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Safety Violation: Ammonium nitrate explosion in Toulouse –France

Abstract:

Friday September 21, 2001, 10:15 am, a big explosion was heard by the inhabitants of Toulouse, France's fourth biggest city. The accident occurred in a warehouse where more than 340 tons of granular ammonium nitrate were stored. The manufacturer, France's largest fertilizer company, AZF (Azote Fertilisants) is owned by TotalFinaElf, the world's fourth biggest oil company. The warehouse was situated 5km from the center of Toulouse.

Lack of control in a chemical plant can lead to a tragedy with striking human, economic, political and ecologic consequences. The tremendous preventable explosion in Toulouse shows the importance of control skills for chemical engineers and the need for conscientiously-followed regulations through every production step.

Introduction:

Before the catastrophe on September 21, 2001, the AZF site produced 1150 tons of ammonia fertilizers per day, mainly Ammonium Nitrate (AN = NH_4NO_3).
AN is produced in industry, with low manufacturing cost, using anhydrous ammonia gas and concentrated nitric acid in a highly exothermic reaction:
$HNO_3(aq) + NH_3(g) \rightarrow NH_4NO_3(aq)$
AN is a white powder at room temperature. It is mainly used:

- in agriculture as a high-nitrogen fertilizer because plants require nitrogen to make proteins
- as an oxidizing agent in explosives, specifically in improvised explosive devices (bombs fabricated by incorporating lethal and incendiary chemicals used in unconventional warfare) : At high temperatures, explosive properties of AN become apparent, for example nitrous oxide is an oxidizer made by heating AN. This latter is used for nitrous oxide based explosives.

The AZF Toulouse site was classified as a high-risk plant by the state of France. The impact of the blast was huge: 31 people were killed, 2442 injured, losses in hundreds of millions dollars, telephone lines were immediately affected up to 100 km from the site, homes and schools were damaged… Discussions continue to this day concerning damages to the economy and environment.

Causes of the explosion:

The cause of the accident was intensively investigated for years. Several hypotheses were circulated: an electromagnetic phenomenon (such as electric discharges in AN mounds or electromagnetic pulses applied for military purposes in Toulouse where e-bombs were tested), other neighboring chemical works, a meteorite, a seism, terrorism act… but the most confirmed hypothesis concerns a

human error in warehouse 221 of the chemical plant. It appears that someone added 500 kg of sodium dichloroisocyanurate ($C_3N_3O_3ClNa$, known as DCCNa) where AN was stored. DCCNa was produced in the south of the AZF site. It is used for eliminating bacteria in swimming pools. It can react with AN to yield a liquid NCl_3.

DCCNa + AN → NCl_3

At 20°C, **NCl_3** is an oily yellow liquid, insoluble in water with a boiling point of 71°C. It decomposes spontaneously and exothermically(heat released = 55 kcal.mol^{-1}) leading to a violent explosion.

This combination of chemicals (DCCNa and AN) constitutes a detonating mixture in the presence of humidity. The explosion occurred because the humidity control of this storage unit failed. Heat flux calorimetry is used to measure the thermal decomposition of AN. By addition of DCCNa, the decomposition temperature of AN decreases since this chlorine derivative catalyzes the decomposition of AN; the rate of decomposition is enhanced by impurities such as chloride salts. Even low concentrations of impurities produce a significant decrease (about 100 °C) in the initial decomposition temperature of AN.

Thus impure, the AN was more subject to explosion and the reaction yielded trichloronitrogen gas. The warehouse contained more than the 500 tons of AN allowed in October 2000. Regulations were not properly controlled on the site.

Improper storage of DCCNa occurred 15 minutes before the explosion; if control of the system had been in place, there would have been enough time for a transducer to detect the error and to get the state variable (temperature or humidity) back to the set point. Under normal storage conditions, ammonium nitrate is inert and does not comprise risks. Only an increase in temperature (between 160 °C and 200 °C) can cause an explosion. Thus controlling temperature was necessary. Further, in the case of an irreversible error, an alarm system could have warned the laborers to evacuate the affected area. Human lives and much damage could have been avoided.

A complete chemical process safety analysis consists of three steps: danger identification, risk analysis and establishment of risk-reducing measures. Thus, building a run-away scenario is required. If we lose temperature or humidity control, the reaction rate will increase and cause the activation of secondary reactions accompanied with a rise in pressure. The maximum temperature achieved by the reaction mixture as well as the time available before a possible thermal explosion are extremely important parameters for the risk assessment of the reaction.

Consequences of the explosion:

This tragedy had serious consequences in several areas: human, economic, ecologic, political.

Human consequences include 30 deaths, at least 10 000 injured and a variety of illnesses, including depression, stress, insomnia, deafness, trauma and coronary thrombosis. Students were affected by school closure. Many people had to relocate…

Economic consequences were tremendous, damages to buildings and infrastructure amounting to several hundred million dollars. A large number of homes, facilities, schools and enterprises were ruined, many state-owned facilities had to be rebuilt (le Petit Palais des Sports, the theater Bikini, the National school of chemical engineers for higher education…). Delocalization of some of the industries around in order to decongest the area from the high concentration of industries and prevent further risks, subcontractors affected by AZF plant's closure, and the loss of 1000 jobs in the industrial zone of Toulouse are to be subsidized by public authorities and the damaged manufacturer.

