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Development of Quantitative Hazard Analysis Method for Inherently Safer Chemical Processes

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This paper shows a method to analyze hazard in chemical plants and to practice inherent safety measures for decreasing consequences. Hazard analysis method of this work is reconsidered about worst case scenario widely has being used in the world. Calculation results are plotted on a graph which takes fatalities and lethality distance on each axis, and hazard potentials of chemical plants are ranked. Furthermore, this work also shows effective inherent safety measures practices about process equipment that have high hazardous potentials.

1. Introduction

Chemical plants have many kinds of chemical hazards, and analysis methods based on worst case scenario have been developed by analysis method of API (2000), U.S. EPA (1999) and so on. There are many studies about consequence based hazard analysis and implementations, e.g. A. Tugnoli (2009) and J. Haddad (2010). They are good way to identify hazard potential in chemical plants fluently by using like datasets in table 1, but those calculation methods are assumed that materials in process equipments are released in normal operation. If operation conditions deviate from normal operation because of any troubles, accidents affecting more significant damage than worst case scenario may occur. For example, there is a reactor which is controlled temperature as normal condition, and if materials in a reactor are released to the outside, consequence would not be so high. But if heat system of a reactor has accident, a reactor would be exploded by reaction runaway and give significant damage. In this case, if release of materials in normal operation is only assumed as worst case scenario, significant accident may be missed and hazard potential of reactor may be underestimated.

2. Definition of “worst case scenario”

In this work, author redefined “worst case scenario”, because consequence calculated as worst case scenario should be most severe. Author defined “abnormal scenario” as scenarios generated by deviated from normal operation, and redefined that “worst case scenario” is constructed with “release scenario” and “abnormal scenario” in this work.

Table 1: Plant information for analysis

Information of process conditions	Information of process equipments	Information of materials	Other information of plant
· Temperature (℃)	· Volume of equipment (m^3)	· Formula of material	· Flow sheet
· Pressure (kPa)	· Internal length (m)	· Molecule weight (g)	· Material balance sheet
· Composition (wt%)	· Hold up volume (m^3)	· Boiling point (℃)	· Equipment list
· Flow rate (kg/hr)	· design temperature (℃)	· Flash point (℃)	· Information of dike
· Phase of material	· design pressure (kPa)		

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3. Procedure of “release scenario”

“Release scenario” is defined as worst case scenario widely used as quantitative hazard analysis in chemical plant in this work. Author reconsidered that “release scenario” reported by M. Nakagawa (2010) is able to analyze more accurately and to get same results even if anyone calculate.

3.1 Selection of equipment

The calculation method is presented by using ammonia model plant as example shown Figure 1. At first, analysis object equipments are selected in PFD or PID. For example, pipeline or pumps have small amount of material compared to tanks, condensers or vessels. It is able to assume that material in pipeline or pumps are included in previous and following equipments, and they are omitted from analysis object. However, in the case that pipeline and pumps have a large amount of material, they should be selected as analysis object equipments. In ammonia model plant, analysis object equipments are 12 circled ones.

3.2 Definition of release scenarios and events

Release scenarios from analysis object equipments and occurrence events are shown as Figure 2. Release scenarios are defined by correlation with process temperature, boiling point, flash point of material and atmospheric temperature. Occurrence events are defined by material phase, flammability and toxicity. Release amounts are defined each event and are shown in Figure 3.

