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BP Process Safety Series

Hazards of Nitrogen and Catalyst Handling

**A collection of booklets
describing hazards and
how to manage them**



This booklet is intended as a safety supplement to operator training courses, operating manuals, and operating procedures. It is provided to help the reader better understand the 'why' of safe operating practices and procedures in our plants. Important engineering design features are included. However, technical advances and other changes made after its publication, while generally not affecting principles, could affect some suggestions made herein. The reader is encouraged to examine such advances and changes when selecting and implementing practices and procedures at his/her facility.

While the information in this booklet is intended to increase the store-house of knowledge in safe operations, it is important for the reader to recognize that this material is generic in nature, that it is not unit specific, and, accordingly, that its contents may not be subject to literal application. Instead, as noted above, it is supplemental information for use in already established training programmes; and it should not be treated as a substitute for otherwise applicable operator training courses, operating manuals or operating procedures. The advice in this booklet is a matter of opinion only and should not be construed as a representation or statement of any kind as to the effect of following such advice and no responsibility for the use of it can be assumed by BP.

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Foreword

Nitrogen is very often used in the chemical or oil industries as a 'safety' tool. However, nitrogen has proved that it can be as deadly as any other gas handled in our plants. In this booklet you will find various descriptions of serious incidents involving nitrogen.

This booklet was created to help share knowledge and improve the understanding on the basic principles for safe use of nitrogen. Due to the serious nature of the incidents along with the widespread use of nitrogen in our industry, BP published a comprehensive 'nitrogen information pack' to complement this booklet.

I strongly recommend you take the time to read this book carefully. The usefulness of this booklet is not limited to operating people; there are many useful applications for the maintenance, design and construction of facilities.

Please feel free to share your experience with others since this is one of the most effective means of communicating lessons learned and avoiding safety incidents in the future.



Frederic Gil, Process Safety and Fire Engineering Advisor

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1

Safe use of nitrogen

79% N₂ + 21% O₂



1.1 Introduction

The atmosphere we live in, the air we breathe every day consists of 79% nitrogen, 21% oxygen and traces of other gases. But only oxygen is vital and essential to human beings for respiration/survival. Without sufficient oxygen, i.e. if oxygen level falls below 16%, we will die of asphyxiation.

Nitrogen gas behaves somewhat like a diluent or buffer gas in the atmosphere. Nitrogen in itself is inert, stable, non-reactive and non-toxic, but too much nitrogen reduces the oxygen content in the atmosphere, creating an invisible condition that can kill. If the earth was without nitrogen but filled with just oxygen, then fires would burn out of control and steel structures would quickly rust away! Therefore, nitrogen is an effective diluent or buffer gas that we can't live without, yet too much of it would deprive us of vital oxygen, which can lead to asphyxiation and even death within seconds.

Nitrogen is widely used for various purposes in refineries and petrochemical plants, for example, to provide an inert atmosphere, to purge a vessel of hydrocarbons, for blanketing and padding storage tanks in order to prevent explosions and fires.

Nitrogen is odourless and colourless. It can kill without warning. Therefore, it is known as the *invisible killer* that has caused many fatalities in the refineries worldwide.

It is one of the most dangerous gases found in refineries and chemical plants.

1.2 Properties of nitrogen

Nitrogen is not toxic since about 79% of the air we breathe is this gas. The mechanism of nitrogen gassing is different to that of hydrogen sulphide (H₂S). Whilst H₂S has a direct toxic effect which is well documented, nitrogen rich atmospheres will asphyxiate due to a reduction in the oxygen content of the inhaled gases. The typical physiological effects of varying degrees of oxygen deficiency are also well documented:

Oxygen (%vol)	Effects & Symptoms
23.5	Maximum 'safe level' (23% is often the high level alarm of most O ₂ detectors)
21	Typical O ₂ concentration in air
19.5	Minimum 'safe level' (19% is often the low level alarm of most O ₂ detectors)
15–19	First sign of hypoxia. Decreased ability to work strenuously. May induce early symptoms in persons with coronary, pulmonary or circulatory problems
12–14	Respiration increases with exertion, pulse up, impaired muscular coordination, perception and judgment
10–12	Respiration further increases in rate and depth, poor judgment, blue lips
8–10	Mental failure, fainting, unconsciousness, ashen face, blueness of lips, nausea, vomiting, inability to move freely
6–8	6 minutes—50% probability of death 8 minutes—100% probability of death
4–6	Coma in 40 seconds, convulsions, respiration ceases, death

When a person enters an oxygen-deprived atmosphere, the oxygen level in the arterial blood drops to a low level within 5 to 7 seconds. Loss of consciousness follows in 10–12 seconds and if the person does not receive any oxygen within 2–4 minutes, heart failure and death follow.

In its case study of fatal incidents (see Bibliography at the end of this book), the US Chemical Safety Board details how nitrogen acts: 'Equipment containing concentrated nitrogen purge gas (oxygen content less than about 10 percent) quickly overcomes the victim without warning (see table above). After only one or two breaths the oxygen concentration in the blood drops dangerously low, and the victim is likely to lose consciousness in less than 60 seconds. Death occurs within a few minutes.

Both the rescuer's attempt to help his coworker, and the possible intentional reactor entry by the first victim, suggest that some workers may believe that they can hold their breath long enough to enter an oxygen-deficient atmosphere and return to safety before being overcome. Workers might mistakenly conclude that they can hold their breath while inside the reactor, similar to their ability to hold their breath when they swim underwater.

Swimmers are acutely aware that inhaling water causes sudden, uncontrollable coughing. This is a powerful stimulus that helps a swimmer resist the body's breathing reflex even after being submerged for a long time. But nitrogen, which is odourless, tasteless, and colourless, provides no stimulus to voluntarily resist the breathing reflex. In a highly emotional and physically demanding emergency, it is extremely unlikely that a person would hold their breath.

Furthermore, workers may be unaware of another dangerous complication—inhaling nitrogen or other inert gas suppresses the brain's breathing reflex response. The breathing reflex is controlled primarily by the amount of carbon dioxide in the blood rather than the shortage of oxygen.

Normally, the ability to voluntarily hold one's breath is eventually overwhelmed by the brain's respiratory control centre, which is triggered by the increased carbon dioxide concentration in the blood, combined with a drop in the blood's pH (acidity). If high-purity nitrogen or other inert gas is inhaled, the body may simply stop breathing, as carbon dioxide accumulation in the blood is insufficient to stimulate the breathing reflex.'

Moving affected and unconscious persons from a N₂ atmosphere into fresh air is not enough to promote recovery, the patient has to be physically resuscitated in order to restore the oxygen supply to the brain.

NOTE: There is also a risk of suffocation with all compressed gases (for example—argon, CO₂, helium, etc.), which either replaces the oxygen or consumes it. This risk also exists in situations where there is a large consumption of oxygen (fires, and rusting in ballast tanks of a ship or water tanks, etc.).

INCIDENT Four fatalities occurred at a construction site during the welding of a stainless steel 54-inch (1.4m) diameter pipe. A grinder entered the pipe (a confined space) without authority for some unknown reason and was overcome by accumulated argon (welding shielding gas). Three additional fatalities occurred when others entered the pipe to rescue the first casualty.

