Process Safety Analysis of Hydrogen Fluoride Production Unit Based on HAZOP-LOPA

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Abstract. In order to improve the accuracy of the risk analysis of the hydrogen fluoride industrial production process, the HAZOP and LOPA methods were combined to conduct a semi-quantitative risk analysis of the rotary reactor in the hydrogen fluoride production unit to study the danger during the reaction. Firstly, HAZOP is used to analyze the possible consequences of the six deviations and propose corresponding safety measures. One hazardous scenarios is selected from the HAZOP analysis and LOPA analysis is performed. The LOPA calculation is used to compare the quantitative values with the risk tolerance values. By taking security measures to reduce the risk of dangerous scenarios that exceed the risk tolerance to an acceptable level. The results show that HAZOP-LOPA analysis can accurately identify potential safety hazards and improve the safety management level of enterprises.

Introduction

Fluoride work is one of the most developed chemical industries. Its products play an extremely important and fundamental role in chemical production. Due to the high risk of fluorination process, it is necessary to carry out safety analysis on its production process to ensure reliable production. An accident occurred during the replacement operation of a company, and a large amount of high acid overflowed, causing two on-site operators to inhale high hydrogen fluoride gas, causing one death and one serious injury[1].

Hazard and operability analysis is one of the most widely used safety analysis methods in the industrial field, especially in high-risk industries such as petroleum and chemical industries. Lin Cui and others developed the HAZOP expert system and proposed a layered directed graph model, which can be used to qualitatively reason the cross-model; Jinlin Li analyzed the system security based on HAZOP; Jun-fang Liu[2] explored the petrochemical industry quantitative basis with LOPA thought as the main line; Ting-ting Zhou[3] combined HAZOP with LOPA to study the process safety risk management of petrochemical projects; Yong-hai Wang introduced the LOPA method into the HAZOP method to conduct safety research on the methanation unit.

This paper studies the process of hydrogen fluoride, focus on the analysis of the highly dangerous rotary reactor in the production process, carry out hazop analysis of the reaction process, and select the high-risk deviation for LOPA analysis to determine the failure probability of the independent protective layer, and then calculate the frequency of occurrence of the scenario, and the effectiveness of the security measures is assessed by comparing the quantified values with the risk tolerances[4]. The flowchart of the process is as follows.

The fluorite and sulfuric acid are pretreated in the initial part of the process[5]. After the fluorite is processed through the baking post, it is placed in a large silo, and then waited for the sulfuric acid washing to enter the rotary reactor together, and the reaction is carried out in the furnace to form crude hydrogen fluoride. The anhydrous hydrogen fluoride and other impurity gases and components obtained in the reactor are collected through a coarse tank, and are purified by entering a distillation column, and then hydrogen fluoride from which sulfuric acid and moisture are removed is obtained through a degassing tower, and then the finished hydrogen fluoride is flowed into the finished tank. At
the end of the process, the hot air post is reached. After a series of reactions and finished product storage, the unreacted material dry slag and tail gas are treated.

Figure 1. Hydrogen fluoride production process flowchart.

**HAZOP and LOPA Basic Steps**

The first step of HAZOP is to analyze the preparation, determine the object, purpose and scope of the analysis, collect the data, determine the analysis team, and develop the meeting process. The second step is to hold an analysis meeting[6]. The node is used as the analysis unit to describe the deviation of the process parameters of the node; the cause of the deviation is analyzed in the form of brainstorming, which may lead to the consequences; the existing security measures of the node are found out and suggestions are made.

The first step of LOPA is to identify and filter the scene. Then confirming the initial event (IE). IE includes external events, device failures, and personnel failures. The Independent Protection Layer (IPL) is then evaluated to determine the failure probability on demand (PFD) of the independent protection layer. Finally, the scene frequency is calculated and the scene risk is determined. Usually, the following calculation method is used:

\[ f_{iC} = f_{iI} \times PFD_{i1} \times PFD_{i2} \times \ldots \times PFD_{ij} \]  

(1)

\( f_{iC} \)—The consequence of the initial event b, the frequency of occurrence of C, the unit is a;
\( f_{iI} \)—The frequency of occurrence of the initial event i ,the unit is a.

**HAZOP-LOPA Analysis Steps**

Firstly, carrying out HAZOP on the device, analyzing the deviation, the consequences of the accident and the safety measures, and obtaining a record sheet. Then filtering LOPA scenes. Doing LOPA analysis, determining the probability of occurrence of initiating events, conditional events and consequential events, calculating the probability of event non-alleviation events; identifying existing independent protection layers and security protection measures, determine their failure probability, and calculate the probability of residual risk reduction[7].
HAZOP Analysis

The rotary reaction furnace is the core process equipment for completing the crude hydrogen fluoride reaction of fluorite sulfuric acid. In the reaction process, the rotary reaction furnace has a great danger. Therefore, the reaction process of the rotary reaction furnace is set as a node, and the reaction unit is subjected to HAZOP analysis. Analysis results are shown in the table below.

