Emanation of Nitrous Gases in Nitration Process
Río Loa Plant - ENAEX Chile

María Virginia Ramírez, BSc & MS; ENAEX Servicios, Santiago, Chile

Tomás Weibel, BSc; ENAEX Servicios, Santiago, Chile

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Abstract

The Nitroglycerin Nitrator feeds the reactor with mixed nitric and sulfuric acid. The tank TK 04 that is fed with such mix has several level sensors linked to the processing pumps, which in turn, open or stop the feeding of acid mix to the tank, as appropriate.

In October, 2017, the Nitrator's cooling system failed, thus evidencing a lack of logic control sequence in the pump that feeds tank TK 04 since it did not stop accordingly.

Said failure enabled then that the mixed acid overflowed through the dam, emanating nitrous gases for about 9 minutes.

We finally concluded that neither changes made in the unit were documented, nor the information was conveyed and therefore such changes were not recorded as 'change management'. Failure to management of change led to lack of revision or updates in the corresponding emergency plans in case of nitrous gas emanation.

Introduction

Río Loa plant dated back from 1920 and during almost its 100 years of operation has gone through several generations and changes to its processes. Therefore, it is key to use the Management Of Change –MOC- tool for its correct operation.

This report clearly shows the importance of reporting and researching these changes and the processes' deviations, if any.

Description of the Incident Area

Background information of the normal operation of Nitrator regarding the incident.

To operate the Nitroglycerin Nitrator, it is necessary to feed the reactor with mixed nitric acid and sulfuric acid. This mix is sent by pump Nº 1 (see figure N° 1) from tank TK 04 to the reactor. Pump Nº 2, sends the mix of acids to tank TK 04 from tanks TK 01 and TK 02 respectively, and located approximately 80 meters away.

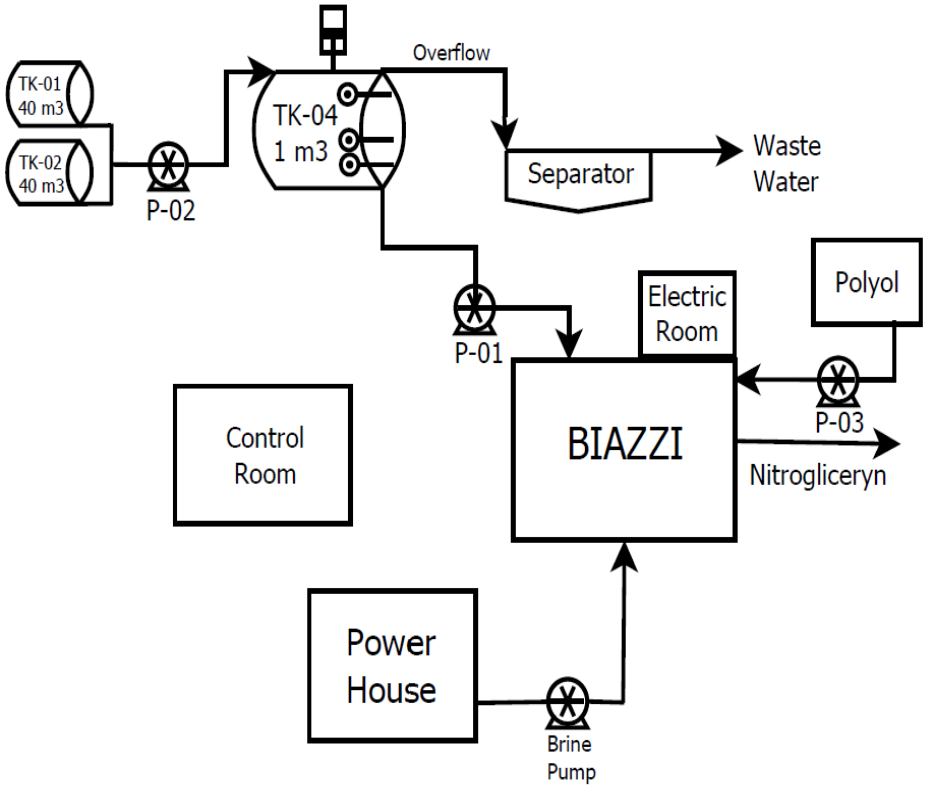

Figure 1. Nitroglycerin Nitrator Process

Tank TK 04 has the following level controls:

- Analog level device that indicates the tank's filling percentage from 0 to 100% and displays it on a computer screen in the control room. This device is not linked to the logic control sequence to stop pump P-02 in case said level indicates 100% filling.
- Tank TK 04 has floating digital sensors on three levels: high, low and low-low. When the acid mix that feeds tank TK 04 reaches the high level, said sensor sends a stop signal to pump P-02.
- As the acid mix in tank TK 04 feeds the nitroglycerin nitrator, its level drops, reaching the low level. At this point, the sensor sends a signal to pump P-02 so that it starts the acid mix feeding process to tank TK 04.
- If, for some reason, the level of tank TK 04 reaches the low-low level, because, for example, the P-02 feeding pump was not activated at that moment, then the low-low sensor signal will stop the nitration process. In other words, both pump P-01, which sends mixed acid, and the P-03 polyol pump stop.
- If the nitration process stops due to other problems, such as failure in the cooling brine pump or else a stop in the sodium hydroxide pump that maintains pH in the nitration process, and, at that point, pump P-02, which feeds mixed acid to tank TK 04 is working, does not stop when reaching the high level, as it does when there are no unexpected stops in the nitration process. In this case, the operator must physically go to the electric room and turn off pump P-02. If pump P-02 is not manually turned off, then the mixed acid would overflow through the tank TK 04.

- The mixed acid that overflows from TK 04 falls into a gutter and then into a pipe that transports it to the industrial wastewater tank.

