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# Analysis of Operational Risks in the Storage of Liquid Ammonium Nitrate in a Petrochemical Plant, through the HAZOP Methodology

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The storage of liquid ammonium nitrate in a petrochemical plant, located at the Caribbean region of Colombia, is analyzed to identify and mitigate the risks present in it. Hazard and Operability (HAZOP) methodology was followed to assess the risks and hazards associated to this process. Initially, the ammonium nitrate storage tank was defined as the node to be studied, together with the instrumentation required for this operation. The diagrams of the node and technical specifications of the equipment and instruments were reviewed. This information, together with the operative, technical and conceptual knowledge of the staff at the plant, allowed to assess the deviations for operational variables such as temperature, pressure and level, among others, in order to identify the hazards and risk scenarios that can take place during the storage of ammonium nitrate. Based on the HAZOP analysis, recommendations were made to mitigate or avoid incidents that have an impact on people, environment or the company. This case study highlights the qualitative deviations and variables that require a constant monitoring and control for a safe storage of ammonium nitrate.

## 1. Introduction

The storage of Ammonium Nitrate (AN) is considered a critical process, due to the risks and hazards related to its own nature, as well as its handling, storage and processing (Labourer et al., 2016). In this work, the development of a Hazard and Operability (HAZOP) analysis is presented to identify and assess the risks associated with the AN storage, and make recommendations for the safe storage conditions of liquid AN in a fertilizer plant, located in the industrial zone of the city of Cartagena, Colombia. Ammonium nitrate is one of the main sources of nitrogen to produce fertilizers. In its liquid state this substance is translucent and colourless or slightly yellowish; in its solid state it is colourless, highly soluble in water and non-combustible. AN is a good oxidizing agent that promotes the burning of other combustible materials, even in the absence of air. When subjected to high temperatures, AN releases toxic and/or corrosive gases. The main risk associated to its storage or handling is its explosiveness. Moreover, Ammonium Nitrate can detonate if one of the following factors occurs: heating, high temperatures under confinement, contamination or strong impact. Besides, it is incompatible with powdered metals, organic materials, strong reducing agents and natural fabrics (EFMA, 2005). Many explosions have been reported as a result of the fire of AN, being the explosion at BASF Plant Oppau in 1921, Texas City in 1947 and the AZF Toulouse Disaster in 2001 the most significant among them (Negovanović et al., 2015). The critical nature of the AN storage requires appropriate studies that allow identifying safety, health and environmental hazards and risks; the structured analysis offered by HAZOP studies, provide this information and also allows to search for potential operating problems (Crawley and Tyler, 2015).

## 2. Production process of Ammonium Nitrate

The production process of AN consists of mixing ammonia and nitric acid. The reaction is highly exothermic:

$NH_3 + HNO_3 \rightarrow NH_4NO_3 + Heat$ (1)

The neutralization of 45-65% solution of $HNO_3$ with gaseous $NH_3$ is accompanied by the release of 100-115 J/mol of $NH_4NO_3$. This heat of reaction partially evaporates the water that accompanies the $HNO_3$ to produce a 83% ammonium nitrate solution. During neutralization, the components must be mixed rapidly and completely in the reactor to avoid local overheating, nitrogen losses and decomposition of AN (Hullman's, 2012). The process, in general, consists of a reactor without agitation (see Figure 1), where vaporized ammonia and 55% nitric acid are injected through the top of the reactor. Ammonia is transported through a tube to the bottom of the reactor, then it rises and goes counterflow with the $HNO_3$ to form ammonium nitrate. During the production of AN, monitoring and control of temperature and pH, online monitoring of NOx and/or $N_2O$, and purity and safety of the AN solution are required. These conditions are described in the document released by EFMA (2005).