Nitrogen (N₂) is a very common and extremely dangerous gas that you may be exposed to at a refinery or chemical plant. You must always be on your guard.

1.3 Uses and hazards of nitrogen

Most useful or most dangerous gas???



What is nitrogen used for?

Nitrogen has numerous safety applications in plants:

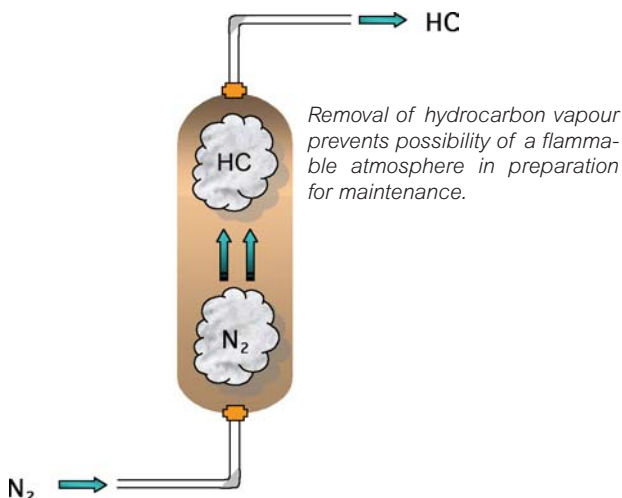
As a gas:

- for inerting equipment to prevent flammable atmospheres;
- for preparing equipment for maintenance by purging out hydrocarbons;
- for removal of air / oxygen in equipment before start-up;
- for blanketing tanks to prevent the ingress of air;
- for specific welding operations;
- for 'mothballing' equipment to avoid the rusting process;
- for use as fire-fighting agent as it removes air.

Some sites may also have a practice of using nitrogen to back-up the instrument air system in case of instrument air supply failure—this is discussed in section 1.8.

As a liquid:

- for cooling purposes in the laboratory, freezing a pipeline, etc.
- for storage and transportation of nitrogen in large quantities.



What are the hazards of nitrogen?

Nitrogen is not toxic since about 79% of the air we breathe contains this gas. However, it is not harmless and it has *no smell*.

As a gas:

- It can cause suffocation by replacing the oxygen in a confined area.
- Its presence will give false readings when using explosimeters or flammable gas detectors.
- Like other compressed gases, there are the risks related to its pressurised containment when it is stored in high pressure cylinders.

When using nitrogen for inerting purposes, it is important to be aware that it does not 'wet' pyrophoric iron sulphide deposits like steam or water do. For more information on pyrophoric materials, refer to BP Process Safety Booklet *Safe Ups and Downs for Process Units*.

As a liquid:

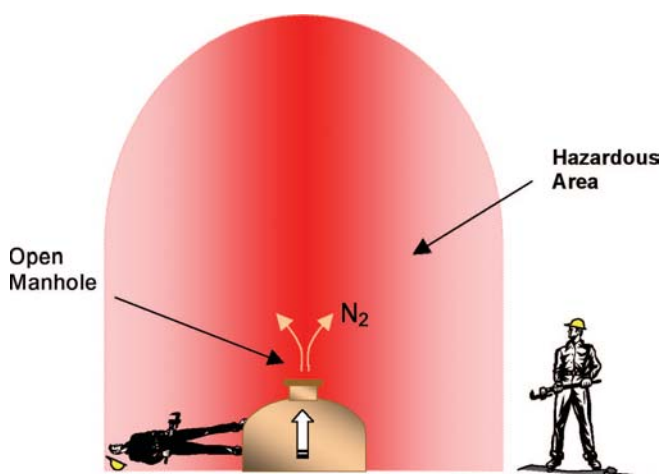
- The same as the gas, when it evaporates.
- By creating an intense coldness (-196°C / -312°F) that can cause frostbite, crack steel equipment and explode tyres.
- It boils at a colder temperature than oxygen thereby condensing the oxygen in the air (which can then form explosive mixtures with other vapours or cause a violent reaction in contact with organic substances).



What is an asphyxiant?

A chemical (gas or vapour) that can cause death or unconsciousness by suffocation. **Simple asphyxiants** such as nitrogen, displace oxygen in air. They become especially dangerous in confined or enclosed spaces. **Chemical asphyxiants**, such as carbon monoxide and hydrogen sulphide, interfere with the body's ability to absorb or transport oxygen to the tissues.

1.4 Hazards of open manholes



The invisible killer: a danger commonly found in refineries

Previous incidents with open vessels under nitrogen include:

- sampling a nitrogen atmosphere for hydrocarbons in the reactor without wearing breathing apparatus;
- attempting to rescue inert entry technicians without suitable breathing apparatus and rescue plan;
- recovering entangled rope or equipment from inside a reactor;
- helping inert entry technicians to move ladder from the outside;
- performing work activities outside reactor e.g. cleaning reactor interior from outside adjacent to open manhole;
- installing blinds nearby an open manhole during catalyst unloading, whilst is adequately protected from nitrogen and catalyst dust;
- opening the top manhole of a vessel under nitrogen purge with unprotected workers located in an oxygen deficient atmosphere.

Oxygen Deficient Atmosphere: An atmosphere with an oxygen content below 19.5% by volume. (OSHA Definition)

CAN YOU **SEE** OR **SMELL** THE INVISIBLE KILLER?!!





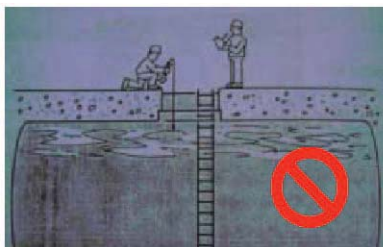
No! And how are you sure it is safe to enter? What are your precautionary measures before entry? Do you carry a portable gas detector that beeps if oxygen falls below 19%? Do you have a standby attendant?

Do you know that you can be overcome by N_2 by just looking into the manhole without wearing breathing apparatus?

ACCIDENT

While in the process of taking a sample of the atmosphere from a reactor under nitrogen purge, a process operator became asphyxiated and fell to his death through this open manhole. He was found on the second tray approximately 20 ft (6m) below the manhole.

It should also be noted that instruction manuals/handbooks on gas-testing, confined space entry, etc . . . must raise awareness on the risk to the operator of doing a gas test or taking a sample from the outside of a vessel. Pictures below are typical illustrations of poor practices.



Initial gas testing should be performed from outside the space by inserting a probe or piece of flexible tubing. However, ensure that the contractor or employee performing gas testing is adequately protected with breathing apparatus and accompanied by a second person.

ACCIDENT

A subcontractor employee (not wearing breathing apparatus or safety harness) entered the barricaded area atop a reactor to assist a confined space entry attendant in lifting the internal access ladder. He was overcome by an oxygen deficient atmosphere around the manhole and fell into the reactor. Without the vital oxygen to sustain respiration, it is very unlikely that anyone could exit the reactor alive!