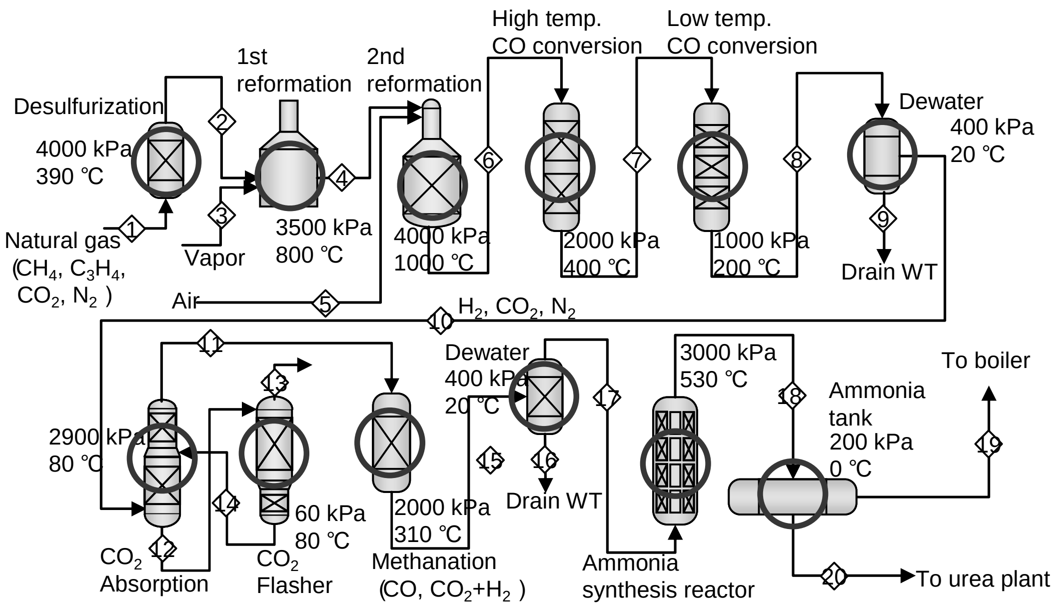


Figure 1: Process flow diagram

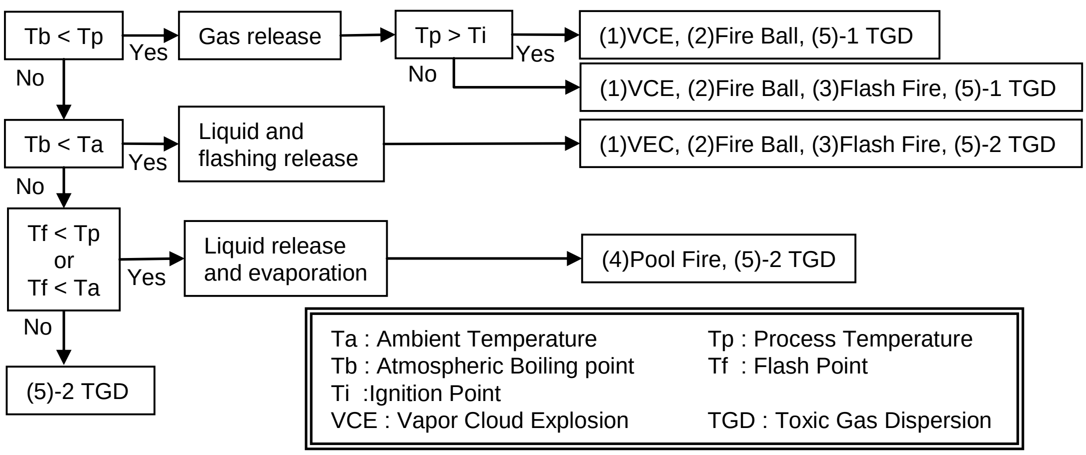
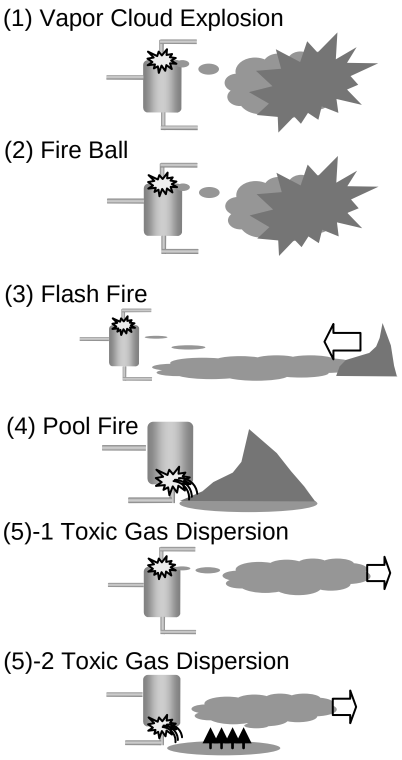


Figure 2: Release scenario and event type



The total mass released
= the quantity of substance present in the vessel
+ the feed of substance from the upstream vessel in 3 min.