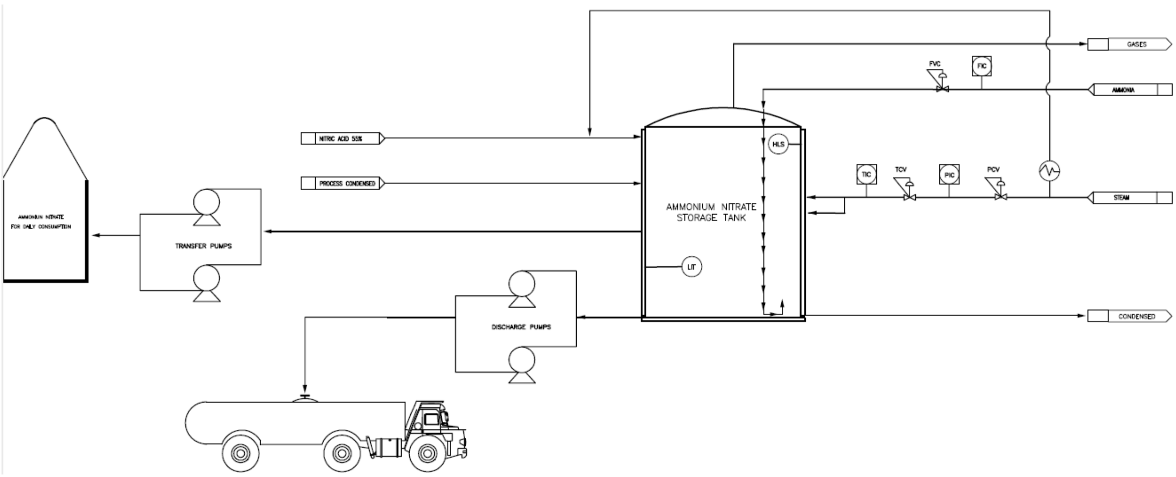


*Figure 1. Production of Ammonium nitrate from gaseous Ammonia and Nitric acid.*

The decomposition of AN is one of the main chemical hazards associated to its storage. The reaction is as follows:

$NH_4NO_3 \rightarrow N_2O + 2H_2O + 44.83\ kJ/mol$ (2)

When AN is heated rapidly and its temperatures reaches the 260 – 290°C range, side reactions are promoted. These side reactions are highly exothermic and rapid. Confinement will result in uncontrolled temperature or pressure, and the decomposition may become explosive (Nygaard, 2006). An explosion is considered as an industrial accident, having consequences in three areas, such as human, environmental and economic, and affecting each one differently. HAZOP analysis provides the information about the hazards and risks in critical processes of a manufacturing company (Crowl and Louvar, 2011). The critical process that will be evaluated in this paper is the storage of liquid AN at high temperatures (130 °C - 150 °C). This is considered a critical process because of the risk represented by AN decomposition, that can cause, among other consequences, detonation due to high temperatures. Another factor that adds to the critical nature of the storage of AN is the confined amount in the tank (approximately 800 tons, which is 85% of the total storage capacity).

## 3. Methodology

The objectives of this work were: 1) to define the node to be evaluated, 2) to analyze the asset profiles corresponding to the liquid AN production plant, 3) to identify the risk and threat scenarios around the node, following the HAZOP methodology, according to the work by Janošovský et al. (2016), and considering the information provided by the staff at the company, 4) to evaluate the risks and operability associated with the liquid AN storage tank and 5) to select a mitigation approach with the basic recommendations, according to the deviations of the node and failures that can occur in the process. The liquid AN storage tank was defined as the node to be analyzed. The analysis of the asset profile of the liquid AN production plant was based on the review of documents such as PFD and P&ID diagrams, operations manual of the storage tank, data of the pumps upstream and downstream of the tank (power, NPSH). Data of instruments and valves, and Safety

Data Sheet for AN at 83% (Pasman and Rogers, 2016). The analysis of the asset profile shows that the tank has:

- Two discharge pumps, one in operation and the other stand-by, each equipped with pressure and temperature indicator in the discharge.
- Condensate discharge lines from the tank.
- Level indicator and level transmitter that sends signal to ammonium nitrate discharge pumps.
- Temperature transmitter that sends signal to the steam supply line to the tank coil.
- Steam supply line to the coil with pressure control valve, pressure transmitter, temperature control valve and temperature transmitter.
- Condensate inlet line.
- Inlet line of liquid ammonium nitrate to 83% to the storage tank.
- Outlet line of gases that will be used in another plant.
- Ammonia inlet line with flow transmitter, flow control valve and pressure gauge.