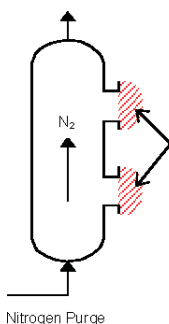
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OPEN MANHOLES ARE DANGEROUS!

WHY?

THE VESSEL COULD BE DEFICIENT OF OXYGEN



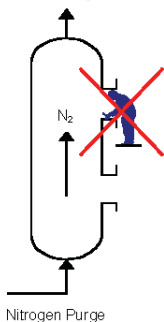
Oxygen
Deficient
Atmosphere

Nitrogen can create an oxygen deficient atmosphere outside the vessel/piping that is being purged with this medium

AND

TECHNICIANS PUT THEIR HEADS INSIDE

THEREFORE



DO NOT PUT
YOUR HEAD
INSIDE
OPEN
MANHOLES

You are asphyxiated with only your head inside an oxygen deficient atmosphere – not your whole body.

INCIDENT

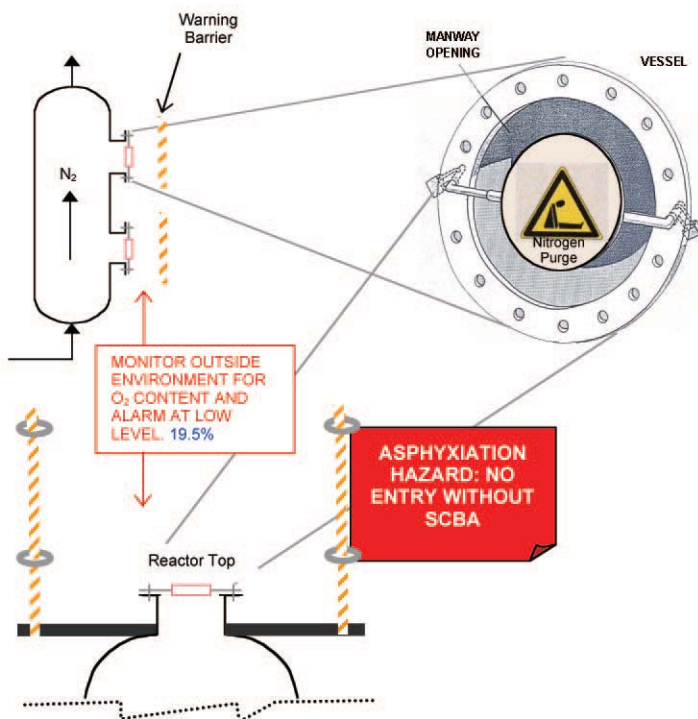
Two workers perished in an incident while working to re-attach piping near the open manway of a hydrocracker reactor that was under nitrogen purge to prevent moisture from reaching the catalyst.

It appears that one of the two contractors likely became disoriented, passed out, and fell into the vessel after he breathed nitrogen near the manway opening on top of the vessel. Upon seeing his colleague fall into the vessel, the second contractor employee then entered it, probably in an attempt to save his coworker. Both men died quickly from nitrogen asphyxiation.

KEEP TECHNICIANS AWAY FROM AREAS OUTSIDE MANHOLES THAT COULD BE DEFICIENT IN O₂ (UNLESS AUTHORISED THROUGH A CONFINED SPACE ENTRY PERMIT).

HOW?

PREVENT ACCESS

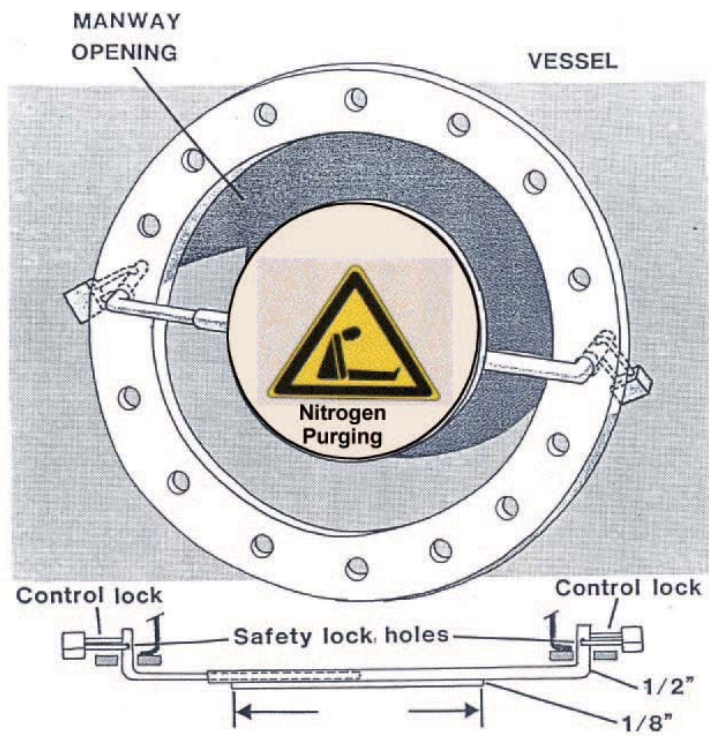


ACCIDENT

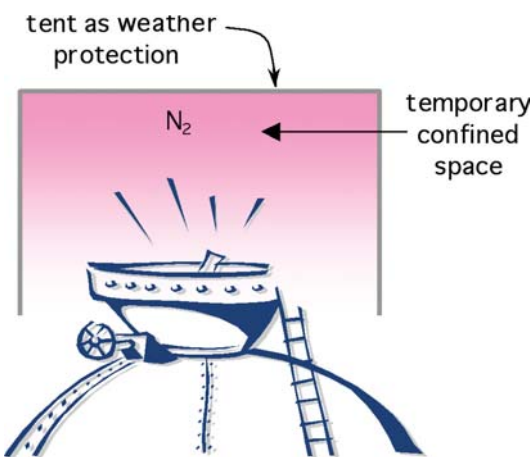
A fixed bed reactor was filled with catalyst under a nitrogen blanket. At the start of a new shift the operator went to inspect the reactor top alone. When he failed to return, a colleague went to look for him and eventually saw him lying on top of the catalyst in one of the reactors. He put his head inside an oxygen deficient atmosphere, knowing all the hazards, but for a moment ignored them.

Good practice

A device was developed for placing across manholes and other openings to confined spaces which may contain an oxygen deficient atmosphere. The device can be locked into place to prevent unauthorized removal and physically prevents access. Removal would only be allowed as a condition of a confined-space entry permit.



1.5 Hazards of temporary confined spaces



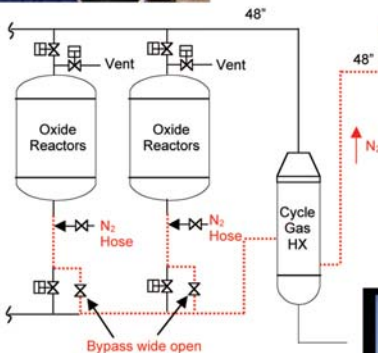
Outside areas can be deficient in oxygen which are exacerbated by any form of closure or tent.