Table 1. Some typical results of HAZOP analysis.

| Guide word | Parameter                  | Deviation                                    | Possible reasons                                                                 | Consequence                                                                 | Safety measures                                                                 | Risk level |
|------------|----------------------------|----------------------------------------------|--------------------------------------------------------------------------------|----------------------------------------------------------------------------|--------------------------------------------------------------------------------|------------|
| more       | temperature                | Excessive temperature increase               | 1. The steam valve is not closed or leaks; 2. The feed rate is too fast; 3. The cooling system is faulty; 4. The coolant temperature is high [8]. | The temperature changes too fast, which may cause a serious reaction and form an explosion accident. | 1. Close the valve, check the maintenance valve to ensure it is in good condition; 2. Control the feeding speed according to the requirements of the process regulations; 3. Check and maintain the cooling equipment to ensure that the cooling system is in good condition. | C3         |
| less       | temperature                | Rotary reactor internal temperature is too low | 1. Temperature indication failure 2. Gas system intake valve failure              | 1. Decreased output 2. When suddenly heating up, it is prone to material accidents and explosions, which may cause danger. | 1. Check the feeding situation; 2. Check the thermometer; 3. Check gas system intake valve; 4. Set gas-temperature interlock system. | C3         |
| other      | Condenser failure          | The condenser structure is severe or corroded | High-temperature materials have the possibility of escaping, causing poisoning accidents. | 1. Regularly checking and repairing the condenser; 2. Replacing old condensers in time; 3. Setting up a toxic gas detection device. |                                                                                         | C2         |
| other      | composition                | Raw and auxiliary materials are not pure     | 1. Impurities are mixed into raw materials during storage and transportation of materials 2. The production equipment is not cleaned which causes impurity inclusion | Foreign matter involved in the reaction may cause a sudden increase in pressure or the risk of a fire explosion. | 1. Strict standards should be used for the procurement of raw materials; 2. Material storage is checked regularly; 3. Sampling and checking the purity before feeding; 4. Clean the rotary reactor regularly. | C4         |

HAZOP-LOPA Analysis

In this paper, the deviation and the consequences of the accident are analyzed. The accidental scene in LOPA analysis is selected as ‘fire and explosion accident caused by excessive temperature increase’.

Then the IE should be confirmed. In this scene, some failures and their failure probabilities are set in Table 2.
Table 2. The failure probability of IE.

| Type                      | Description            | Failure probability[a] |
|---------------------------|------------------------|------------------------|
| Initial event             | Steam valve failure    | 0.1                    |
| Conditional event         | Cooling system failure | 0.1                    |
|                           | Increased pressure     | 1                      |
| Consequence modification event | Ignition probability | 0.01                   |

The PFD of IPL in the event of fire or explosion which causes by the rapid rise of temperature and pressure will be as shown in the following table.

Table 3. The PFD of IPL.

| IPL          | Description                  | PFD[a] |
|--------------|------------------------------|--------|
| 1            | Safety shut-off valve works  | 0.1    |
| 2            | Standby cooling system intervention | 0.01   |
| 3            | Increased pressure emergency pull over | 0.01   |

Risk tolerance value is set to $10^{-5}$/a. From Table 2, the value of $f_i^1$ is $10^{-4}$/a, which means its risk level is medium and unacceptable. And then from Table 3, the value of $f_i^C$ is $10^{-9}$/a by equation (1). The risk level is low and is acceptable.

Conclusion

The following conclusions can be reached through a semi-quantitative risk analysis of the hydrogen fluoride production process by a combination of HAZOP and LOPA:

(1) Through HAZOP analysis, finding out the danger of reaction in the production process of hydrogen fluoride, and proposing corresponding safety measures for different dangers[9]; then determining the scene by LOPA, calculating the probability of occurrence of initial event and the probability of occurrence after safety intervention, and comparing two results. The combination of analytical methods can effectively improve the reliability of safety analysis results.

(2) Using the LOPA method to quantify the effectiveness of security protection measures and mitigate the residual risk of events, not only enrich the HAZOP results, but also provide managers with security decision information to reduce security risks and improve risk analysis accuracy and security management[10].

(3) The HAZOP-LOPA analysis method achieves the quantification of risk targets by probability values. By comparing the quantified values with the risk tolerances, it is possible to more intuitively assess the effectiveness of security measures and make up for the traditional HAZOP defects.

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