The HAZOP analysis allowed to identify hazards and threat scenarios present in the node, as well as the selection of the mitigation approach and basic recommendations according to each deviation. 32 deviations were analyzed, of which 18 apply for this node and will be explained below. The operation variables considered were: Pressure, level, temperature, volumetric flow, time, concentration, pH, mass flow and power.

## 4. Results

A typical layout of an ammonium nitrate storage tank has been prepared formerly by the European Fertilizers Manufacturers Association - EFMA (2005). This storage tank has the following characteristics: in its upper part it has a vent for the exit of the decomposition gases and the steam coming from the added water; an overflow point to avoid spills of ammonium nitrate; a steam coil to evaporate the water that is added and to keep the temperature and concentration in the tank, in order to avoid explosions, it has a line of recirculation and discharge of ammonium nitrate and an a line for ammonia addition, to maintain the pH of the ammonium nitrate. Also, the tank has the following instrumentation: a high and low level alarm, a high temperature switch, a low level switch, a high and low temperature alarm, and a low flow and pH alarm in the recirculation line. After selecting the node to be evaluated, HAZOP analysis allowed to identify risks and threat scenarios present in the node, as well as the risk assessment, selection of mitigation approach and basic recommendations according to each deviation.

### 4.1 Flow deviations

Table 1 shows, as an example, the results of the HAZOP analysis for flow deviations. Other deviations (pressure, temperature, level) are commented below, according to the structure of the Table 1. The Table 1 lists the possible causes of the absence of flow, as well as the causes of higher or lower quantity of flow. It also shows the consequences of the deviations, together with the recommendations that help avoiding or mitigating the causes or consequences of each deviation. The letter that indicates the event frequency is also shown in the column of the causes for each deviation. It is observed that the causes for flow deviations are mainly of low to medium frequency (indicated by letters D and E respectively); a low frequency (letter D) means that the event can happen in a frequency from 0.01 to 0.1 times per year, while the medium frequency (letter E) means that the event can happen in a frequency from 0.1 to 1 times per year. These values of frequency are given in the risk assessment matrix (Crawley and Tyler, 2015).

### 4.2 Pressure deviations

In relation to the pressure, the "high pressure" deviation may be caused by failure of the pressure gauge, which, in turns, would cause a high pressure in the coil. It is recommended that the safety valve is included in the program of periodic calibration, to ensure its proper operation. Even though the deviation "Less Pressure" does not apply for this node, it is considered important for the integrity of the tank and the substance; a lower pressure is due to a less than required amount of air that enters through the vent while discharging AN, or due to condensation taking place inside of the tank. This can lead to a deformation of the tank, due to the vacuum formed inside. To avoid this, it is recommended to install a wider vent, so the air that enters through it can keep a stable internal pressure of the tank.