ACCIDENT

A process column had been taken out of service for maintenance for several weeks. The column had been cleaned, several manholes were open, and a nitrogen purge was on the column. Two experienced workers were examining the flange surface of a remote manhole for stress cracks. They sprayed dye on the flanges and used a black light to identify the suspect areas. The weather conditions were sunny, windy and mild.

A tarpaulin was draped over the flange but it is unclear whether this was to block the wind while they were using dye penetrant or to facilitate using the black light, or both. The confined space created by the tarpaulin was soon filled with nitrogen which asphyxiated both men. One man died as a result of the exposure and the other survived because he collapsed face down on the expanded metal grating, which allowed sufficient oxygen to sustain his life.

The immediate cause of the accident was the inadvertent creation of a confined space environment around an open manhole that was being purged with nitrogen. The basic causes were the failure to recognise a confined space and the risk of asphyxiation from nitrogen coming out of the manhole, and inadequate control of work on a column that was being nitrogen purged.



NOTE: The nitrogen injection points were a considerable distance from the location where the nitrogen gas was being emitted through the opening.



Examples of temporary confined spaces

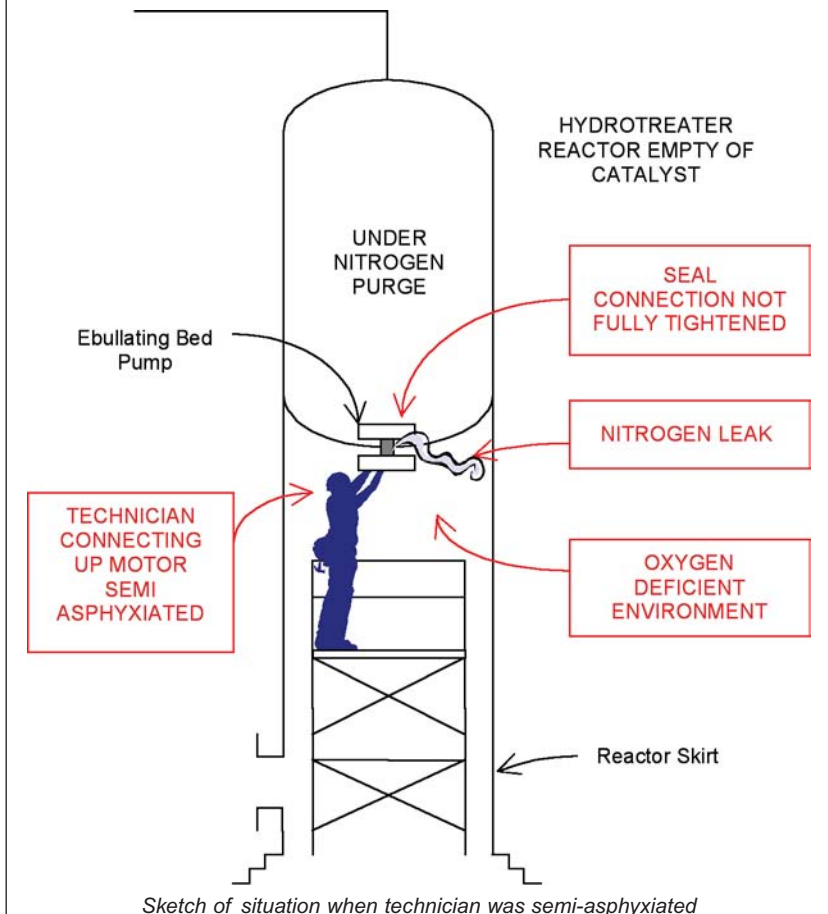


ACCIDENT

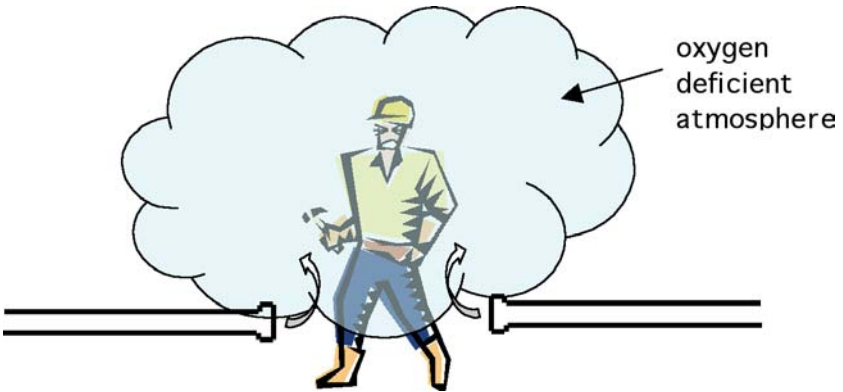
A technician was overcome by an oxygen deficient atmosphere while connecting up a motor. The catalyst had been removed and the reactor was floating on nitrogen. The pump seal on the reactor was leaking, allowing nitrogen to enter the reactor skirt. The supervisor assumed that the reactor seal was tight and there was no requirement for either:

- air-line breathing apparatus;
- air movers;
- continuous oxygen monitoring with alarm.

Skirts surrounding the bottom of vessels must be considered a Permit-Required Confined Space.



1.6 Hazards of piping under nitrogen purge

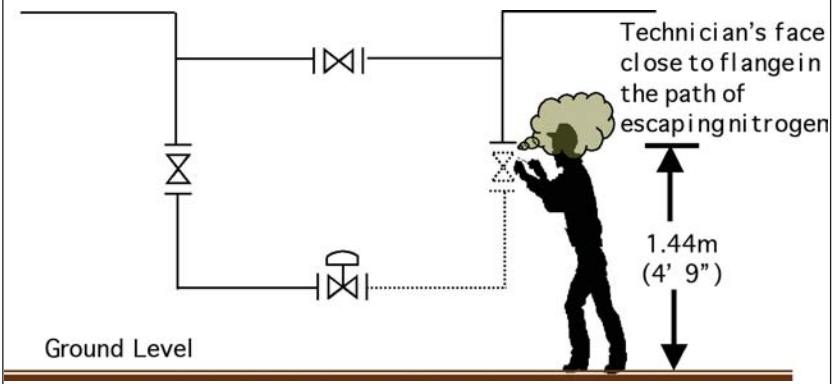


Beware of changing fittings on piping being purged with nitrogen:

- changing a valve;
- replacing a section of pipe;
- turning a spectacle plate;
- installing or removing full face blinds.

ACCIDENT

A technician collapsed during reinstallation of valve and section of pipe shown by dotted line.



Good practice

- Breathing apparatus must be worn where there is risk of exposure to a level of nitrogen that could cause oxygen deficiency in the local surrounding atmosphere.
- All persons, and in particular supervisors, must be made aware of the risks associated with nitrogen to ensure that suitable precautionary measures are taken when vessels and pipelines are being purged with nitrogen.

1.7 Hazards of inerting equipment leaving a site

ACCIDENT

Railcars were used to move Decene (C10 hydrocarbon) to and from a chemical site. A railcar was identified as having a problem with a leak on a vent valve on the top of the railcar and was subsequently notified for repair. A few days later, after being moved to a repair workshop, a worker was found unconscious inside the railcar and was pronounced dead at the scene.

