top event probability (TEP). However, lots of uncertainities are involved in evaluation of fault tree through conventional approach arising due to: system behaviour because to complexity of operation, maintenance of log book data and its analysis and environmental and operating conditions for components (instruments). Hence, it is necessary to tackle these uncertainities to prevent a more realistic picture of top event probability. This is done taking recourse to Fuzzy set theory (FST)\(^{1,8}\).

One of the intermediate event (Flash vessel empty) shown in Fig. 7, is reduced to a logically equivalent form using union and intersection operators as:

Minimum cutsets:
\[ \{X_1, X_2, X_3\}, \{X_1, X_2, X_4\} \ldots (1) \]

Event relationship: 
\[ TEP = X_1 \cap A_1 \]  \ldots (2)

where 
\[ A_1 = X_2 \cap A_2 \] and 
\[ A_2 = X_3 \cup X_4 \]

Top event probability (TEP) is given by the expression:
\[ P_{\text{TEP}} = p_{X_1} \times p_{A_1} \]

Hence the expression for TEP becomes:
\[ P_{\text{TEP}} = p_{X_1} \times p_{X_2} \times [1 - (1 - p_{X_3}) \times (1 - p_{X_4})] \ldots (3) \]

In view of the above mentioned uncertainities, it is appropriate to consider the interval estimates for the probability of various component failures rather than working with point estimates. Accordingly, the component failure probabilities are characterized using trapezoidal representation of fuzzy numbers\(^{8}\) as shown in Fig. 8. The estimation of TEP according to the Eq. (3) would now be termed as Fuzzy top event probability (FTEP) and is computed using following arithmetic operations:

Multiplication Operation
\[ P_{X_i} \times P_{X_j} = (\alpha_{i1} \times \alpha_{j1}, \alpha_{i2} \times \alpha_{j2}, \beta_{i1} \times \beta_{j1}, \beta_{i2} \times \beta_{j2}) \ldots (4) \]

Complementation Operation
\[ P_{\bar{X}_i} = 1 - P_{X_i} = (1 - \beta_{i1}, 1 - \beta_{i2}, 1 - \alpha_{i1}, 1 - \alpha_{i2}) \ldots (5) \]

Fig. 5—Consequence analysis for ammonia plant.
where, $P_{xi}$ = trapezoidal representation of failure probability for the event $X_i$, $\mu$ = membership grade function, and $\alpha, \beta$ = failure probabilities.

The concept of fuzzy probability in fault tree presents fuzzy number, the value of which ranges between zero and one of each primary event.

The shape of fuzzy probabilities of primary events could take various forms. Trapezoidal representation of fuzzy number could be one such shape that was used. Fuzzy probabilities of the basic events must be combined according to the
rule of combination (multiplication and complementation are the two operators used in the present study) of fuzzy numbers to arrive at fuzzy probability of the top event in FFTA.

The TEP of the hazardous event (release of ammonia from the storage tank) using conventional FTA approach has been estimated as $1.00 \times 10^{-5}$ f/yr. as shown in Fig. 6. Random combination of the fuzzy probability of primary events were used as per the procedure outlined in previous section for membership grade function $\mu = 1$ and the range of FTEP was estimated which is presented in Fig. 9. It is seen that the occurr-

Fig. 9—Fuzzy top event probability for ammonia storage tank

Fig. 10—Reliability block diagram for primary reformer
ence of fuzzy top event probability (FTEP) has the most likely interval of \(5 \times 10^{-5} - 5 \times 10^{-4}\) with possibility \(\mu = 1\). Employing conventional approach, top event probability works out to \(1.00 \times 10^{-5}\), i.e., a value that lies outside this interval.

Reliability Analysis

Reliability has been commonly defined as the probability that an item will perform its intended function for a specified interval of time under given operational conditions. In a large chemical plant as that of ammonia, the process control instruments form a complex system and it is, therefore, essential to study integrity of such components/instruments and the behaviour of individual instrument, the failure of which would affect the performance of the entire system. The occurrence of a hazard due to instrument failure or human error follows a pathway. This pathway is logical, i.e., the path followed to control a variable, such as pressure, temperature and flow.

The pathway may be preceded or followed by a valve or similar pathways. The indicators, recorders and alarms are sensed by the human operator and the control action is propagated through human action by a switch, manual valve and set point. All paths that contribute to an accident or failure of an equipment can be drawn. Since each component of a path has a failure rate the pathway reliability can be computed for all the paths. The lowest pathway reliability amongst all paths gives the reliability of that event. The reliability of a pathway can be improved by redundancies or improving the control loop where control is manual. The logical representation through reliability block diagrams for primary reformer which handles large quantities of flammable gas at elevated temperature is presented in Fig. 10.

Reliability of instruments decreases exponentially with time and is given by following equation:

\[ R = e^{-\lambda t} \]  
where \(\lambda\) = failure rate (yr.\(^{-1}\)) and \(t\) = preventive maintenance schedule (yr.)

As could be seen from Fig. 10, path number 1 is divided into four paths, i.e., 1, 1A, 1B and 1C. The components in these paths are detailed as under:

- **Path 1**: \(HT \rightarrow HIC \rightarrow HO \rightarrow HCV\) (Series)
- **Path 1A**: \(FT \rightarrow FIC \rightarrow FCV \rightarrow PSV\) (Series)
- **Path 1B**: \(HT \rightarrow HIC \rightarrow HO \rightarrow HCV\) (Series)
- **Path 1C**: \(HT \rightarrow HIC \rightarrow HO \rightarrow HCV\) (Series)

The sample calculation for estimation of pathway reliability for path 1C for seven days preventive maintenance scheduling is shown below:

\[ \text{Reliability (1C)} = \left(0.983 \times 0.989 \times 0.999 \times 0.988 \right) \times \left(0.988\right) - \left(0.983 \times 0.989 \times 0.999 \times 0.988\right) \times \left(0.995\right) \]

\[ = 0.9949 \]

Fig. 11 shows the variation of reliability with time. The maintenance scheduling could be worked out for maintaining the minimum reliability of 0.9 which is the management decision.

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**Nomenclature**

- **FT, HT, PT** = transmitter (flow, pressure etc.)
- **FIC, HIC, PIC** = indicator and controller (flow, pressure etc.)
- **FCV, HCV, PCV** = control valve (flow, pressure etc.)
- **FAL, PAL** = alarm for low flow, pressure
- **FAH, PAH** = alarm for high flow, pressure
- **FY, FFFY** = flow ratio controller
- **FRC** = flow recorder and controller
- **FSAL** = switch [and alarm] for flow
- **PV** = human operator
- **PSV** = pressure valve
- **PV** = pressure safety valve
E-204A/B, E-202B = heat exchanger
TAH = high temperature alarm
TAL = low temperature alarm
TRC = temperature recorder and controller
TCV = temperature control valve
USY = quick shut off switch (valve)
ISI = interlock switch system

References
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