The total mass released
= the quantity of substance present in the vessel
+ the feed of substance from the upstream vessel in 3 min.

The total mass released
= (the quantity of substance present in the vessel / 10 min.
+ the feed of substance from the upstream vessel) * 10 min.

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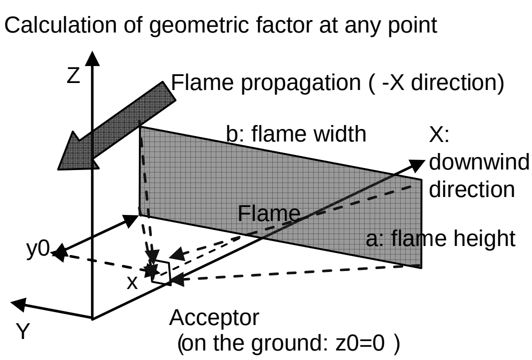
+ the feed of substance from the upstream vessel) * 10 min.

Figure 3: Release amounts defined by each release event

3.3 Calculation of consequence model

Consequences caused by each event are calculated by TRACE software by SAFER Inc. Fatality numbers are calculated by probit function with reference to TNO (1999).

Author reconsidered about calculation method of flash fire, because representative calculation methods are that all people will die in flammable gas dispersion area or people are received maximum radiation while flame burning. These methods are possible to overestimate consequence. Therefore, author calculates flash fire as below. Flammable gas dispersion phenomena are calculated by TRACE at first, and change with time of radiation received by any point and geometric factor between flame and arbitrary point during flame moving are calculated by gPROMS, PSE Inc.(Figure 4 and 5). In Figure 5, radiation intensity is moving with flame front, and fatalities are gradually increasing with burning time.



$$F_{1,2} = \frac{z_0}{2\pi\sqrt{{z_0}^2 + x^2}}\left\{\tan^{-1}\frac{b-y_0}{\sqrt{{z_0}^2+x^2}} + \tan^{-1}\frac{y_0}{\sqrt{{z_0}^2+x^2}}\right\}$$

$$+\frac{y_0}{2\pi\sqrt{{y_0}^2 + x^2}}\left\{\tan^{-1}\frac{a-z_0}{\sqrt{{y_0}^2+x^2}} + \tan^{-1}\frac{z_0}{\sqrt{{y_0}^2+x^2}}\right\}$$

$$+\frac{a-z_0}{2\pi\sqrt{(a-z_0)^2 + x^2}}\left\{\tan^{-1}\frac{b-y_0}{\sqrt{(a-z_0)^2+x^2}} + \tan^{-1}\frac{y_0}{\sqrt{(a-z_0)^2+x^2}}\right\}$$

$$+\frac{b-y_0}{2\pi\sqrt{(b-y_0)^2 + x^2}}\left\{\tan^{-1}\frac{a-z_0}{\sqrt{(b-y_0)^2+x^2}} + \tan^{-1}\frac{z_0}{\sqrt{(b-y_0)^2+x^2}}\right\}$$