*Table 1: Input-Output table of flow deviations*

| Guide words | Causes | Consequences | Recommendations |
|---|---|---|---|
| NOT FLOW | • Failure in the discharge pump of the tank (E)<br>• Closure of the discharge or suction in the discharge pump of the tank (D)<br>• Closed valve between the pump that carries AN and the storage tank (D)<br>• Obstruction of the valve between the pump that carries AN and the storage tank (D)<br>• No level in the AN storage tank due to failure of the tank level transmitter (D) | • Crystallization of AN<br>• Pipe obstruction<br>• Production losses<br>• Pump cavitation<br>• Heating of AN<br>• Decomposition and explosion | Install:<br>• Temperature transmitter in the recirculation line of the AN storage tank, with alarm<br>• Alarm for low flow in the pump discharge<br>• Low amperage or vibration alarm<br>• High temperature alarm<br>• Alarm for high and low pressure in the pump discharge |
| LESS FLOW | • Closing or partial obstruction of the valve (D)<br>• Inefficiency of the discharge pump of the tank (E)<br>• Leak in pipes (D) | • Crystallization of AN<br>• Obstruction in pipes<br>• Production losses<br>• Crystallization in the pipes due to low speed<br>• Contamination<br>• Affectation to people<br>• Plant stop. | • Reduction in the number of flanges and leak points<br>• Inspection of critical pipes (maintenance program and mechanical integrity of the plant) |
| MORE FLOW | • More flow of ammonia to the tank, due to failure of control loop of the flow indicator in the line that carries ammonia to the tank (D)<br>• Condensate inlet to the AN storage tank, through the flood line (D)<br>• Failure in the flow indicator control loop, in the ammonia line to the tank (D)<br>• Flow of ammonia to the AN tank, due to operational error when improperly entering the set point of the control valve of the line that transports ammonia to the tank (B)<br>• Condensate inlet to the AN storage tank, through the washing line (D)<br>• Input of more steam to the coil, due to failure of the temperature indicator control in the steam line to the tank (D)<br>• Coil rupture of the AN storage tank | • Dilution of AN<br>• Economic loss<br>• Ammoniacal gases<br>• Environmental impact<br>• Affectation to people<br>• Uncontrolled heating of AN<br>• Decomposition of AN<br>• Risk of explosion | • Implement online pH measurement in the AN storage tank<br>• Implement tempering system to lower heating steam temperature<br>• Implement SIF SIL 3, so that high temperature stops the passage of steam to the coil, and floods the AN storage tank<br>• Verify inspection plan of AN storage tank coil |

## 4.3 Temperature deviations

A "High Temperature" deviation can be due to the entry of more steam to the coil, due to a failure in the temperature indicator. This deviation would cause an uncontrolled heating of AN, decomposition of AN, and risk of explosion. Recommendations associated with this deviation include installing of a tempering system, to implement SIF SIL 3, and to verify the inspection plan of the coil in the AN storage tank. On the other hand, the causes of "Low Temperature" deviation may be due to closure of steam supply to the tank, which, in turns, is due to failure of the coolant temperature gauge, and failure in the steam supply to the tracing of lines; this low temperature deviation would result in the crystallization of AN and obstruction of the lines, and loss of production. The recommendations are to install a temperature transmitter in the recirculation line of the AN storage tank, with an alarm. Also, a low flow of steam alarm is recommended.

## 4.4 Level deviations

The "High Level" deviation causes can be related to condensate entering the wash line, due to an operational error during clean-up activities; consequently, the AN will get diluted and economic losses will follow. Other causes are condensate entering the flood line in test activities; pump not stopping during transfer of AN to the tank; failure in the level transmitter during transfer of AN to the tank, or due to flood water entering the tank. These will cause AN spills, environmental impact and possible affectation to people. To prevent high-level deviations and its consequences, it is recommended to locate the tank in a safe place; also, it is recommended to check if the signals from the level transmitter and the high-level switch go to different I/O cards. The “Low Level” deviation can be due to failure of the level transmitter during transfer, operational error by leaving drains open, by leaving samples open or during transfer from the tank. A low-level deviation, results in cavitation of the suction pumps at the outlet of tank, heating and/or decomposition of the AN with subsequent explosion, soil contamination with AN, possible damages to people and unscheduled downtime. To minimize these risks, it is recommended to install the drainage to a safe place and implement protections such as low-flow alarm when discharging the tank, as well as turning off the suction pump if low amperage or vibration, high temperature or low/high pressure are detected at the pump discharge.

## 4.5 Deviations during start-up and stopping of node

If condensate enters the node due to operational errors, it will cause the dilution of AN and economic losses; other deviation during start-up is the lack of heat to the lines and remnants of crystallized AN at the pumps before starting up. These operational errors cause plugging of the lines, delay in start-up, economic loss, damage to the pump, heating and/or decomposition of AN with subsequent explosion. To minimize these risks, it is recommended to implement protections such as low-flow alarm when discharging the tank, as well as turning off the suction pump if low amperage, low vibration, high temperature or low/high pressure are detected at the pump discharge.

## 4.6 Deviations related to composition

This type of deviation occurs when there is rapid decomposition, contamination, or change in the composition of the liquid AN contained in the tank. The possible causes are condensate or ammonia entering the tank. This can cause AN dilution and economic losses. Another cause is low pH in the tank, due to feed coming from another tank. This leads to decomposition of AN and risk of explosion. It is recommended to install safety instruments/devices that flood the tank in case of detecting high temperature.

