

## Learning lessons from eight gas explosions

EGAN Simon Mark, Corporate Process Safety Expert, Solvay, 85 avenue des Frères Perret, BP 62 – 69192 Saint-Fons Cedex, France

Eight cases of gas phase explosion in industrial facilities are presented, together with root causes and learning lessons for each one of them. The examples are drawn from the author's professional experience with Rhône-Poulenc (1975-2000), Rhodia (2001-2010) and Solvay (2011 onwards). Following the examples, the issue of flame blow-back in vent lines and inerting of process vessels are discussed. It is shown that avoiding injuries and fatalities caused by gas phase explosions in process units requires:

- Risk analysis,
- Feedback from past accidents and incidents,
- Accurate data on materials used and made,
- Thorough understanding of technical issues concerning explosions.

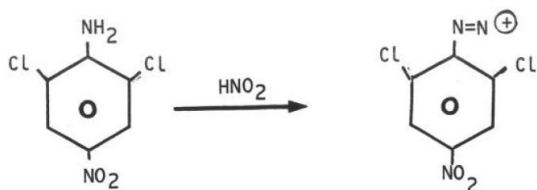
### 1984: gas phase explosion in a chemical reactor

#### Description

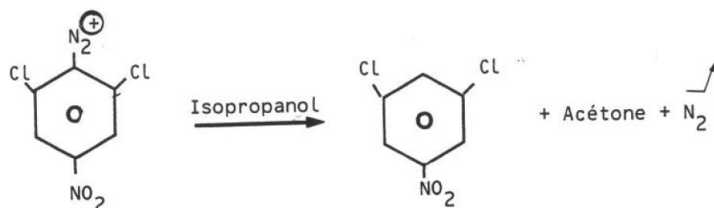
In 1984 a gas phase explosion occurred inside a 16 m<sup>3</sup> Glass Lined Mild Steel reactor. One person was injured as a result although there was no environmental impact and material damage was limited.

#### The facts

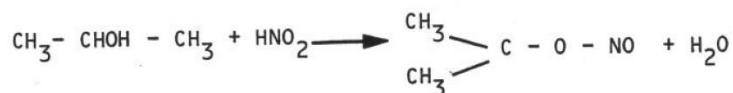
The reactor was used to carry reactions of diazotisation and reduction of 2,6-dichloro-4-nitroaniline (DCNA). The diazotisation reaction carried out may be written as follows:



The reduction reaction may be written as follows. It led to formation of 3,5-dichloronitrobenzene, which was the wanted product as well as nitrogen off-gas. The reducing agent was isopropanol and this was oxidised to acetone as shown below.



A known side reaction led to the formation of isopropyl nitrite, which is volatile (atmospheric boiling point 40 °C).



On the day of the incident, the normal procedure had been followed. The reactor had been charged with the following (the figures in brackets indicate molar ratio):

- recycled isopropanol/acetone mixture (3.933/0.464),
- 2,6-dichloro-4-nitroaniline (1.000),
- copper sulphate (0.004),
- sulphuric acid (1.863),
- water (23).

The mixture was stirred and the temperature adjusted to 42 °C under atmospheric pressure. The addition of an aqueous solution of sodium nitrite (1.980) over an eight hour period at 40-45 °C was started. Six and a quarter hours into the addition there was a shift change, during which the addition was stopped for thirty minutes, following the Standard Operating Procedure. The addition was restarted at a slightly lower temperature of 41 °C and an explosion occurred. A reinforced glass tube on the top of the reactor shattered, slightly injuring one person. The bottom run-off valve of the reactor blew off: the reactor contents flowed out and caught fire. The fire was extinguished rapidly and the liquid was collected in a containment pit. The reactor itself did not rupture but suffered a vertical crack in its glass lining. From the damage to the vessel, the maximum pressure reached during the incident was estimated to have been between 10 and 40 bar gauge. After the incident the inside of the bottom section of the condenser was found to be coated with soot.

### The explanation

Prior to the accident it had been thought that there was no hazard of a gas phase explosion because the reduction reaction gave off nitrogen such that the headspace of the reactor contained an inert mixture of nitrogen with vapours of isopropyl nitrite, acetone and isopropanol. Extensive laboratory work was carried out on the reaction after the incident. It showed that both nitric oxide (NO) and nitrous oxide (N<sub>2</sub>O) form during the reaction, especially towards the end of the addition and are present in the headspace. It was estimated that towards the end of the sodium nitrite addition period the off-gas from the reaction contained about 60% v/v N<sub>2</sub>O, 39% v/v NO and 1% v/v NO<sub>2</sub>.

The headspace of the reactor would have contained vapours of isopropyl nitrite, acetone and isopropanol. The explosivity characteristics of acetone were determined in NO and N<sub>2</sub>O. A mixture of isopropyl nitrite (20% w/w), acetone (30% w/w), isopropanol (30% w/w), water (6% w/w) and various low boiling impurities (4% w/w) was also tested in both N<sub>2</sub>O and a gas mixture intended to represent the reaction off-gas (60% v/v N<sub>2</sub>O, 39% v/v NO and 1% v/v NO<sub>2</sub>). The explosivity characteristics were determined in a 4.6 litre steel cylinder. All the tests were carried out at atmospheric pressure and 60 °C. The ignition source was a hot wire or an electrostatic discharge.

Table 1 Explosivity characteristics of acetone in air, NO, N<sub>2</sub>O and reaction off-gas mixture determined in 4.6 litre cylinder

Fuel gas	Acetone		Isopropyl nitrite (20% w/w) Acetone (30% w/w) Isopropanol (30% w/w) Water (6% w/w) Various lights (4% w/w)		Units
	NO	N <sub>2</sub> O	N <sub>2</sub> O	60% N <sub>2</sub> O 39% NO 1% NO <sub>2</sub>	
Oxidant gas	NO	N <sub>2</sub> O	N <sub>2</sub> O	60% N <sub>2</sub> O 39% NO 1% NO <sub>2</sub>	
Upper explosive limit	22	35	38	33	% v/v
Lower explosive limit	4	1	1	1	% v/v
Maximum explosion pressure	14.8	22.5	19.3	17.1	bar
Maximum rate of pressure rise	450	17000	12000	3000	bar s <sup>-1</sup>

A series of twenty-five experiments was then carried out in a 2 litre stirred pressure vessel designed to reproduce the conditions of the reactor involved in the incident. One experiment followed the standard procedure exactly and the others had slight variations in procedure and quantities used. During each experiment sparks were generated at fifteen minute intervals in the headspace to see whether the gas mixture was explosive or not. One of the twenty-five experiments, where the sodium nitrite addition had been interrupted and the temperature slightly reduced, gave such an explosion and was reproducible. None of the other experiments gave an explosion.