Figure 4: Calculation of geometric factor

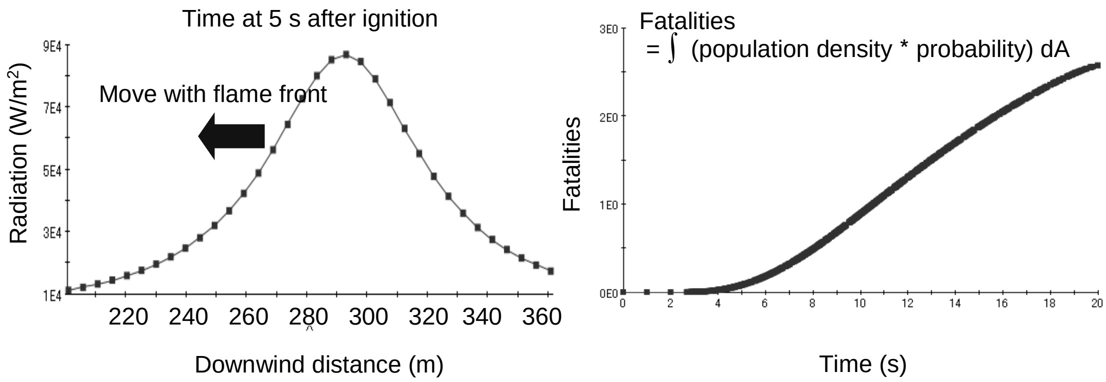
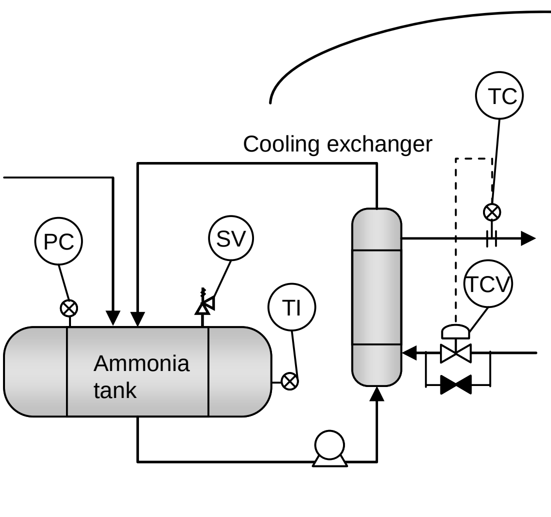


Figure 5: Result examples of radiation intensity and time dependence of fatalities

4. Procedure of “abnormal scenario”

“Abnormal scenario” is considered that process is deviated from normal operation. “Abnormal scenario” has scenarios analyzed by what-if analysis, HAZOP or HAZchart analysis which is developed by M. Nakagawa (2004) in Mitsubishi Chemical Corp.

An example of “abnormal scenario” around ammonia tank in ammonia production process plant is shown Figure 6. “Abnormal scenario” is selected from plotted in high consequence level in risk matrix (Figure 7) which likely cause larger fatality numbers than “release scenario”. For example, it assumes that a control valve which control feed rate of cooling medium toward a heat exchanger is failed and feed of cooling medium is stopped. If feed of cooling medium is stopped, internal temperature of ammonia tank gradually rises and at the same time internal pressure rises involved with ammonia vapor pressure. Then, alarms of temperature and pressure are sounded and operators try to do recovery work. But if it is impossible to recovery, pressure in ammonia tank rises continuously. Safety valve is installed on ammonia tank so that pressure is released outside from ammonia tank at set-point below tank design pressure. However, if safety valve is not activated, tank will be ruptured and ammonia is released at higher temperature than normal operation. According to scenario analysis and probability calculation performed by HAZchart, probability of tank rupture is not high. Because there is enough time to do recovery work during pressure-rise up to design pressure and safety valve is installed on ammonia tank. But if ammonia tank rupture occur, ammonia is released at higher temperature from tank and it causes flash of larger amount of ammonia, and large amount of ammonia gas will give more sever consequence. In the aspect of analysis of hazard potential assumed worst case scenario, it needs to calculate such scenario. Calculation results are described in Section 5.



