Journal of Hazardous Materials 142 (2007) 771–775

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

A real-life example of choosing an inherently safer process option

Karen Study *

Risk Management Services Department, Rohm and Haas Company, 6519 State Highway 225, Deer Park, TX 77536, United States

Available online 30 June 2006

Abstract

While choosing an inherently safer alternative may seem straightforward, sometimes what seems to be the most obvious alternative may not provide the best risk reduction. The process designer must maintain a broad perspective to be able to recognize all potential hazards when evaluating design options. All aspects of operation such as start-up, shut-down, utility failure, as well as normal operation should be considered. Choosing the inherently safer option is best accomplished early in the option selection phase of a project; however, recycle back to the option selection phase may be needed if an option is not thoroughly evaluated early in the process. In this paper, a project to supply ammonia to a catalytic reactor will be reviewed. During the course of the project, an "inherently safer" alternative was selected and later discarded due to issues uncovered during the detail design phase. The final option chosen will be compared to (1) the original design and (2) the initial "inherently safer" alternative. The final option was inherently safer than both the original design and the initial "inherently safer" alternative even though the design team initially believed that it would not be.

Keywords: Inherently; Safer; Design; Ammonia; Risk

1. Introduction

Choosing an inherently safer design (ISD) can be a difficult task at times. The four main strategies used to choose an inherently safer design are (1) minimize, (2) substitute, (3) moderate and (4) simplify [1]. Minimize refers to using smaller quantities of hazardous substances. Substitute refers to using a less hazardous substance. Moderate refers to using less hazardous conditions such as a less hazardous form of a material, lower pressure, or facilities which minimize the impact of a release of hazardous material or energy. Simplify refers to designing facilities which eliminate unnecessary complexity and make operating errors less likely, and which are forgiving of errors which might be made [2]. Although these options appear straightforward, changing a process design can have unforeseen consequences.

This paper will follow the course of a project to modify a steam production facility. The project illustrates the benefits of applying inherently safer design practices as well as illustrates the difficulties that can be encountered during selection of an ISD option. It also reinforces the need to evaluate design options critically early in the project stages. During the option selection and detailed design phases of the project, the "safer" design alternative was not at first obvious to the project team. Implementation of the perceived ISD may have actually increased some aspects of the risks involved with the project. Consequence modeling was used to understand the safety benefits of the proposed changes.

2. Facility description

The unit produces a large amount of steam using a multiple-burner boiler with natural gas and a low-BTU off-gas as its fuel sources. The boiler waste gas (flue gas) is sent to an elevated stack where it is discharged to the environment. This flue gas is mainly nitrogen and water vapor with oxygen and carbon dioxide. As with all boilers, there is also NOx present in the flue gas. NOx refers to compounds of nitrogen and oxygen that include nitric oxide (NO) and nitrogen dioxide (NO_2) gases. NOx contributes to the formation of ozone in the presence of volatile organic compounds and sunlight [3]. Also, NOx can react with water in the air to form nitric acid, resulting in acid rain [4]. After many years of operation, the steam production unit was required by new environmental regulations to reduce these NOx emissions. A team was formed to assess different NOx reduction options. After evaluating several options to achieve the required NOx emission reduction targets, the design team chose to install a selective catalytic reactor (SCR).

* Tel.: +1 281 228 8679; fax: +1 281 228 8675.
E-mail address: KStudy@rohmhaas.com.

0304-3894/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2006.06.097

The purpose of the SCR is to reduce the NOx in the boiler flue gas into nitrogen and water. This is done by reacting the NOx with ammonia in the SCR catalyst bed. The reaction equations for NOx reduction are [5]:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \quad (2)$$

3. Properties of ammonia

Ammonia (NH_3) is easily recognized by its pungent, penetrating, suffocating odor. Its common forms are anhydrous ammonia (without water) and ammonium hydroxide or aqua ammonia (a solution of ammonia and water). At standard conditions, atmospheric pressure and 32 °F, ammonia is a light gas. However, if the auto-refrigeration effect from a pipe or flange leak brings the temperature down sufficiently upon release, it can be heavier than air.

Exposure to ammonia vapors or liquid has the potential for serious injury or fatality. Inhalation of vapor or mist can cause severe irritation of the nose, throat and lungs, shortness of breath, breathing difficulty, headache, nausea, bronchial spasm, pulmonary edema (fluid in lung and air spaces), and possible death [6]. Exposure to 2700 ppm ammonia for 10 minutes could be life threatening [7]. Table 1 summarizes some of the physical and toxicological properties of ammonia.