The conclusions drawn from this work were as follows:

1. Explosions of acetone or an artificial fuel mixture in NO, N<sub>2</sub>O or a mixture of those gases gave pressures rising from atmospheric to between 10 and 25 bar gauge, which corresponded to the damage to the reactor (an explosion in air would only have given between 8 and 10 bar gauge).
2. The upper explosive limit for acetone in the off-gas mixture is 33% v/v. Now the temperature in the reactor was 41 °C when the explosion occurred. The vapour pressure of pure acetone at 41 °C is 0.587 bar absolute. The vapour pressure of acetone above the mixture actually present in the reactor would be less than this because water was present. Normally the gas mixture was too rich to give an explosion, but a variation in conditions (lower temperature, more sodium nitrite etc.) would have given a mixture just inside explosive limits.

The ignition source could not be identified.

## Learning lesson

An unsafe process may operate for many years with no apparent problem. It can be very difficult to identify gas phase explosion hazards in cases like this. Detailed knowledge of the main reactions, side reactions and especially gaseous by-products is required. An obvious difficulty is that not everyone is at ease with chemistry. However there are two tell-tale signs of trouble in any organic chemical reaction. One is the presence of an oxidising agent, such as sodium nitrite, somewhere in the process and ready to generate an oxidant gas such as NO or N<sub>2</sub>O under certain conditions. Another is when the molar ratios used in a process are far removed from the official stoichiometry. This process used a 100 % excess of sodium nitrite. Always ask why the excess is necessary. If the chemists reply “you have to use a large excess to get the reaction to go to completion” that means there are side reactions going on and you need to know what they are.

### 1988: gas phase explosion in a centrifuge

#### Description

In 1988 a gas phase explosion occurred inside a centrifuge and led to a generalised fire in the plant building. There were no significant injuries or damage to the environment although the building was extensively damaged.

#### The facts

A suspension of a solid (which was the wanted product) in methanol, was fed to a centrifuge to separate it from the liquid phase (or “mother liquors”). The methanol was fed to another part of the plant so that the solvent could be recovered. The methanol-damp solid was transferred via a screw feed system to a pneumatic drier, where it met a stream of warm air which transported it to a hopper and dried it at the same time. The entire process operated under air. The incident occurred when a bolt fell into the centrifuge, leading to ignition. The explosion and fire spread via the screw feed to the pneumatic drier. The centrifuge and the drier had explosion vents which discharged flames inside the building, leading to a generalised fire.

#### The explanation

Methanol is a flammable solvent whose flash point is 11 °C and the process was operating above this temperature with no inerting. It only required an ignition source to cause the explosions and fire.

#### Learning lesson

As in the previous example, an unsafe process may operate for many years with no apparent problem. But this time the problem should have been relatively obvious. Today nobody would operate a centrifuge with a flammable solvent without first installing a rigorous inerting system using a continuous purge of nitrogen or other inert gas and interlocks on loss of nitrogen flow to shut down the centrifuge in case of low flow.

### 1989 gas phase explosion in a sulphuric acid tank

#### Description

In 1989 a gas phase explosion occurred inside a sulphuric acid tank, leading to the death of one person and serious injuries to two others.

#### The facts

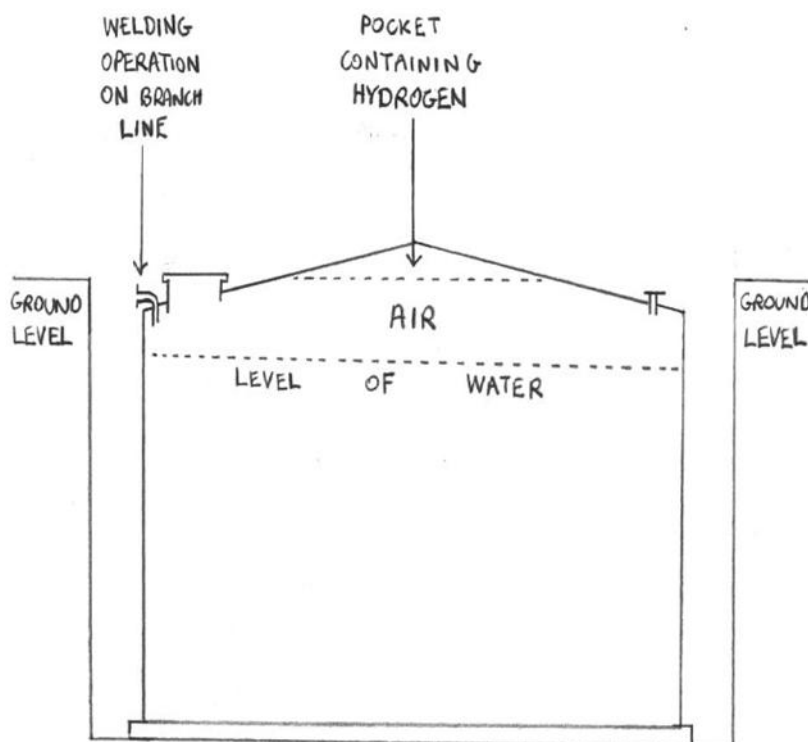
The 50 m<sup>3</sup> tank was made of mild steel and situated in a pit below ground level (see Figure 1). It was used to store 96 % sulphuric acid. It became necessary to repair a line connected to the top of the vessel. The sulphuric acid was pumped out of the tank to another vessel. At this point, the tank was observed to contain a layer of sediment. Eight bags of sodium carbonate powder were added via the manhole. The tank was then filled with water to within 15 cm of the top. For various reasons the repair work was carried out six days after the addition of sodium carbonate and water to the tank. During this period and immediately before starting the repair work, checks for hydrogen were carried out inside the pit, at ground level and inside the tank. All the tests proved negative. Grinding work duly started on the line to be repaired. There was an explosion inside the tank. The tank did not rupture but it must have shaken violently because its ground fixation points gave way and the three people on the roof of the tank were thrown into the air. One of those persons was killed and the other two were seriously injured.