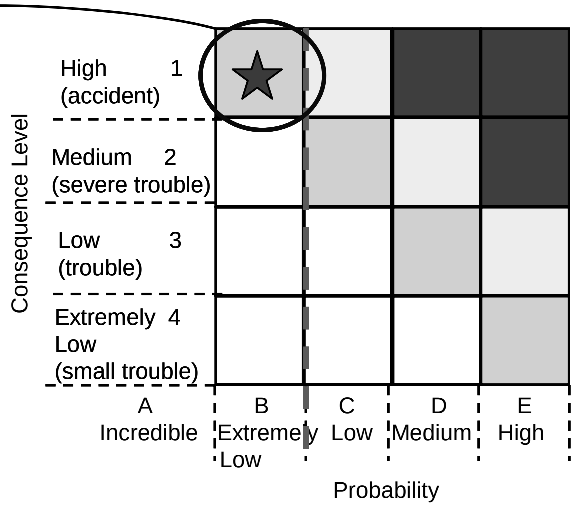


Figure 6: “Abnormal scenario” around ammonia tank

Figure 7: Risk Matrix calculated by HAZchart

5. The presentation of results; “release scenario” and “abnormal scenario”

Results analyzed by “release scenario” and “abnormal scenario” are plotted on a graph such as Figure 8. Graph takes fatality number caused by unlikable events such as explosion, fireball, etc on the vertical axis. Graph takes lethality distance which author defined as unlikable events affect people 10 % death probability on the horizontal axis. Furthermore, plant borderline is taken on the horizontal axis, and the graph is divided 3 color parts and ranked by severity of results. If process equipments plotted in red area that unlikable events affect over plant borderline and cause more than 1 fatality, safety practice should be considered immediately. In this work, ammonia tank and ammonia synthesis reactor have high hazard potential in ammonia plant. Practicing safety measures are described in Section 6.
About flash fire in Section 3, representative calculation method gives 9 fatalities, and this work gives 5 fatalities. This work calculates in detail about integration of radiation on arbitrary point that representative method overestimates, and it seems that fatality number is smaller than result of representative method.
Consequence of “abnormal scenario” in Section 4 got bigger result than “release scenario”. The reason is that ammonia release temperature and flash gas amount of “abnormal scenario” are higher. In this way, “abnormal scenario” has possibility that have larger consequence. Furthermore, it is possible to image how large accident would occur by comparing to past accident by plotting on the same graph. Table 2 shows past accident examples. Calculated fatalities and 10 % lethality distance are calculated by TRACE. Past accident examples are plotted on a graph in Figure 9 added results of ammonia plant. Calculation result of toxic exposure of ammonia released from 2500 t tank implies higher hazard than Bhopal accident.

6. Inherently safety practices

Though ammonia tank and ammonia synthesis reactor have severe hazard potential, it is possible to decrease hazard potential by practicing inherently safety measures. As inherently safety measures there are four measures, moderate, minimize, substitute and simplify. In case of example of ammonia tank and ammonia synthesis reactor, moderate and minimize are possible to adapt and are described below.

6.1 Moderate

In the case of practicing safety measure ”moderate” to ammonia tank and ammonia synthesis reactor, dilution and cooling are considered effective. In the case of dilution, diluting ammonia liquid with water and changing ammonia liquid to ammonia aqueous are possible to decrease the amount of ammonia flashed when ammonia release from tank and also to decrease vaporization rate from a dike. In the case of cooling, cooling ammonia tank temperature below boiling point is possible to remove ammonia flash phenomena and to significantly decrease vaporization rate from a dike.

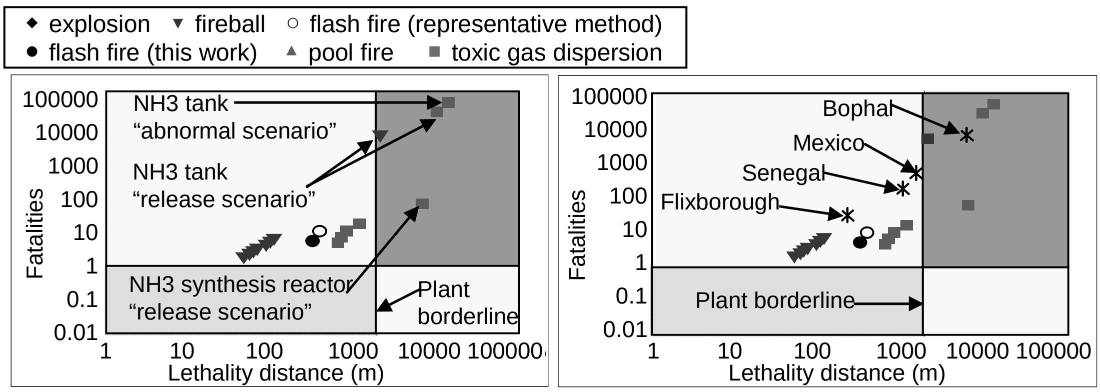


Figure 8: Consequence of ammonia plant *Figure 9: Comparison to past accident examples*