## 4.7 Deviations associated to sampling and steam supply.

These involve failure in the sampling procedure (in this case, the sample is taken three times a day). A failure in the test sample may result in skin burns due to contact with AN. It is recommended to redesign the sampling system and review the sampling frequency. A "No Steam Supply" deviation will cause crystallization of AN, obstruction in the lines and production loss.

## 4.8 Deviations due to effects from surroundings

These are due to external conditions that can cause some type of deviation. For example, a collision of vehicles can affect the tank structure, and it has the effect of breaking, leakage and loss of containment in the tank, generating production losses. It is recommended to clearly define the perimeter of the plant.

## 4.10 Deviations related to explosion, emissions and commissioning

This node (AN storage tank) has the necessary security barriers, however, it is important to carry out the periodic maintenance and monitoring to the tank, piping, valves and instruments, and to report their actual status, to prevent controllers and indicators from sending false signals to the control room and/or to the valves.

The process usually has a security system such as a bypass and relief, as well as a venting system to avoid overpressure explosions in the tank, given the nature of the AN and its storage conditions; therefore, constant checks are necessary to prevent leaks and ensure correct operation. Also, efficient communication among the workers is crucial to mitigate the consequences of any of the causes analysed above; it is also highly recommended that all operators to have training on behaviour-based safety to ensure good practices that are implemented in the plant. Also, daily and weekly inspection and maintenance plans are followed to ensure the proper operation of the tank, the condition of its components (instruments, pumps, piping, coil, dikes) and the safe storage of AN. A strict maintenance is carried out when the plant is stopped, and the inside of the tank can be accessed. Operators receive regular training on the handling of hazardous materials, First Aid and Emergency Care. Operators have appropriate clothing to meet an emergency, such as fire suits equipped with the safety accessories, hazmat suits for handling spills of hazardous chemicals, tools to stop spills and implements to give first aid in case of an emergency with people; talks about the proper use of equipment, instruments and electronic devices are given on a daily basis so that, in case of an emergency, operators can proceed to mitigate it while the corresponding discipline arrives at the place. In addition, new staff receive a training on safety and environment before entering the facility and follows a training program for three months.

## 5. Conclusions

HAZOP methodology was followed in this study to identify and analyze the operability risks associated to the liquid Ammonium Nitrate storage tank, considering the operational, technical and conceptual variables in a petrochemical plant located at the Caribbean region of Colombia. Mitigation strategies were established according to the risks identified, and HAZOP methodology showed a relevant tool that helps identifying and minimizing risks in an industrial process. Key parameters that showed representative deviations were tank pressure, temperature and level. These variables are crucial when storing liquid Ammonium Nitrate, due to its explosive nature, so the constant monitoring of these variables is necessary, to avoid incidents. Also, continuous control and maintenance must be carried out on the equipment and control instruments used in the process to avoid the emergence of new risks. An important fact that requires a continuous monitoring is the temperature of the inlet to the tank, and the temperature inside the tank, so it keeps in the range of (130°C – 150°C). If these temperatures exceed this range, an explosion would follow. Also, pH in the tank must be monitored and controlled, as well as the flow to the pumps at the outlet of the tank, so cavitation is avoided. Any deviation from normal parameters in this process could result in decomposition of the Ammonium Nitrate followed by explosion. However, it is noted that the tank has the necessary instrumentation to maintain the parameters of temperature and pressure in control, however, continuous monitoring is recommended due to possible human failures. The frequency of the HAZOP can be established by the company, as a strategy to help avoiding incidents in the processes. HAZOP analysis, thanks to its qualitative results, is recommended before implementing quantitative process safety as LOPA or SIL, since HAZOP provides the frequency of the events occurrence that can be quantified more easily when doing a LOPA or SIL. For future research, it is recommended to implement a quantitative methodology in the Ammonium Nitrate storage process, to establish comparisons between quantitative and qualitative analysis and optimize the process. Finally, it is evident the need to develop a regulation system for the Colombian chemical industry that promotes the safety management of processes; so far, the laws that apply are only in safety and health at work.

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