#### The explanation

Clearly, the sulphuric acid was not neutralised. No attempt had been made to stir the contents of the tank in any way. No pH check was carried out on the mixture. Hydrogen forms when aqueous sulphuric acid is in contact with mild steel. This reaction may be written as follows:  $\text{Fe (s)} + \text{H}_2\text{SO}_4 \text{ (aq.)} \rightarrow \text{FeSO}_4 \text{ (aq.)} + \text{H}_2 \text{ (g)}$ . For 92-98 % sulphuric acid, which is the normal range for storage in mild steel, the corrosion rate is reduced by the formation of a protective layer of solid ferrous sulphate (FeSO<sub>4</sub>) which does not dissolve. But when water is added, forming more dilute acid, the ferrous sulphate dissolves and the protective layer is lost. Corrosion and the formation of hydrogen are then more rapid. It was calculated that the corrosion rate would have been about 10 mm per year, leading to the formation of 50 g (0.6 m<sup>3</sup>) of hydrogen over a six day period. Given that the Lower Explosive Limit of hydrogen is only 4 % v/v, this would be enough to make 15 m<sup>3</sup> of an explosive hydrogen-air mixture.

As hydrogen is much lighter than air it collected inside the conical top section of the tank, which was not vented. After the accident, tests showed that hydrogen was indeed present inside the conical top section. Hydrogen has a very low Minimum Ignition Energy (0.017 mJ) so it is not surprising that it was ignited.

Figure 1 Sulphuric acid tank



### Learning lessons

Concentrated sulphuric acid can be safely stored in mild steel vessels but:

1. There should always be a vent at the highest point of the vessel.
2. Great care is needed when doing maintenance work. The tank must be emptied. The remaining sulphuric acid must be immediately neutralised with an excess of sodium carbonate or other suitable alkali. The mixture formed must have a pH over 7. The tank must then be thoroughly vented to remove all traces of hydrogen.

### 2001 Gas phase explosion in a catalyst washing vessel

#### Description

In order to carry out maintenance work, a catalyst washing vessel was drained then opened. An explosion occurred, causing injuries to three people. There was no impact on the environment and no damage to equipment.

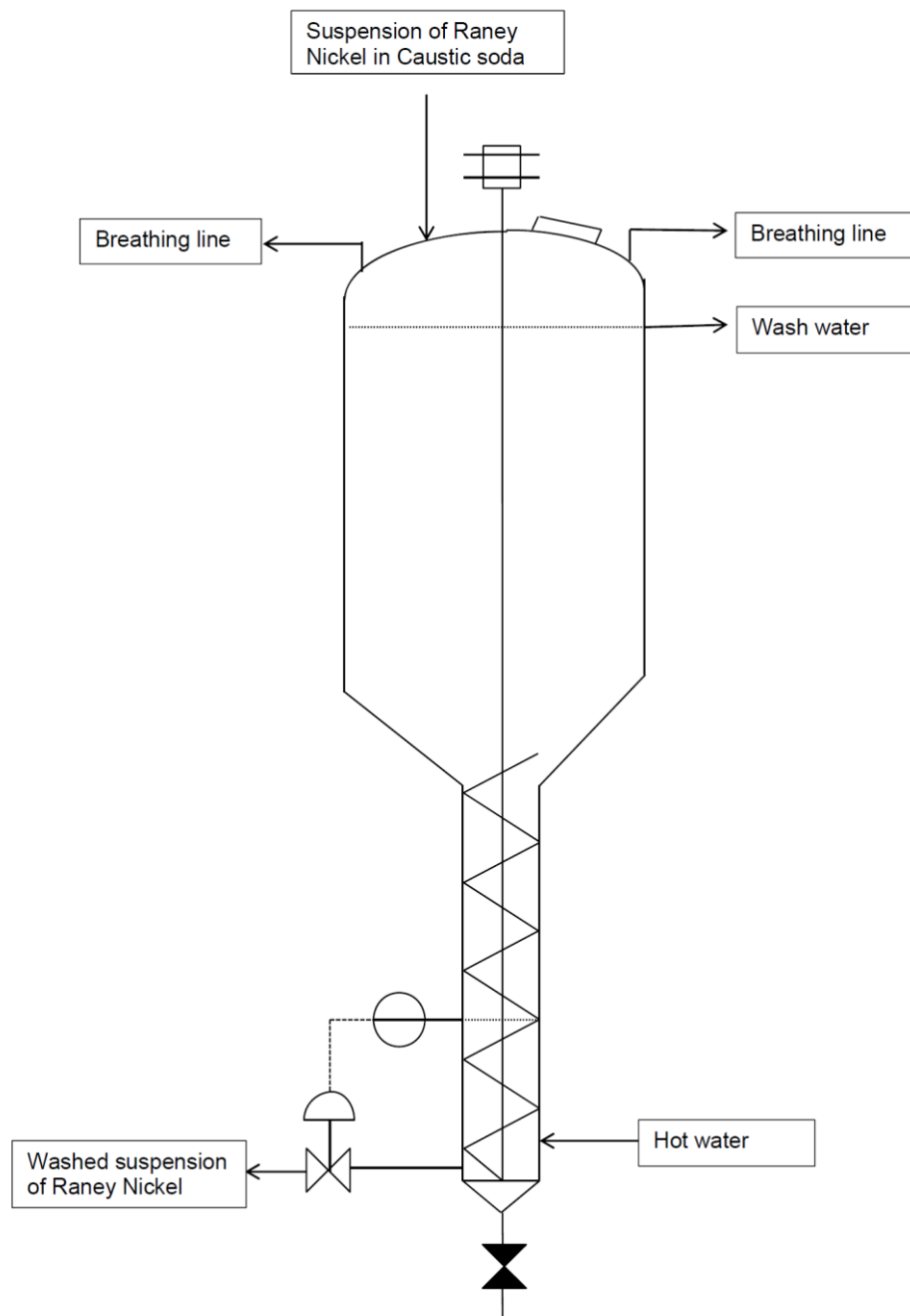
#### The facts

The vessel was used to wash activated Raney Nickel catalyst, used elsewhere in the plant in a hydrogenation process. Raney Nickel is an alloy of nickel and aluminium, bought in the form of granules. It is activated by treatment with caustic soda, which dissolves the aluminium and generates hydrogen:  $\text{Al (s)} + \text{NaOH (aq.)} + \text{H}_2\text{O} \rightarrow \text{NaAlO}_2 \text{ (aq.)} + 1.5 \text{ H}_2 \text{ (g)}$ . It leaves granules of nickel in a very finely divided form that is able to catalyse hydrogenation reactions. The vessel involved in the accident was used to carry out continuous counter current washing of a suspension of activated catalyst with hot water (see Figure 2). During the normal process, the suspension of Raney Nickel in caustic soda was fed in at top of the vessel at a constant rate. Hot water was fed in at bottom at a constant rate. A suspension of washed Raney Nickel catalyst was run off at the bottom to a mixing vessel, whilst the wash water ran off at the top. The incident started with a blockage in the washed catalyst run-off line. The vessel was emptied and rinsed through with water. The manhole was opened on top of vessel and an explosion occurred in or near the vessel. Three workers were standing on a platform next to the manhole. They fell to the ground: one of them was seriously injured.