A few months earlier, it had been decided to inert the railcars to solve reliability problems. The Management of Change process only covered the engineering requirements, not the safety aspects, and the railcar sent for repair had no sticker or documentation attached that mentioned the hazard of an inert atmosphere.



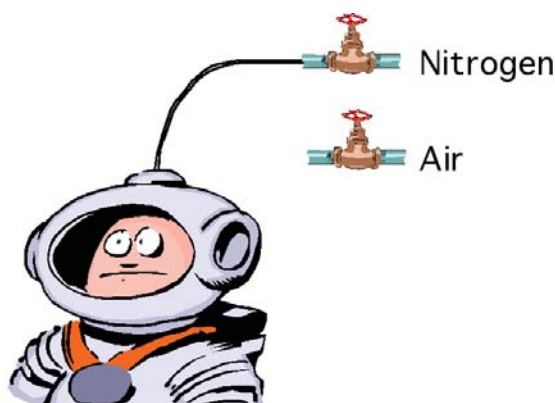
Valve which was due for repairs.

Good practice

- Provide a visible and overt warning of the hazardous atmosphere present in equipment leaving facilities.
- Rigorous discipline on documenting communications should be practised.
- Fully comprehend safety practices of contractors and subcontractors and the consequences through the Management of Change (MOC) process when procedures/practices change.

- Do not assume that personnel outside your facility understand safety practices necessary to safely manage hazards with which you may be intimately familiar.
- Implementation plans and training materials need to be provided when new procedures or practices are installed.

1.8 Hazards of confusing nitrogen with air



Previous incidents of confusing nitrogen with air include:

- no unique bayonet fittings for breathing air supply;
- air-line system was not checked or verified prior to connection;
- air-line system isolated and used as a nitrogen header, but the operator was not aware of the change after returning from his rest days.

ACCIDENT

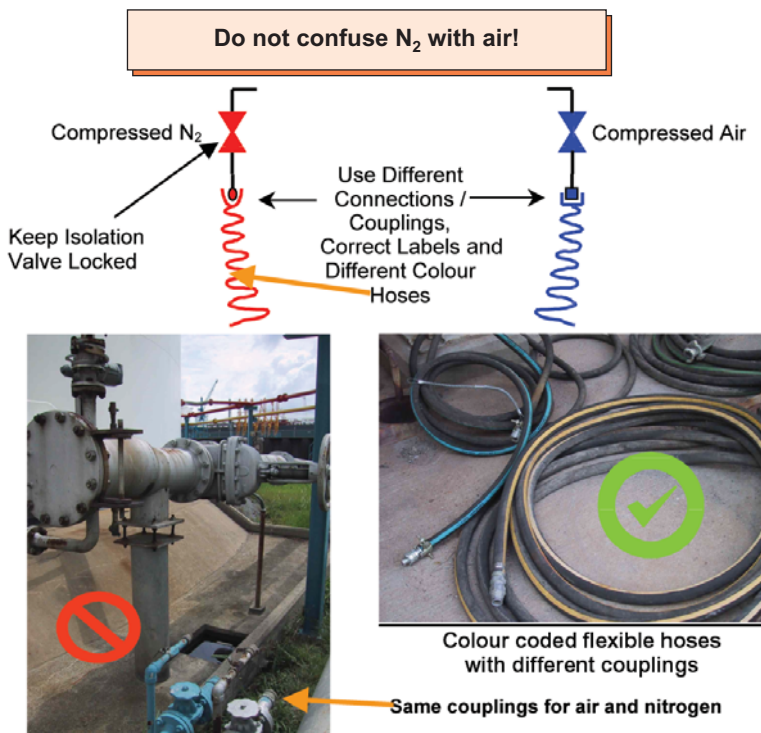
An incident occurred on a Monday when the foreman instructed the technician to connect up the breathing air supply to the air receivers of the plant's instrument air system, as he had done the previous Friday. Instead the technician connected the hoses to a regeneration air manifold which had been blinded/blanked from the air system and was being used as a nitrogen header. No reason for this change was established other than it may have been 'more convenient'. The 'Management of Change' procedure had not been initiated prior to making this temporary modification.

Good practice

- Never use nitrogen instead of compressed air (for instance with pneumatic tools).
- Use different couplings. Although special couplings for nitrogen connections are a good practice, they should not be relied upon during turnarounds. The valve should be kept chain-locked as contractors have all kind of couplings to defeat the system. Locking of the isolation valves should be mandatory

on utility stations for nitrogen to prevent misuse by contractors and control usage through the Lockout-Tagout Procedure.

- Never store bottles of compressed nitrogen in confined unventilated areas (a 50-litre [13 US gallons] bottle at 200 bars can cause the oxygen level in an average 9 sq. metre [97 ft²] room to drop to 12%).
- Never use nitrogen to back-up an air system without a formal risk assessment.



Good utility station:

- colour coding;
- signage and labels;
- specific fool-proof couplings;
- check valves;
- all piping and accessories welded on nitrogen to prevent dismantling;
- non-threaded vents/drains on nitrogen to prevent connection of different couplings;
- nitrogen valve locked close when not in use and key delivery controlled.

Always use dedicated breathing air supply

A mobile, self-contained, high pressure cylinder storage system undoubtedly provides the highest integrity, freedom of operation and safety when using air-line breathing apparatus. Most sites prefer to either use bottled air, supplied from a trolley set (wheeled trolley with air bottles on it) or from a bank of dedicated air bottles located on the plant. There is a requirement to ensure that the quality of air in supply bottles is correct, whether they are refinery filled or otherwise by a respectable external company.

ACCIDENT

Following a total power blackout at the process site, an instrument technician was found unconscious in an analyser house. He was rushed to a local hospital but pronounced dead on arrival. During the power failure, instrument air was replaced with nitrogen. It was suspected that a nitrogen leak was the cause of the fatality.



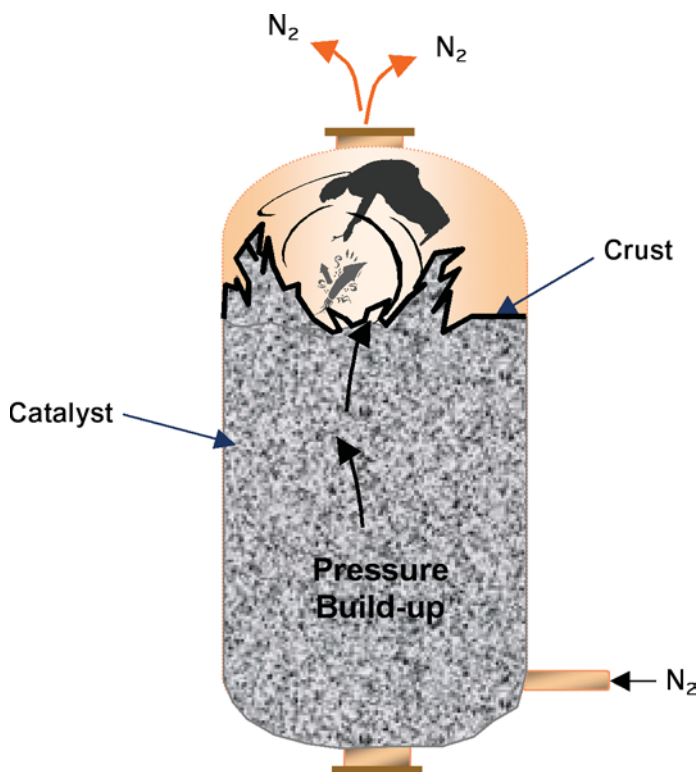
Analyser house with atmosphere warning signs.