For this analysis, the ammonia toxicity dose–response relationship was expressed in the form of a "Probit" equation. Probit equations are generally derived from animal exposure data. The use of Probit equations to describe the toxicity dose-relationship for toxic gases is described by CCPS in the Guidelines for Consequence Analysis of Chemical Releases [10]. For this analysis, the following Probit equation was used:

$$\text{Probit} = A + B\ln(L), \quad L = C^N t \quad (3)$$

where L is the toxic load associated with exposure at concentration C (in ppm) for a time t (in minutes). A, B and N are constants derived from experimental vapor exposure data as determined by the Rohm and Haas Toxicology Department [11]:

$$A_{\text{Ammonia}} = -47.8, \quad B_{\text{Ammonia}} = 2.3, \quad N_{\text{Ammonia}} = 2 \quad (4)$$

Table 1
Properties of ammonia [8]

Color	Colorless
State	Gas
Relative density, gas	0.6 (air = 1)
Relative density, liquid	0.7 (water = 1)
Vapor pressure	124 psi at 20 °C (68 °F)
Boiling point	−33 °C (−27 °F)
Solubility in water	Completely soluble
Percent volatility (%)	100
Lower explosive limit (%)	15
Upper explosive limit (%)	30
Immediately dangerous to life and health (IDLH)	300 ppm [9]
Acute exposure guideline levels (AEGL) for 10 minutes exposure durations [7]	
AEGL 1	30 ppm
AEGL 2	270 ppm
AEGL 3	2700 ppm

4. Initial design proposal (liquid anhydrous ammonia)

To supply ammonia to the SCR, the design team considered using anhydrous ammonia in the vapor form but rejected this option fairly early. The vapor delivery system was rejected because the team believed that flow control would be less reliable for the vapor compared to the liquid system, and they were also unsure if the vapor supplier would be able to meet the project on-stream requirements. Therefore, the project team chose to tap into an existing liquid anhydrous ammonia piping header that supplied a nearby processing unit. Piping was minimized as much as possible to ∼600 ft of 2 in. pipe. A vaporizer skid using steam to vaporize the liquid ammonia prior to injecting into the SCR would be installed near the boiler. See Fig. 1 for a high level overview of this option.

After the option was selected, the process safety group was consulted to provide input. Due to concerns regarding

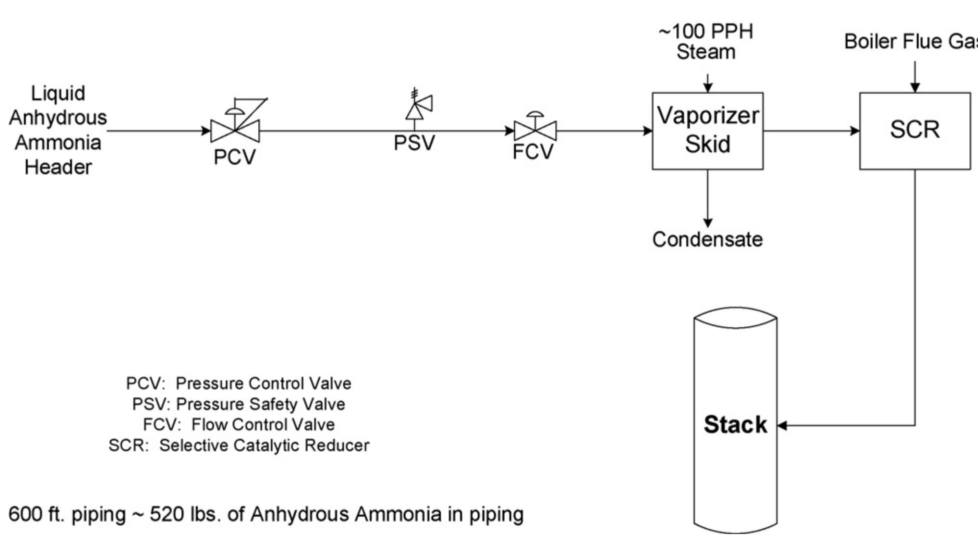

Fig. 1. Initial ammonia supply proposal—liquid anhydrous ammonia supply.