### The explanation

The reaction of the aluminium in Raney Nickel with alkali generated hydrogen. This reaction was still going on the catalyst washing vessel because the pH was alkaline and traces of aluminium were left in the granules. Also common breathing lines with other vessels had not been blanked off, so a mixture of hydrogen and air was present in the headspace of the vessel. As discussed in the previous incident, hydrogen is very easy to ignite. Slight friction between metal parts when opening the manhole would have been enough to ignite the gas mixture inside the vessel.

Figure 2 Continuous counter-current catalyst washing vessel



### Learning lesson

All process vessels contain flammable gas or vapour until proven otherwise. Lines to other vessels should have been blanked off by placing metal discs (or "spades") into flanges. The vessel should have been completely filled with water or else thoroughly ventilated before opening it.

## 2005 Gas phase explosion in a chlorine pipeline

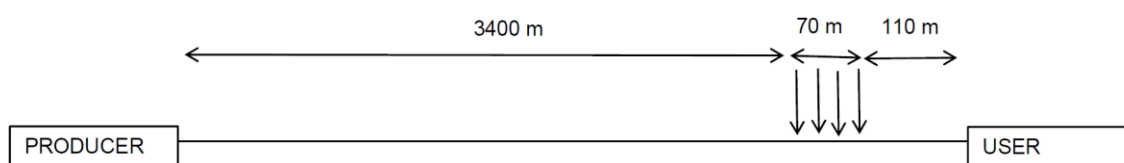
### Description

A pipeline used to supply chlorine gas exploded. There was no significant leak of chlorine as the incident occurred during a shutdown. Nobody was injured and there was no environmental impact although the pipeline was damaged.

### The facts

The pipeline was 3.6 km long, 200 mm in diameter and made from carbon steel. It was first used to supply recovered hydrogen chloride to a client company from 1961 to 1975. It was out of service for the next six years. In 1981 it was recommissioned for the supply of chlorine gas at 5.3 bar gauge. The pipeline was heated electrically to avoid condensation of liquid chlorine inside the pipe. The heating was regulated to maintain the skin temperature at 25-30 °C. In 2001 some maintenance was carried out at the client's end of the line. It is known that about 240 kg water got into the line at this time. The pipeline was operated normally from 2001 onwards and was again shut down for maintenance in 2005. The chlorine pressure was reduced to 0.25 bar gauge. The cable of one of the temperature transmitters was accidentally cut. Three days later the pipeline exploded in four places near to the user's end (see Figure 3). Fragments of several kg were projected up to 150 m. After the accident 2500 to 3000 kg of a solid deposit was found inside the pipeline. The solid deposit was found to be thermally unstable: differential scanning calorimetry showed an exotherm of 300 J/g.

Figure 3 Chlorine pipeline with arrows to show where the ruptures occurred (not to scale)



### The explanation

The pipe was never cleaned between its construction in 1961 and the incident of 2005. The solid deposits are supposed to have originated from the use of the pipeline to supply recovered hydrogen chloride. This would have contained impurities which condensed in the pipe and it is thought that the deposit of solid built up over a period of years. The entry of water during maintenance in 2001 led to the formation of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  which is solid at 25-30 °C. The broken cable to temperature probe led to false low temperature readings, so the pipeline heating came full on and it is estimated that the skin temperature would have reached 90 °C. At 90 °C,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  melted to give an acidic solution of  $\text{FeCl}_3$  in water. This solution corroded the steel, generating hydrogen and forming an explosive mixture of hydrogen and chlorine. Such mixtures are very easy to ignite: even ultraviolet light is enough. In this case the ignition source may have been the solid deposit. This was thermally unstable and the heating of the pipeline to 90 °C may have caused its decomposition, forming a localised hotspot at about 200 °C. The explosion would have started in deflagration mode. But then the configuration of pipework, which had several bends, would have led to acceleration of the flame approaching a detonation regime, as shown by the rupture of the pipe in several places.

### Learning lessons

1. Explosion of chlorine pipelines due to presence of hydrogen is common. The hydrogen may come from the electrolysis reaction used to synthesise it or, as here, from corrosion of carbon steel piping.
2. We need to analyse the risks during transitory phases just as much as normal running.

## 2008 Gas phase explosion in a treatment system for hydrocarbon off-gases

### Description

In 2008 a gas phase explosion occurred in a treatment system for hydrocarbon off-gases. A fibre reinforced plastic (FRP) seal pot in the vent system ruptured. No one was injured and no significant environmental emissions occurred.