As for the ecology, the blast created a 50-meter-diameter crater more than 10meters deep. Experts compared the explosion to an earthquake measuring 3.4 on the Richter scale. .. The red cloud seen near the factory right after the blast was tested but the results showed no danger of poisoning and the alert was lifted so that local people were allowed to leave their homes. Depollution of the site was undertaken by Total to eliminate thousands of tons of residue of ammonium nitrates and other substances kept in the installation. Also, to further their efforts toward a clean environment, Total Energie created a Solar Panel Production Plant in the area providing a source of renewable energy. The facility has a capacity of 5MW, sufficient to equip 2500 European households. Total also created a European Safety Institute in cooperation with Toulouse University.

A large legal case was initiated, influenced by politics:

About 9 people were arrested at first for lack of observation of rules but finally, only Serge Biechlin the director of the manufacture was detained and the Grande Paroisse Corporation (AZF owner) was convicted for involuntary homicide as the investigation in charge of the case confirmed the thesis of a chemical accident, ruling out other hypothetical causes for the explosion. Many questions were raised by the court: What made the ammonium nitrate oxidizer become explosive? Was it the presence of contaminants like chlorides or metals such as chromium, copper, cobalt or nickel which enhanced the propagation of the explosion? Was it due to the electromagnetic effect of the e-bomb (experiments in wireless transmission of energy with microwave beams), a new bomb tested secretly in Toulouse by the French army? A seism that might have occurred simultaneously?

The high concentration of chemical units in the Toulouse urban zone was criticized. In July 2006, another hypothesis was proposed: the neighboring SNPE manufacturing UDMH (asymmetric dimethyl hydrazine) whose fumes, in the presence of air, cause an explosion. These fumes carry an ammonia smell. That site was closed for maintenance on the explosion day where a large quantity of UDMH was stored. That UDMH would have spread to warehouse 221 and reacted with the nitrates to form an explosive: BLU-73 normally used in anti-bunker bombs. This could have aggravated the explosion. At this time, in late 2001, there was tension between the US and France who used to sell weapons to Saddam Hussein .SNPE was manufacturing the deadly gas in these weapons. The unsafe manufacturing process in that area was probably masked by state strategic secret operations. Moreover, the AZF accident occurred only 10 days after September 11, when the Twin Towers were destroyed in New York.

To file pertinent lawsuits, chemical engineers are called upon to select and confirm the most likely hypothesis, classify the conditions for the occurrence of each one and obtain the necessary scientific proof. In this process, they interact with experts in different domains such as law, politics, ecology…

Qualified engineers were present at the time when DCCNa was stored. However, they neglected control of the humidity level and responsible management of the dumping of potentially dangerous chemicals.

The inquiry commission denounced unsafe storage and errors in handling, as well as underestimation of the potential risks for an AN storage unit: the 221 unit was old and rusty with a thick ammonium crust on the ground. It was especially humid and dark, with no fire alarm system. Conditions were worse during the winter. Financial reasons were responsible for not taking appropriate measures and cleaning the storage unit.

Steps toward prevention of future explosion:

According to the European Union regulations for the AN processing (concerning the pH, the presence of heavy metals, the size of granules…) and the chemical industry in general, the manufacturer must ensure that specifications and requirements are met (safe processes, control of raw materials, storage conditions, transportation..). Unfortunately, this accident is not unique. Frequently, small explosions initiated with a small amount of AN in a confined space (like a blocked pipe) provoke explosion of a larger quantity of chemicals present on the site. AN with more than 0.2 % combustible substances is classified as explosive.

As a result of such accidents (mainly the Seveso[1] accident) and of subsequent studies of the properties of AN, legislation was adopted in Europe, the so-called Seveso Directive. This directive, followed by the Seveso II directive, was reviewed many times. The Directive aims first, to prevent major accident hazards involving dangerous substances and second, to limit the consequences of such accidents not only for humans (safety and health) but also for the environment. Companies holding quantities of dangerous substances, as well as the member countries, have obligations stated by Seveso II and should establish periodic Safety reports, Safety management system and an Emergency plan..
The land-use planning provision of Seveso II is one of the Directive's most challenging requirements to control major accident hazards.

[1] Bursting of a rupture disc on a chemical reactor of the Icmesa chemical company in Seveso, Italy on July 9th 1976 which resulted in hazardous releases.

Conclusion:

Appropriate controls as well as the existing tools for Emergency Responses to chemical emergencies, show great disparities between countries; if regulations become too strict, some manufacturers will be tempted to move to less developed countries… Jobs created by the chemical industry as well as taxes paid by these companies to local collectivities are vital for the economy but, in principle, public authorities cannot prefer higher revenues to public safety.
Chemical engineers and other experts work for enforcement of prevention policies to maintain safety in manufacturing processes, storage and transportation of dangerous substances … Following 2001, the French's slogan during protests was "Never Again". However, the emergency funds paid to the victims by the state will not erase the human trauma and stress due to the AZF accident.

Five years after the AZF-Toulouse accident and the depollution phase, a research center for cancer has been created on the site. The health complex comprises a hospital, laboratories of worldwide pharmaceutical companies such as Pierre Fabre and Sanofi Aventis, as well as public and private research facilities with over 2400 researchers. This complex is estimated at 1 billion euros and should cover 2.2 km^2.

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