1.9 Hazards of trapped pressure

ACCIDENT A contract employee was fatally injured while removing catalyst from a Hydrodesulphurisation (HDS) Reactor.

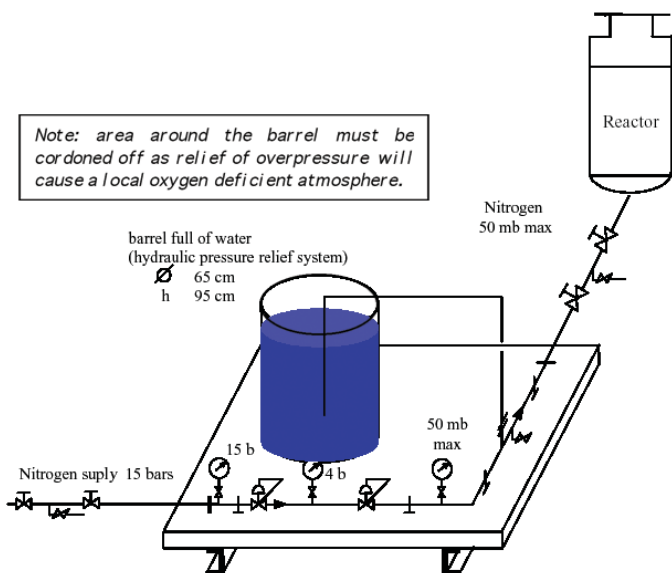
After shutdown and a nitrogen purge, the reactor inlets and outlets were blinded, and a nitrogen hookup provided to supply a continuous purge for use by the catalyst unloading contractor. The atmosphere at the reactor top opening was checked for oxygen, flammable material and hydrogen sulphide and found to be satisfactory. Wearing respiratory equipment suitable for inert gas entry work, the worker went inside the top of the reactor to remove the internal structure.

There was a crusted layer on top of the catalyst bed below the distribution tray in the top of the reactor. What was unknown to everyone was the build-up of nitrogen pressure under the crusted layer. When the worker inside the reactor chipped the crust, the sudden release of pressure killed him. His equipment and part of the reactor contents were expelled upwards through a 22 feet (0.6 m) diameter manhole.



Precautions

Nitrogen injection pressure should be lowered to less than 0.7 psig (50 mbar), or strict formal checking procedures enforced. An example of a pressure regulating system with simple pressure relief device is given below:

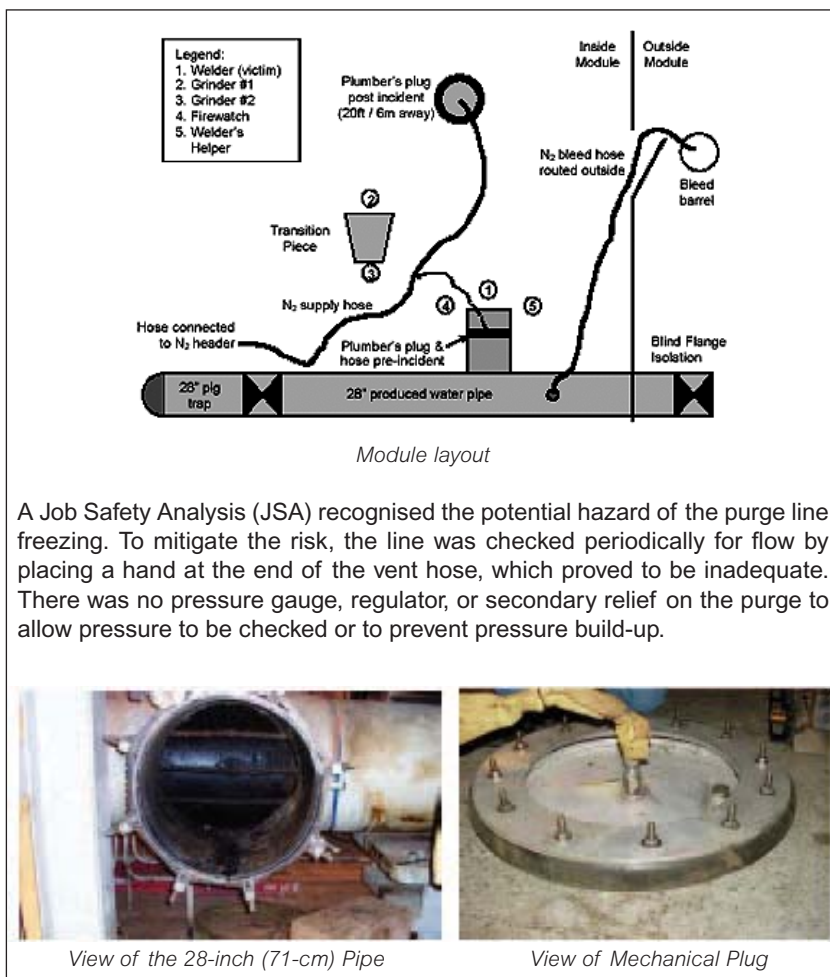


NOTE: Remember that nitrogen (or any other gas) should never be used for strength testing of pressure vessels except in very special circumstances following a risk assessment and approval process.

ACCIDENT

A mechanical plug installed inside a pipe to isolate hot work from process fluids released suddenly striking and killing the welder. The work in this incident involved a welding operation on a 28-inch (71 cm) water line that had residual water and hydrocarbons in it. A non-pressure containing mechanical plug (also known as 'plumber's plug') had been installed about 12-inch (30 cm) inside the pipe as a barrier against process fluids. The pipe area behind the plug was blinded at both ends, and was being purged with plant nitrogen to carry away potential hydrocarbon vapours. Nitrogen at 30 psig (2.07 barg) was introduced by a $\frac{3}{4}$ -inch (2 cm) hose through a connection at the centre of the plug, and was being vented by a separate $\frac{3}{4}$ -inch (2 cm) hose coming from the top of the pipe. The vent line ran out of the module through a door, to prevent the build-up of nitrogen in the atmosphere inside the module. The nitrogen absorbed residual water in the pipe and the water condensed and froze inside the nitrogen vent line when exposed to the cold temperatures outside, approximately 0°F (–18°C). The frozen water blocked the nitrogen vent line, causing pressure to build behind the 63 lb (29 kg) plug and blew it off.

continued...



When purging systems using such plugs, procedures should address the size of inlet and vent hoses, placement of vent hoses, use of regulators to control flow, use of secondary pressure relief to prevent overpressure, positioning of workers away from the plug, and work crew training and hazard awareness.