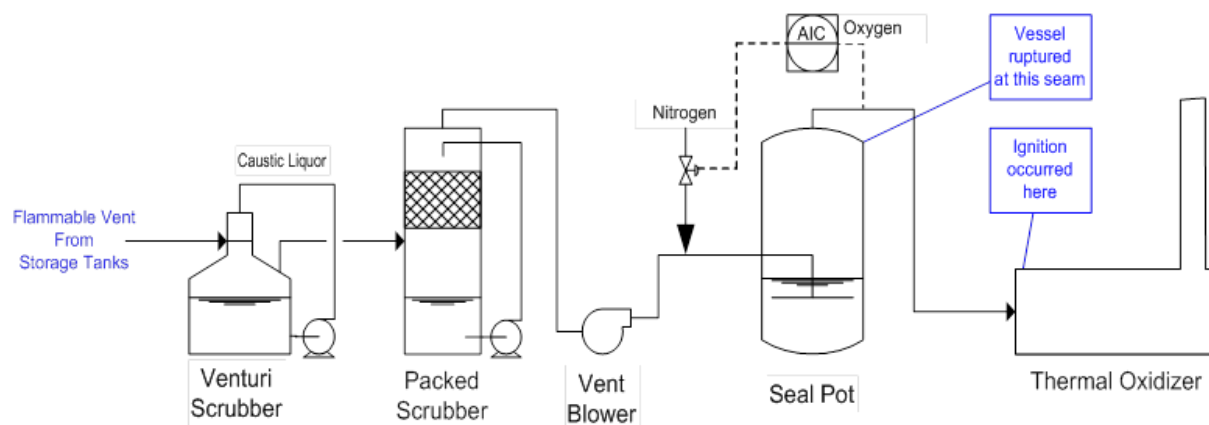
### The facts

The incident occurred in a plant used to treat used sulphuric acid from oil refineries. Sulphuric acid serves as a catalyst in the alkylation reaction which is used to raise the octane rating of light petroleum fractions. In that reaction, butadiene is introduced in the presence of concentrated sulphuric acid and reacts with olefins in the petroleum fraction to give longer chain hydrocarbons, so raising the octane rating. Various impurities build up in the sulphuric acid over a period of time so this has to be purified.

Our plant was built to carry out this purification or treatment process. There were a number of large stock tanks for the acid to be treated. This acid was contaminated with light hydrocarbons and indeed generated hydrocarbons during storage. For this reason, the off-gas from the storage tanks was treated to remove both sulphuric acid and hydrocarbons. The vent system consisted of a venturi caustic scrubber, a caustic column scrubber a vent blower, a seal pot filled with water, and a thermal oxidizer unit (see Figure 4). The storage tanks were maintained at positive pressure using nitrogen. Since air leaks into the vent system could occur, the oxygen concentration was normally maintained below the Limiting Oxygen Concentration (estimated to be 8%) by adding additional nitrogen upstream of the thermal oxidizer.

The explosion occurred without warning. The seal pot ruptured and a flanged, 400 mm diameter metal elbow attached to the top dome of the seal pot came to rest about 15 metres away. Fragments of the seal pot, which was made of Fibre Reinforced Plastic were found up to 50 metres away.

Figure 4 Off-gas treatment system for sulphuric acid tanks



### The explanation

On the day of the explosion, the oxygen analyser was out of service for repairs. It had been taken out of service some weeks previously. This was recognised as a process change. The site Management Of Change (MOC) procedure had been followed, but no measures had been taken to compensate for the absence of the analyser. As a result, no nitrogen was being fed into the off-gas stream. Under these conditions, the level of oxygen would have been close to 21 % v/v. The level of hydrocarbons would have varied, following the level of impurities in the sulphuric acid in the storage tanks. At some point the hydrocarbon concentration in the off-gas exceeded the Lower Explosive Limit and a flammable mixture was fed to the thermal oxidiser, where it ignited. The flame blew back along the vent line and reached the seal pot, which ruptured. The seal pot was intended to prevent such a blow back reaching the scrubber system and the storage tanks. It fulfilled its role, except that it did not resist the explosion pressure.

### Learning lesson

In this case the hazard was recognised during the HAZOP carried out during the design phase. The oxygen analyser and the injection of nitrogen were intended to reduce the risk to an acceptable level. The analyser was put out of service as a result of a breakdown. We should always analyse process changes to see if they introduce an additional hazard or aggravate an existing one or remove a means of prevention, as in this case.

## 2011 Gas phase explosion in a treatment system for exhaust air containing acetone

### Description

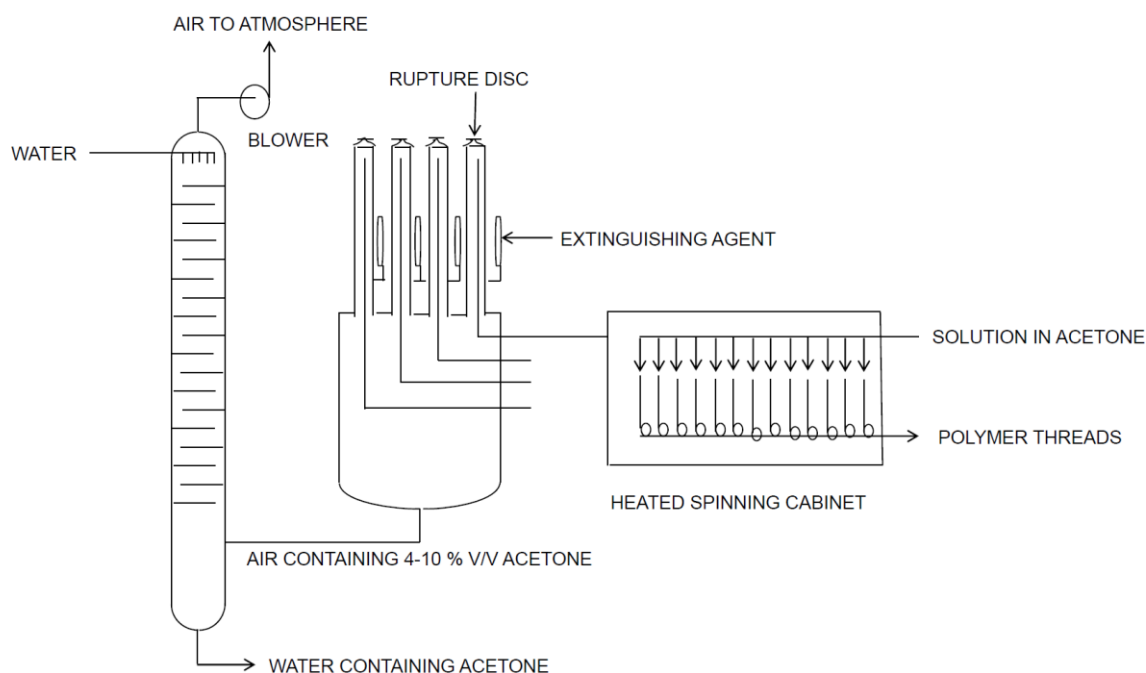
Acetone vapours ignited in a spinning cabinet used to generate fibres of polymer. The flame was transmitted through the ducts of the vacuum suction system. The flame was detected and automatically set off the extinction system, which put out the flames. A rupture disc on a disconnection vessel opened as it should have done. There was no damage to the plant, no impact on the environment and nobody was hurt.

### The facts

A warm solution of polymer in acetone is extruded in spinning cells inside a ventilated cabinet maintained at about 70 °C. As the acetone evaporates threads of solid polymer are formed inside the spinning cells. They pass over a system of pulleys and are gathered together into a yarn. Air is extracted from the spinning cells and the cabinet itself by a vacuum suction system. The air from this and other cabinets, containing acetone vapours permanently within explosive limits, is fed to a water washing column of the acetone recovery unit (see Figure 5).