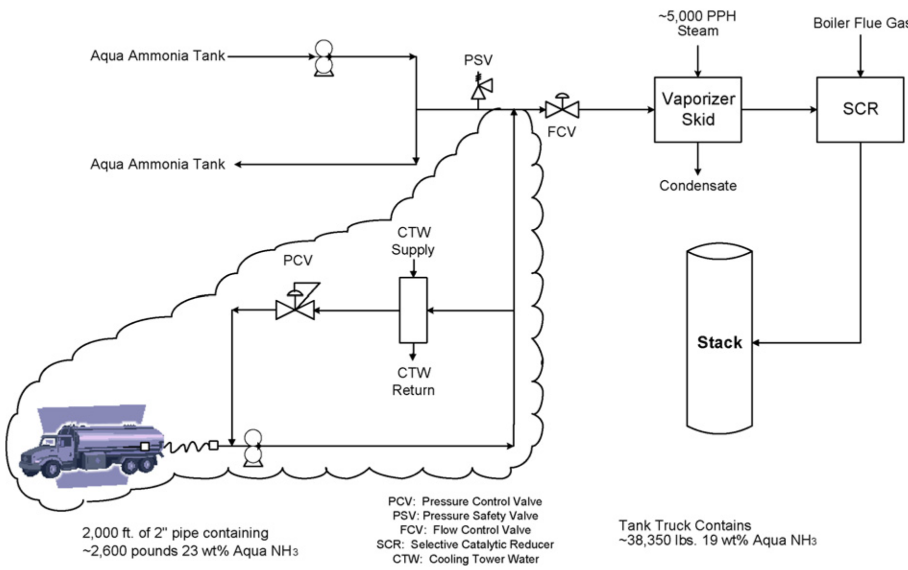

Fig. 2. Aqueous ammonia supply proposal.

incrementally increasing risks associated with the current liquid anhydrous ammonia piping system, the safety group recommended using the ISD practices to evaluate another alternative. Using the "moderate" option for ISD, an option to use aqueous ammonia was developed by the design team. The aqueous ammonia alternative would supply a less hazardous form of ammonia, thus minimizing the impact of any loss of containment. Since aqueous ammonia was available at a nearby processing unit, this seemed to be a straightforward alternative.

5. Aqueous ammonia design proposal

An aqueous ammonia user in the plant could provide aqueous ammonia to the boiler facility via a connection downstream of their aqueous ammonia storage tank. Since this storage tank was much farther from the boiler than the anhydrous ammonia header, the length of piping required was much greater. Also, new positive displacement pumps, located at the tank, were required to supply the aqueous ammonia. A temporary supply alternative also had to be built into the design, since periodic shutdowns were required at the aqueous ammonia tank. To accommodate these periodic supply needs, additional connections and provisions were made for tank truck deliveries of aqueous ammonia. See Fig. 2 for an overview of the aqueous supply option.

After the detailed package was almost complete, a hazard and operability analysis was conducted. Several concerns were raised regarding the tank truck delivery system and associated operations. The review team felt that the risk of spills and operator errors for the tank truck portion of the delivery system was higher for this option than an anhydrous ammonia system. Also, this option had much higher capital, operating and maintenance costs. There were also issues with reliability related to the addition of pumps in the system. So, the project was recycled back to the option selection phase once again.

6. Final round of option selection

During the third round of option selection, use of anhydrous ammonia vapor was re-evaluated. The anhydrous ammonia

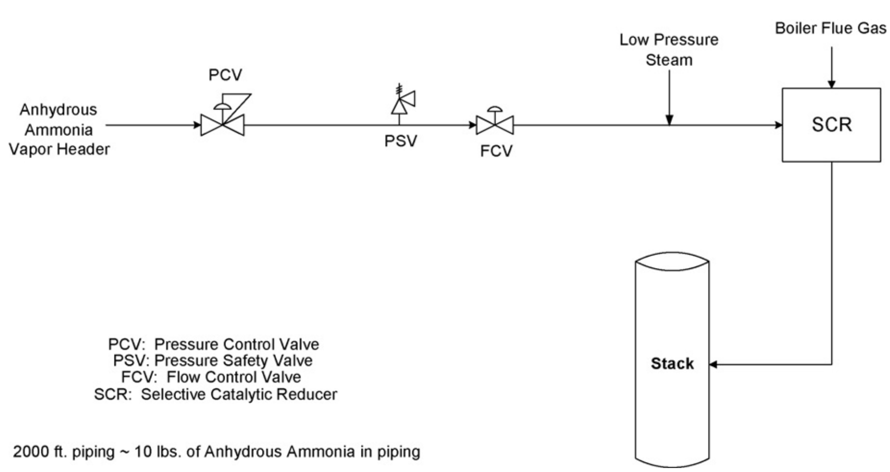

Fig. 3. Anhydrous ammonia vapor option.