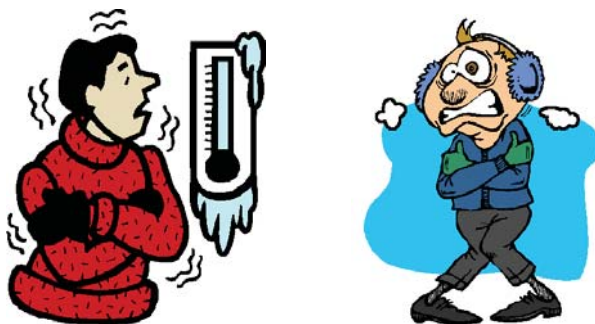
Where possible, the best option is to design tie-ins so that isolation plugs between hot work and hydrocarbons are not needed. Alternatively, evaluate the use of better plug types, including double-sealing hydraulic plugs (Car-Ber type) and pressure rated plugs (Thaxton) that have the potential to be used with or without purging.

For more details on the hazards of trapped pressure, refer to the BP Process Safety Booklet *Hazards of Trapped Pressure and Vacuum*.

1.10 Hazards of liquid nitrogen

ACCIDENT A 30 ft. (9 m) section of a 2 inch (0.05 m) carbon steel nitrogen transfer line at a refinery failed as a result of brief low temperature embrittlement arising from the malfunction of a solenoid valve. The failure was potentially serious and one witness described the noise as an explosion and saw the line lift 6 ft (1.8 m) into the air before disintegrating. At the time of the fracture part of the pipe was covered by a layer of frost about 1/8-inch (0.003 m) thick. Hazardous bulk nitrogen systems at four different sites were modified by fitting a low temperature sensor connected to magnetic or air-operated shut-off valves.

ACCIDENT When a High Pressure Lube Oil Hydrogenation Unit (HPH) was being decommissioned and cooled down for a statutory overhaul, liquid nitrogen from the associated nitrogen vaporizer was inadvertently discharged into three reactors via temporarily installed hoses. The initial cooling rates for the reactor were found to be too low so the decision was taken to abandon the normal decommissioning procedure and instead supply nitrogen using hoses from a nitrogen vaporizer. This new procedure represented a major departure from the existing one and no hazard analysis was undertaken as part of a Management of Change procedure prior to making the change. The injection of liquid nitrogen caused damage to the vessel. Magnetic crack detection and dye penetrant methods carried out detected several cracks in the weld metals. Three thermowell nozzles on the top of the reactor were severely damaged through excessive shrinkage caused by thermal shock. The cracks, which were as long as 40 mm (1.6 inch), were grinded out and made good by rewelding. Repair costs were significant.



Safe handling of liquid nitrogen in laboratories

Liquid nitrogen is frequently used in chemical research laboratories for the purpose of cooling. Liquid nitrogen is a valuable coolant because of its low

boiling point of -196°C / -321°F , inexpensive price, and low toxicity. In comparison to liquid air, which was previously used as a popular coolant, liquid nitrogen has the advantage that it does not support combustion.

Cold traps cooled with liquid nitrogen

A common use of liquid nitrogen is as a coolant for cold traps incorporated in vacuum lines. A cold trap is used in vacuum lines to collect organic/toxic vapour specimens by cooling and condensation. In addition, a cold trap helps the system to achieve a better vacuum with a smaller vacuum pump.

Care must be employed when using liquid nitrogen as a cold trap coolant. Systems including liquid nitrogen traps must never be opened to the atmosphere until the trap is removed from the coolant. This is because oxygen has a higher boiling point (-183°C / -283°F) than nitrogen (-196°C / -321°F) and will condense out of the atmosphere and collect in a liquid-nitrogen cooled vessel open to the air.

ACCIDENT

This phenomenon was confirmed during an experiment reported by a research engineer at a laboratory. He reported that after leaving an open cold vent, with the liquid nitrogen still in the dewar, in the hood, for about five minutes, it was later found full of liquid.

He suspected that the incident was caused by a very small leak in the vacuum system such that air got into the line downstream of the glassware apparatus. The oxygen in the air then condensed inside the cold trap, together with other chemical vapours. This would have caused a highly flammable (explosive) mixture. Upon ignition this would cause serious injuries to laboratory personnel.

ACCIDENT

A similar incident was reported in the food industry by the Loss Prevention Bulletin (no. 191): Finely ground baked pork rinds were cooled with liquid nitrogen to make them brittle, before being processed through a grinder. On the day of the incident, pork rinds were left in nitrogen over a meal break. When the grinder was started, an explosion occurred because the rinds became oxygen-enriched to the point where the energy generated by the rotating blades of the grinder was sufficient to cause the grease in the rinds to detonate.

Liquid oxygen may also be mistaken for water by laboratory personnel, and direct contact with unprotected skin will cause serious cold burns. If the liquid oxygen is disposed of as water, it may react violently with some organic materials and explode.

Recommendations

- Prepare an inspection and maintenance program to check for any leakage in the vacuum system and other associated systems.
- If you suspect liquid oxygen has condensed in a cold trap, then shield the trap (with an explosion shield, closed hood window, etc.), post a sign

indicating the danger, and allow the trap (vented to the atmosphere) to slowly warm to room temperature.

Other recommendations regarding use of liquid nitrogen:

- Cryogenic liquids such as liquid nitrogen can cause very severe burns upon eye or skin contact. Splashes are common when handling liquid nitrogen, so safety goggles must therefore be worn at all times when working with this material.
- In addition, protective gloves that can easily be removed in the event of a spill should be worn when handling liquid nitrogen (alternatively, potholders may sometimes be more convenient for handling small containers of cryogenic materials).
- Particular care must be taken to prevent uninsulated vessels containing liquid nitrogen from coming into contact with unprotected parts of the body, since extremely cold materials can become firmly bonded to the skin such that separation is not possible without serious injury.
- Contact of the skin with liquid nitrogen can cause severe cryogenic burns. The tissue damage that results is similar to that caused by frostbite or thermal burns. Since small amounts of liquid nitrogen quickly evaporate from the surface of exposed skin, some inexperienced employees may mistakenly underestimate the risk of cryogenic burns when working with this material. In fact, it is not unusual for spills and splashes of liquid nitrogen to become trapped under rings, bracelets, watchbands, or inside gloves, and this can result in serious and painful burns.

Containers for liquid nitrogen

- The properties of some materials (including metals) change drastically when exposed to cryogenic liquids such as liquid nitrogen. Containers for such liquids must therefore be selected carefully to ensure that they can withstand the temperatures and pressures they may be exposed to. Liquid nitrogen is commonly stored in Dewar flasks which should be taped to minimize the hazard in the event of an implosion.
- A Dewar flask is a container after which the common thermos bottle is patterned. It consists of two flasks, one placed inside the other, with a vacuum in between. The vacuum prevents the conduction of heat from one flask to the other. For greater efficiency the flasks are silvered to reflect heat. The substance to be kept hot or cold, such as liquid nitrogen, is contained in the inner flask.