After the incident the burnt remains of a cloth, containing traces of a flammable solvent, were found in the cabinet. The solvent was identified. It has a Lower Explosion Limit (LEL) of 1.1 % v/v and a flash point of 70 °C.

Figure 5 Spinning cabinet and off-gas treatment system (not to scale)



### The explanation

Normally cleaning of spinning cells is carried out using a cloth impregnated with a mixture of water (96 %) and paraffin oil of high flash point (> 200 °C). But it seems to have become a common practice to use a cloth impregnated with a lubricant containing some solvent of low flash point (70 °C) for cleaning spinning cells. This lubricant is used as a separating fluid on spinnerets.

On this occasion, a cloth impregnated with this lubricant was left in the cabinet for about two days because the cabinet could not be unplugged. The cabinet continued to be heated at 70 °C which corresponds to the flash point of the solvent. Now heating a liquid to its flash point does not cause ignition: it just means that the concentration of vapour in the air in contact with the liquid will reach the Lower Explosive Limit (LEL). Ignition still requires a spark or hot-spot.

But heating a cloth impregnated with such a fluid to 70 °C is a quite different matter. The cloth gives a large surface area for the air to react with the fluid. An exothermic oxidation reaction starts, slowly at first. The cloth retains the heat and its temperature rises until it catches fire. This phenomenon is especially common when heat transfer fluids leak into open cell (e.g. Rockwool) insulation. Fires can develop, even below the flash point of the liquid. For example we found the following values for paraffin oil (Kaydol):

Autoignition point (immediate ignition on a hot surface)	350 °C
Flash point (vapour in contact with the liquid catches fire if ignited)	216 °C
Rockwool insulation soaked with liquid catches fire spontaneously	130 °C

In view of this, it was normal for the cloth impregnated flammable solvent and left in a spinning cell at around 70 °C for two days to catch fire.

### Learning lessons

1. This incident occurred because the official cleaning procedure was deliberately not followed by operating personnel. This was a violation. Procedures are necessary to guarantee safety. They need to be explained and enforced.
2. In all of our plants, we must ensure that the materials used for cleaning are compatible with working conditions and do not pose ignition risks.



## 2012: gas phase explosion in a distillation column

### Description

An explosion occurred in a distillation column. A process operator suffered burns but was treated successfully. There was no environmental impact. Damage to the plant was light.

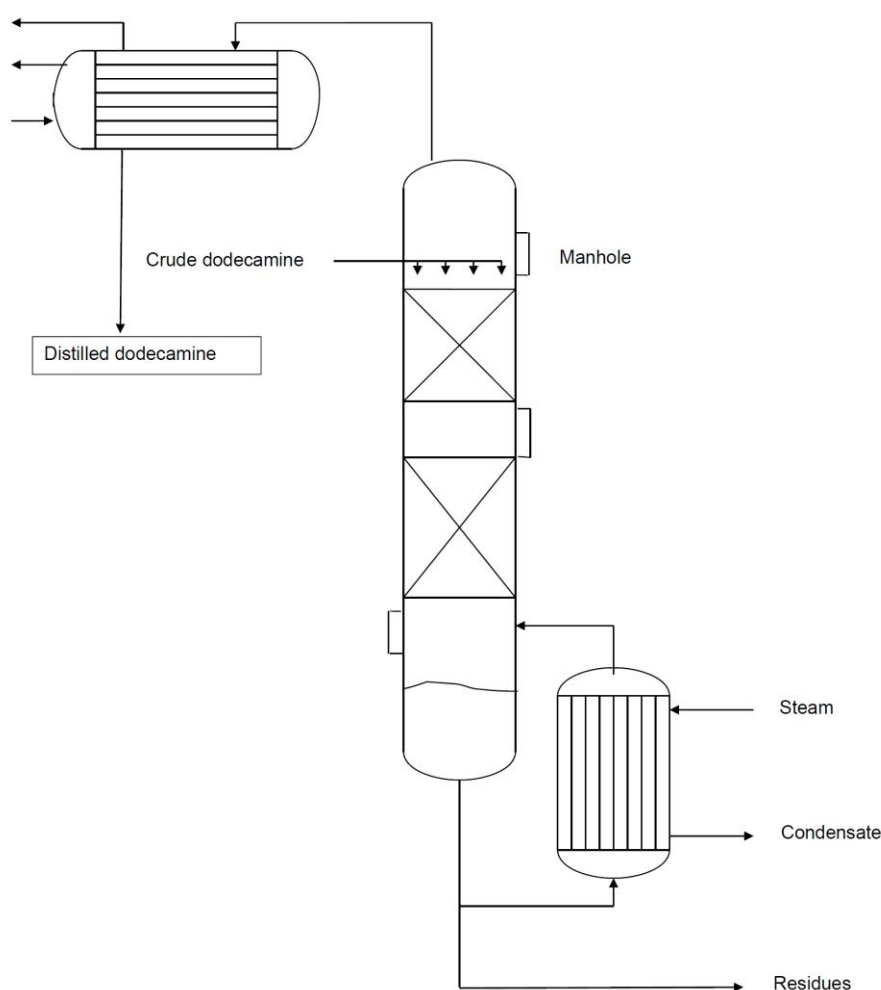
### The facts

The distillation column was part of a plant used to make dodecanamine by hydrogenation of the corresponding nitrile. The reaction can be written as follows:  $C_{11}H_{23}CN(l) + 2 H_2(g) \rightarrow C_{12}H_{25}NH_2(l)$ . Raney nickel was used as the catalyst. The crude product was filtered then purified by fractional distillation (see Figure 6). Two process modifications were introduced:

1. Finer granules of Raney Nickel catalyst were used.
2. The number of filtration stages was reduced from one to two.

Following the modification, the distributor of the distillation column, where crude filtered product was fed in, was found to be blocked up. The column was shut down at 150 °C and the vacuum was released with nitrogen. A manhole cover near the top of the column was removed in order to clean the distributor. A jet of flame burnt one operator.