Timeline of the Events

On Tuesday, October 4 at 6:00 am, the Nitroglycerin Nitrator operators of shift A began their production work normally.

At 11:19 am, the outside operator was at the Polyol house when he heard the Nitrator's alarm. He immediately went to check why the Nitrator had stopped and alarmed. Then, he went to the control room to let the indoor operator know that there was no brine. On his way, he passed through the industrial wastewater tank area, without noticing the gas emanation.

At 11:20 am, the indoor operator called the powerhouse to inform and inquire about the reason for the brine pump's stoppage. The powerhouse operator told him that he was going to check on site and call him back. Once he checked, he returned the call and confirmed that the brine pump had, in effect, stopped.

In the control room, the indoor operator informed him that the brine pump had stopped, which caused the nitration process to stop automatically.

At 11:24 am, the indoor operator called the General Supervisor who did not answer the call and therefore the call was handed to the Shift Supervisor, who was informed of the nitration process stoppage.

At 11:25 am, the outside operator called the Shift Supervisor to let him know about the nitration process stoppage.

Figure 2. Emanation of Nitrous gases in the Separator

At that time, the nitroglycerin nitrator indoor operator sees on the computer screen that the signal of the level sensor was 100%, so he went to the electric room to stop pump P-02. It was then that the indoor operator realized that nitrous gases were being generated in the industrial wastewater tank. Therefore, he quickly went to stop the pump and, together with the outside operator, began to add water to the tank in order to control the gas emanation.

At 11:31 am, the HSEC Chief received a phone call from the Shift Supervisor about the presence of gases in the Nitrator sector, so he immediately went to the sector, where he could see that the emanation was being controlled by the operators and the General Supervisor. He confirmed that the wind was directing and dissipating the gases quickly towards a sector where there were no workers.

At 11:33 am, the HSEC Chief warned the HSEC Supervisor, who was in touch with Central Control Room, to not give the emergency alarm that activates the siren, because the event was already under control.

Findings

1. A failure occurred in the logic control sequence of the pump that feeds mixed acid into tank TK 04 when the nitration process stopped while acid was being fed into said tank.

2. There is no emergency stop button in the control room of the pump that feeds tank TK 04.

3. Low water flow in the nitrator of nitroglycerin, without a flood system for the industrial wastewater tank.

4. The Operator did not act in a timely manner to stop the feed pump from the electric room.

5. No action was taken on this irregularity by reviewing the unit's operation control loops.

6. When the process goes from automatic to manual, some links stop working.

7. The stop controls for the pump are located approximately 100 meters away from the control room.

8. The separator is currently flooded with a 1" hose, which is used in case of a decomposition of acid.

9. There is no document with the logic diagram of the unit.

10. The way to perform this task was known among more experienced operators. It was not formalized or described in the work procedure.

11. There was no record of previous occurrences; therefore, there had been no need to flood the industrial wastewater tank.

12. The Operators knew that they had to manually stop the feed pump of tank TK 04 from the electric room if the nitration process happened to stop unexpectedly.

13. Two workers from the quality department saw the emanation of nitrous gases that was occurring in the nitroglycerin nitrator when they were heading to their offices, after finishing a quality control at the Starret house (see figure Nº 2). They decided to stay in the sector, since the wind was carrying the nitrous gases in a different direction from where they were. Notwithstanding the above, a co-worker called them on the phone because all the quality area staff were evacuating their offices and going to the meeting points/security zone (EPP). Therefore, in order to get to that security zone, they had to pass through the gases, although these had already dissipated.

Corrective Actions

Findings	Corrective Actions
• There is no stop interlocking for the pump that feeds mixed acid to tank TK 04 when, for some reason, the nitration process stops.	• Modify the security interlocking logic.
• In the Control Room, there are no push buttons or a stop software system for pumps 1 and 2 that feed tank TK 04.	• Carry out a project to install a pump stop push button in the control room.
• **Protection and Containment**: There is no flooding, cooling or abatement of gas system for the industrial wastewater tank.	• Carry out a project to install a flood system in the industrial wastewater tank.
• The Operator did not take timely actions to stop the feed pump from the Electric Room.	• Incorporate alarms in the level transmitter and level indicators (limit switches).
• **Design:** When the Programmable Logic Controller (PLC) system was implemented, the different operation scenarios and, in this case, the load of tank TK 04 were not foreseen.	• Create a logical diagram for emergency stop.
• **Procedure:** Tasks that are not documented are performed and the information is transmitted verbally.	• Review the IPER –Hazards Identification and Risk Assessment and Control- to ensure that all tasks are included in said analysis and Procedure. • Re-Train Operators and generate records of the training.
• **Risk Management:** There is no analysis of the different emergency scenarios that allow applying preventive actions.	• Perform a Hazop/What If analysis to detect risk operational situations not contemplated.
• The correct assignment of operations is not ensured.	• Prepare instructions about the current way of operating, in the meantime, while a logical definitive solution is established.
• **Emergency Control:** SIA –Superintendence of Applied Research- and Quality staff received the order from their superiors to go to the Emergency Meeting Point –PEE.	• Re-educate the staff about the Emergency Plan and their corresponding responsibilities.

Conclusion

1. Changes made in the unit were not documented, nor the information was conveyed and therefore such changes were not recorded as ‘manage of change’.

2. Failure to manage of change led to lack of revision or updates in the corresponding emergency plans in case of nitrous gas emanation.

Acknowledgement

We would like to particularly thank people who work in production in the Acid & Nitrate Department and people from HSEC Department from Río Loa Plant for their valuable contribution in carrying out an ICAM which finally allowed us visualize this important failure in our processes.

Appendix

Aerial view of the Nitroglycerine Nitrator Unit