Table 2: Plant information for analysis

Places accident occur	substances	events	amount t	fatalities(actual) person	fatalities(cal.) person	lethality distance m
Flixborough	cyclohexane	vapor cloud explosion	13	28	50	227
Bhopal	MIC	toxic gas dispersion	57	6,000	3,413	6,013
Mexico	LPG	fireball	800	500	338	1,476
Senegal	ammonia	toxic gas dispersion	22	129	163	1,052

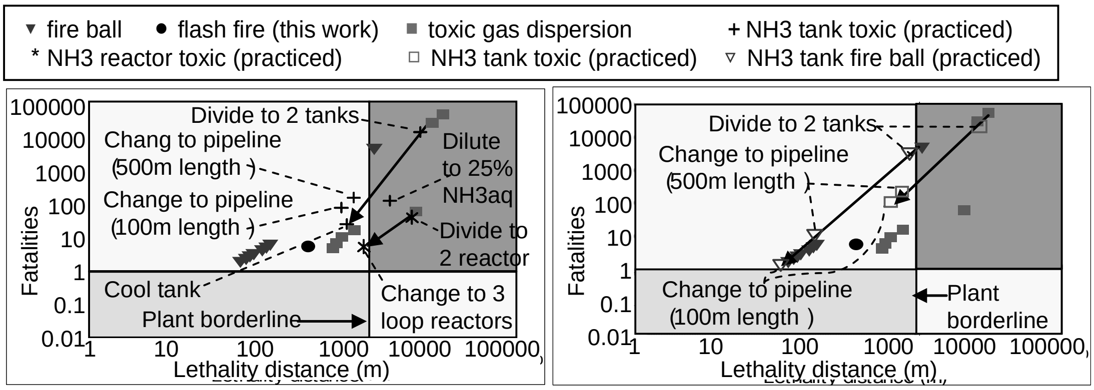


Figure 10: Inherently safer measurement -1 *Figure 11: Inherently safer measurement -2*

6.2 Minimize

In the case of practicing safety measure "minimize" to ammonia tank and ammonia synthesis reactor, dividing a tank and changing from tank to pipeline are considered effective. Changing to pipeline means that plant does not have ammonia tank and feed product ammonia directly to other process plant or customers. To decrease hold up of ammonia is possible to decrease hazard potential and consequence.

6.3 Result of inherently safety practices

Results practiced safety measures to toxic exposure of ammonia tank and ammonia synthesis reactor in "release scenario" are shown Figure 10. Results practiced safety measures to toxic exposure of ammonia tank in "abnormal scenario" and radiation from fireball of ammonia synthesis reactor in "release scenario" are shown Figure 11. They show that inherently safety practices can decrease hazard potential and consequence of each accident quantitatively.

7. Conclusion

Hazard calculation method of this work is able to analyze which equipment has how large hazard potential in Figure.8, and to express how large accidents would occur by comparing to past accident examples in Figure.9. If analyzed equipment has high hazard potential, it is necessary to consider which safety measure should be done and if it generates other hazardous factors. In Figure.10 and 11, each plot practiced safety measures looks like effective deceptively, but it is hard to say all of safety measures are effective. For example, in case of decreasing ammonia tank temperature by "moderate" safety measure, it is effective to decrease hazard potential in "release scenario". On the other hand, in "abnormal scenario" it is not effective. Because in "abnormal scenario" ammonia cooling system failure is assumed and ammonia tank will be higher temperature, and ammonia will be released at higher temperature. That is, in normal operating condition hazard potential is under control, but if process goes abnormal condition hazard potential is revealed. Therefore, it is better way to change tank to pipeline in the aspect of inherently safety practice. Or the possibility that an "abnormal scenario" will occur have to be kept low by further practicing safety measure, though hazard potential is not decreased. By using this analysis method, it would be able to practice more effective inherently safety measures for high hazardous chemical plants.

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