Figure 6 Dodecanamine distillation column



### The explanation

The finer catalyst was not completely removed during by filtration, especially as this was only one stage. Fine particles of catalyst remained in the crude product and caused blockage of the distributor. The column was at 150 °C when the manhole was opened. Inside was hot nitrogen containing dodecanamine vapours above the Lower Explosive Limit (the flash point of dodecanamine is 127 °C). The density of the gas mixture inside the column would have been about  $0.81 \text{ kg m}^{-3}$ , whereas the density of the air outside the column would have been about  $1.25 \text{ kg m}^{-3}$ . The difference in densities led to rapid mixing, forming a mixture of air, nitrogen and dodecanamine vapours within explosive limits. As air came into the column it came into contact with activated Raney Nickel. Now activated Raney Nickel becomes incandescent on contact with air and we suppose that this was the ignition source.

## Learning lessons

1. Vessels must be decontaminated before they are opened.
2. Differences in gas may lead to mixing, as in this case. In other cases layers of denser gas, containing heavy hydrocarbons, may persist in drains etc.
3. Activated Raney Nickel acts as a potent ignition source in the case of entry of air into equipment.

## Prevention of blow-back in vent lines

### Why worry?

Modern chemical plants are increasingly equipped with equipment designed to purify exhaust air, to avoid damage to the environment by reducing emissions of gases such as sulphur dioxide, nitrogen oxides and of course Volatile Organic Compounds (VOC). A common method of treating off-gas containing VOC's is to use a thermal oxidiser unit, as indeed was used for the off gas from storage tanks for recovered sulphuric acid from one of the incidents described previously. A thermal oxidiser unit typically has a hot ceramic bed where VOC's are oxidised to carbon dioxide, water etc. However it is clear that we must ensure that the gas mixture fed to the oxidiser is outside explosive limits. Two aspects of blow-back merit discussion because they are not always understood:

1. Can a high velocity of off-gas in the vent pipe prevent blow-back?
2. Why are so many protection layers necessary to prevent blow-back?

### Can a high velocity of off-gas in the vent pipe prevent blow-back?

The fundamental burning velocity of most hydrocarbons in air is less than  $1 \text{ m s}^{-1}$ . It might be thought that if the velocity of the off gas is well in excess of the fundamental burning velocity then blow-back cannot occur. Unfortunately it does occur and it is worth explaining why. A system consisting simply of a vent line from a process to a thermal oxidiser system is shown in Figure 7 (before ignition) and Figure 8 (after ignition). In each case the graph shows the pressure profile. The process system is supposed to operate at atmospheric pressure. The off-gas is extracted by a blower situated downstream of the oxidiser. Before ignition the pressure drops slowly along the vent line and the air flows from higher to lower pressure in the direction shown by the arrow. Then ignition of the mixture occurs at the entry to the thermal oxidiser. Even if the gas mixture is close to its explosive limits the pressure generated at the point where ignition occurs will be at least 2 bar gauge. So from the pressure peak at the point of ignition a flame front will spread in both directions. The flame front travelling forwards will be extinguished because the gas in front of it is inside the oxidiser and it not explosive as the hydrocarbons have been depleted on the hot ceramic bed. But the flame front travelling backwards towards the process system will feed on the explosive mixture in the line. It will accelerate to reach and even exceed the speed of sound in air (340 m/s) in which case a detonation wave will be formed with a pressure peak twenty or more times atmospheric. The important point is that the direction and speed of flow is determined by the pressure profile which changes completely once ignition has occurred.

Figure 7 Off-gas treatment system - before ignition

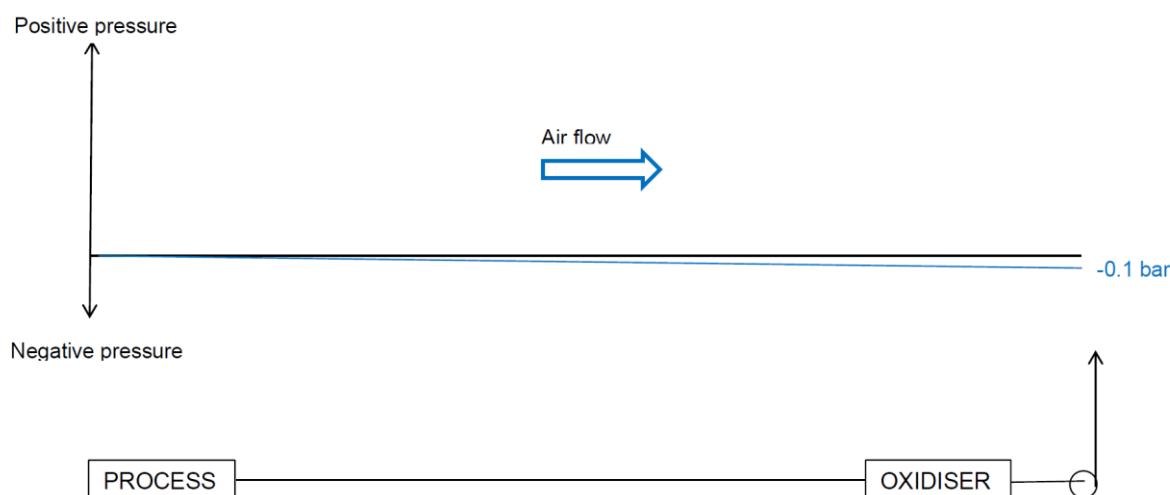
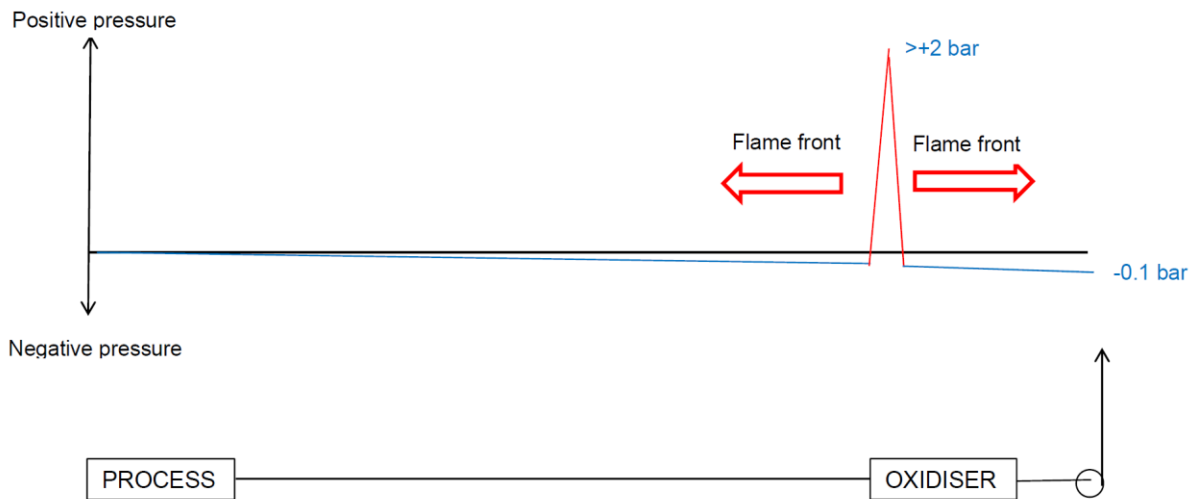