Table 2
Mass comparison for ammonia transfer options

Option	Piping length (ft)	Volume (ft^3)	NH_3 mass[a] (lbs)
Anhydrous ammonia liquid	600	14	520
Aqueous ammonia (23 wt.% NH_3)	2000	47	600
Aqueous ammonia tank truck (19 wt.% NH_3)	N/A	652	7300
Anhydrous ammonia vapor	2000	47	10

Note that 2 in. piping was used for all three options due to structural integrity concerns.
[a] Density of ammonia and water at 80 °F; 37 and 62 lb/ft^3, respectively.

vapor option had not been fully evaluated previously, based on early assumptions that the availability of anhydrous ammonia vapor would not be high enough for the SCR, that aqueous ammonia was a safer alternative, and that it might be more difficult to control the mass flow measurement of the vapor stream compared to the liquid stream. There was a nearby processing unit that vaporized anhydrous ammonia from the plant header prior to using it within their unit. Based on an evaluation of the downtime of their system, they would be able to supply anhydrous ammonia vapor to the SCR at a sufficiently high on-stream reliability so that a secondary supply system would not be needed. Flow control issues were addressed by using redundant instruments which had a good operating history in a similar service. To prevent condensation in the transfer piping, the ammonia pressure was dropped to 25 psig at the tie-in point to the header. This made the risks associated with use of anhydrous ammonia vapor less than if high pressure vapor were used. Redundant instrumentation was used for the control valves and letdown regulators to reduce downtime for the system. A small amount of low pressure steam was added to the ammonia prior to injection into the SCR. The steam was added as a diluent to more evenly disperse the ammonia in the SCR catalyst bed. The anhydrous ammonia vapor option is depicted in Fig. 3. For simplicity, redundant instrumentation is not shown.

7. Consequence analysis

Consequence modeling was completed to evaluate the relative hazards associated with each of the three options under review. Modeling of potential releases was done using the PHAST (version 6.42) chemical release consequence modeling software available from DNV Software. Although there are issues regarding ammonia/water reactions and auto refrigeration when modeling ammonia releases in PHAST, the modeling results were adequate for a comparative analysis of the three options.

For the comparison, a complete break in the piping supplying the SCR was modeled. This resulted in an almost instantaneous release of the entire pipe contents. The concentration of interest used to compare the results was 300 ppm ammonia, the IDLH (immediately dangerous to life and health) value for ammonia [12]. It is also very near the AEGL 2 (acute exposure guideline level) for a 10 min exposure to ammonia, which is 270 ppm [7]. The AEGL 2 is the concentration at which the public could experience irreversible or serious long-term health problems. All of the results are for the equivalent toxic dose calculated using the toxicity dose-relationship (the Probit equation) for toxic gases discussed earlier in this paper.

The consequence analysis for liquid anhydrous ammonia estimated a maximum distance of 1170 ft to the IDLH concentration of ammonia under the worst case weather conditions (F atmospheric stability, 1.5 m/s wind speed) and an ambient temperature of 85 °F. For the aqueous ammonia piping system using the same leak scenario, weather conditions, and a temperature of 45 °F (due to the aqueous ammonia supply being cooled prior to delivery), the impact distance for IDLH level results was 930 feet. The ammonia vapor scenario impact distance for the same conditions and an ambient temperature of 85 °F was 125 ft.

For the aqueous ammonia scenario, it can be expected that a pool of aqueous ammonia would form upon release from the piping system. PHAST does not adequately predict formation of the pool and the evolution rate of ammonia from the pool. If this were accounted for, the results would indicate much longer exposure durations and a smaller impact zone.

Modeling aside, one significant difference between all three options is simply the mass of material inside the transfer piping and associated equipment. The anhydrous ammonia vapor system contained an order of magnitude less ammonia than the other piping systems and two orders of magnitude less than the aqueous ammonia tank truck. See Table 2 for a comparison of the options based on mass differences.

Another issue considered in evaluating the aqueous ammonia system is the temporary tank truck needed when the primary source is not available. Connecting and disconnecting hoses to the truck introduces new release scenarios involving smaller amounts of ammonia in close proximity to production operators. Additionally, the large tank truck inventory greatly increases risks during a catastrophic failure scenario.

Toxicity was the primary concern for this analysis. Hazards due to ammonia flammability are not expected because of the high lower and upper flammable limits (15% and 30%, respectively) and the high ignition energy requirements. These properties usually cause fires to occur where ammonia vapors are enclosed which is not the case for the SCR ammonia transfer system.