Figure 8 Off-gas treatment system - after ignition



**Why are so many protection layers necessary to prevent blow-back?**

At first glance government regulations (for example those of the US coastguard, which applied to our storage tanks for recovered sulphuric acid) seem to require redundant protection layers such as flame arrestors as well as interlocks to close block valves on the line in case of high levels of hydrocarbon or of oxygen. It is important to realise that these layers are not redundant at all, rather they are complementary.

A simplified diagram of such a system is shown in Figure 9. There is an in-line gas analyser for flammable gas concentration and a block valve which is closed automatically if that concentration exceeds say 50 % of the Lower Explosive Limit. The analyser and block valve are placed close to the process producing the off-gas. At the other end of the pipe, close to the oxidiser, there is a flame arrestor. A typical flame arrestor contains a metallic honeycomb structure. The gap between the metal parts is less than or equal to the Maximum Experimental Quenching Distance of the flammable gas being handled. When a flame reaches the metal honeycomb structure it cannot pass through, because the metal takes too much heat away from it.

The flame arrestor could be placed close to the process, but then it would have to be specified for a flame in a detonation regime, which would be more expensive. Also, the entire pipeline would have to resist the pressure generated by a detonation wave, which could be twenty to thirty times atmospheric.

Consider what happens if the concentration of flammable gas reaches 100 % LEL but the valve stays open because its mechanism is jammed. A typical flame arrestor will only hold for some minutes before getting hot and allowing the flame to pass through. So the flame will eventually be transmitted back to the process system.

Now consider a similar system with no flame arrestor. Assuming that the analyser detects the high level of flammable gas and the block valve closes, it might be supposed that blow-back would be prevented. In fact such a system would not be adequate because the valve would take up to about one minute to close (the higher the line diameter the longer will be the time for the valve to close). By the time the valve closes the flame may already have blown back as this only takes a few seconds.

So a typical prevention system with an analyser plus a block valve plus a flame arrestor is in reality one safeguard or one layer of protection.

Figure 9 Simplified diagram to show means of prevention of blow-back



## Pitfalls of inerting process vessels

It is often asserted that process vessels are “inerted” or “blanketed” with nitrogen or other inert gas. However it is difficult to ensure that this is really the case, as the following two examples show.

### Example 1

The first example was a stirred reactor used in a batch process, where operations such as charging of liquids and solids, reaction and distillation were carried out successively (see Figure 10). The solvent was flammable and at one point in each batch cycle the reactor charging port was open and solids were added whilst the reactor already contained the flammable solvent. There was an obvious hazard of gas phase explosion so a steady nitrogen purge was applied during this operation. As part of the HAZOP study we decided to lower a portable oxygen meter into the headspace during the solids charging operation and some of us were surprised that the reading was 21 % O<sub>2</sub>.

### Learning lesson

To maintain a nitrogen atmosphere, solids must always be added via a hopper with a rotary valve etc.

### Example 2

The second example was a reactor used in a similar type of process, except that solids were added via a charging hopper. The solids were transferred from the hopper to the reactor via a rotary valve and nitrogen was injected into the body of the valve during the addition (see Figure 11). The reactor was maintained above atmospheric pressure with nitrogen at all times during the process. As part of the HAZOP study we decided to sample the headspace during the first batch of a new manufacturing campaign. As in the first example, the oxygen level was 21 %.

### Learning lesson

At start of a manufacturing campaign the vessels may well contain air, so we must pull vacuum then purge with nitrogen three times to get a low oxygen level.

Figure 10 : Charging solids directly

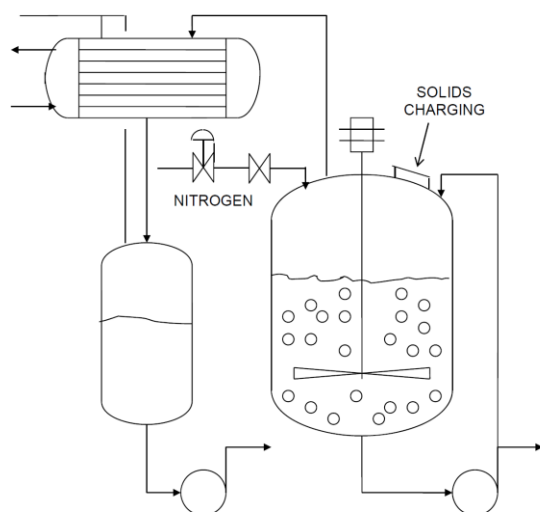
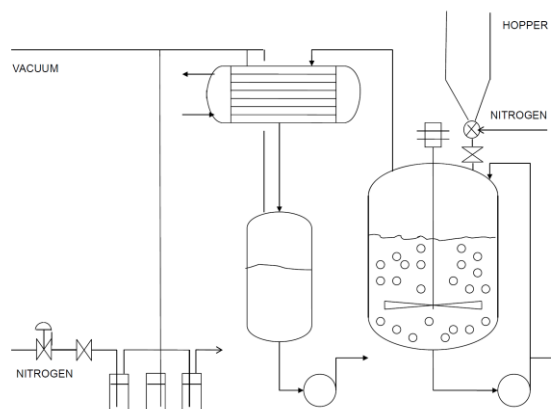


Figure 11 : Charging solids via a hopper with a rotary valve



## Conclusions

Avoiding injuries and fatalities caused by gas phase explosions in chemical process units requires:

- systematic risk analysis,
- feedback from past accidents and incidents,
- accurate data on materials used and made,
- thorough understanding of technical issues concerning explosions.

All of these things are well known since at least twenty years, yet disastrous industrial accidents continue to occur with depressing regularity. So it seems that we are still waiting for the accident and explaining it afterwards, instead of anticipating it and applying sufficient means of prevention and protection beforehand. Why?