8. Conclusion and action

The design team chose to use anhydrous ammonia vapor to supply the SCR. Receiving ammonia in the anhydrous vapor form was determined to be an economically viable option, and the safety analysis indicated that the vapor form of anhydrous ammonia was safer than design options incorporating either liquid anhydrous ammonia or aqueous ammonia.

In comparing both ISD options to the liquid ammonia supply option, the anhydrous vapor supply option decreases risks along the piping run without introducing new risks to the system. Implementation of the liquid aqueous ammonia system, which was first selected as an inherently safer alternative, appeared to have slightly lower risks compared to the liquid anhydrous ammonia system based on modeling analysis performed for the piping run. Unfortunately, a new problem would have been introduced by the aqueous system. The need to have a temporary supply station would have increased the risk to operating personnel due to hose handling while hooking up and disconnecting the tank truck. Plus, for aqueous ammonia releases, there are longer timeframes for exposure due to pool evaporation. In looking at the mass of ammonia contained in the piping system, the anhydrous ammonia vapor system contained an order of magnitude less ammonia than the other systems considered. As such, the vapor option follows the minimize strategy for ISD.

Judging both ISD options from an economic standpoint, the vapor system had lower capital costs. The vapor system also had lower operating costs since very little steam was required prior to injection into the SCR. The vapor system had lower maintenance costs since no pumps were required in the system. Also, the vapor system is predicted to be more reliable due to the simple design and absence of moving parts. As such, the vapor option follows the simplify strategy for ISD.

This project illustrates the principle that decision-making between inherently safer designs involves evaluating several different metrics, including volume of hazardous material, distances affected by a release, frequency of release (for example, during tank-truck connections for aqueous), risk (including consequence severity and frequency), and life cycle cost. The option selected depends upon the metrics used in the decision-making and the weighting factors among those metrics. There is not a single metric that can be considered as the "correct" metric for selecting one inherently safer design over another option. It is always a trade-off.

It should be noted that the review of the design options for inherently safer characteristics was conducted as part of the normal process hazard analysis work process. Some organizations have a formal inherently safer design review separate from the HAZOP or other process hazard analysis. Our practice is to integrate the inherently safer designs review into the other process hazard analysis activities. This project illustrates that the analysis may need to be performed multiple times to get to the optimum solution if the issues are not thoroughly evaluated early in the project stages.

References

[1] Inherently Safer Chemical Processes, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, 1996, p. 22.
[2] D. Hendershot, J. Loss Prevent. Process Ind. 10 (3) (1997) 151–157.
[3] Environmental Protection Agency, Region 5 Air—Ozone. No date, as downloaded from http://www.epa.gov/ARD-R5/naaqs/ozone.htm.
[4] Environmental Protection Agency, Clean Air Markets—Environmental Issues. No date, as downloaded from http://www.epa.gov/airmarkets/acidrain/index.html.
[5] Japanese Advance Environment Equipment, SCR De-NOx System. No date, as downloaded from http://www.nett21.gec.jp/JSIM_DATA/AIR/AIR_3/html/Doc_081.html.
[6] Air Products Material Safety Data Sheet #1003. December, 1999. as downloaded from http://www.mne.umd.edu/LAMP/Safety/Msds/MSDS_GAS/Ammonia.doc.
[7] Environmental Protection Agency Acute Exposure Guidelines. No date, as downloaded from http://www.epa.gov/oppt/aegl/results88.htm.
[8] Air Liquide, Safety Data Sheet, Ammonia. July 31, 2002, as downloaded from http://www.airliquide.com/safety/msds/en/002_AL_EN.pdf.
[9] NIOSH Documentation for Immediately Dangerous to Life or Health Concentrations (IDLH): NIOSH Chemical Listing and Documentation of Revised IDLH Values (as of 3/1/1995). As downloaded from http://www.cdc.gov/niosh/idlh/intridl4.html.
[10] Guidelines for Consequence Analysis of Chemical Releases, American Institute of Chemical Engineers, New York, 1999, pp. 238–240.
[11] Per Rohm and Haas Toxicology Department.
[12] NIOSH Documentation for Immediately Dangerous to Life or Health Concentrations (IDLH): NIOSH Chemical Listing and Documentation of Revised IDLH Values (as of 3/1/1995). As downloaded from http://www.cdc.gov/niosh/idlh/intridl4.html.