Liquid nitrogen and condensed argon

Argon, a gas commonly employed as an 'inert atmosphere' for chemical reactions, distillations, and other laboratory operations, also has a boiling point (-186°C / -303°F) which is higher than that of nitrogen. Consequently, liquid argon will condense in a reaction vessel under an argon atmosphere which is cooled with liquid nitrogen. This creates an extremely hazardous situation, since if the vessel is then removed from the coolant, the liquid argon will instantly vaporize, expanding in volume by a factor of 847! Even if the vessel is vented (to an inert gas line, for example), an explosion is very likely due to the rapid increase in pressure in the vessel. Consequently, never cool an apparatus that is under an argon atmosphere using liquid nitrogen.

1.11 Hazards of explosimeter use in nitrogen atmospheres

Explosimeters (flammable gas detectors) do not tell the truth in nitrogen atmospheres:

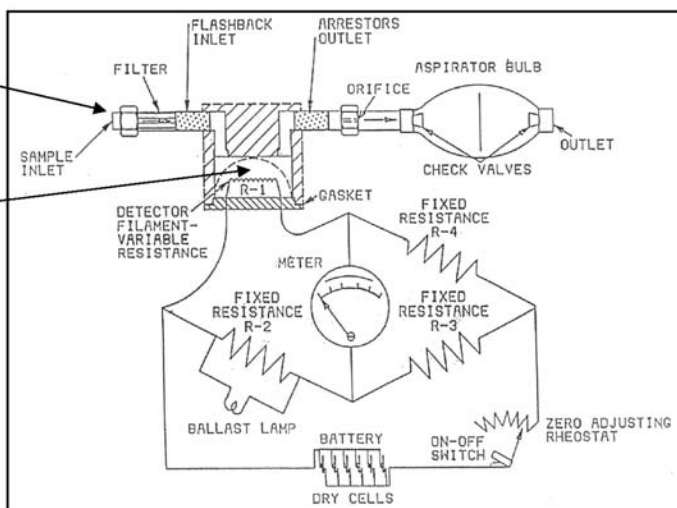
- Explosimeters or gas detectors give false readings in an oxygen deficient atmosphere.
- The types of portable flammable gas detectors in use in refineries usually operate by the catalytic combustion of a flammable gas on a heated filament (usually platinum), to give a reading of the %LEL*/LFL*. Accordingly, there must be approximately 21% oxygen in the sample to give an accurate reading. If the atmosphere being tested is deficient in oxygen, for example when purging with nitrogen, it is not possible to use a standard type of flammable gas detector in its normal mode of operation to detect hydrocarbon vapours.
- A standard catalytic gas detector, therefore, can only be used to give a reading of flammable gas in an inert atmosphere by using special techniques involving air dilution attachments. The interpretation of results is difficult, and hence is not recommended for day-to-day plant use.
- A review of operating and commissioning procedures highlighted a common practice of purging equipment and plant free of hydrocarbon vapours with nitrogen using hydrocarbon / air flammable gas detectors at sample points to determine the presence of hydrocarbon gas. The use of a standard flammable gas detector is not suitable for this purpose.
- Portable instruments are currently available that can be used in hazardous areas and which can give true indication of the level of flammable gas in a nitrogen atmosphere. These include infrared sensors and 'Tankscope' gas indicators used on ships.

Always check the oxygen level first before carrying out a flammable gas test using an explosimeter in preparation for hot work or confined space entry.

* LEL = Lower Explosive Level

* LFL = Lower Flammable Level

Must have
air/oxygen in
sample.



Controlled combustion takes place here:

Oxygen + Flammable gases $\Rightarrow$ CO₂ + H₂O + Heat.

Working Principle of an Catalytic Explosimeter

1.12 Hazards of contaminated nitrogen

Contamination of nitrogen presents two hazards:

- toxics or flammables may be carried to another part of the plant;
- nitrogen that is used for inerting equipment to prevent flammable atmospheres may not be inert anymore if enough air has entered the nitrogen supply.

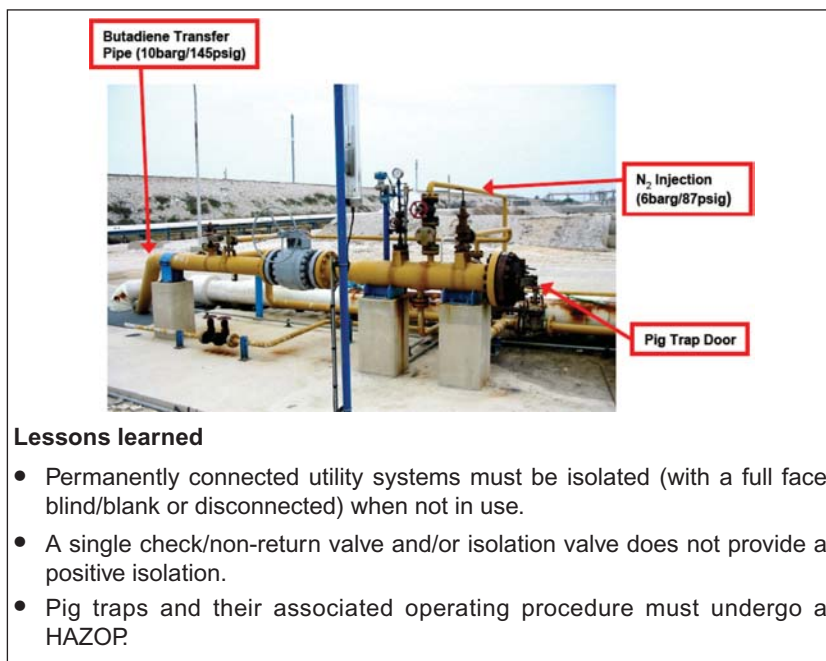
ACCIDENT

Flammable gas was detected at various locations on the nitrogen network of a refinery. A chromatograph in a laboratory caught fire. All N₂ flexible hoses connected to process equipment were immediately removed and the N₂ network purged. Within an hour all the LPG within the nitrogen system had been eliminated.

Investigation

The contaminant was butadiene that had entered the nitrogen stream at a pig receiver station during a pigging operation. The isolation and check/non-return valves on the fixed 6 barg (87 psig) N₂ supply line to the pig receiver were passing/leaking. The butadiene was at a higher pressure (10 barg/145 psig) which allowed it to back flow through the permanent N₂ connection since it was not positively isolated.

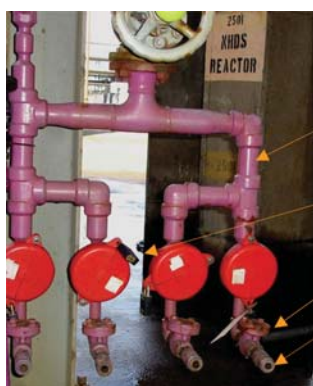
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Nitrogen connections to process equipment containing liquid or gaseous hydrocarbon streams which are **not required** for safety or process reasons, must be disconnected or blinded when not in use to prevent potential contamination of the nitrogen system.

Utility stations on a nitrogen distribution system must also have a non-return device (for example, check valve), must be clearly identified and use special connectors and hoses which are not common to any other system. Other good practices on these utility stations to avoid unauthorised use are to:

- lock the valves;
- weld the nitrogen specific connectors.



Nitrogen utility station

Clear identification of nitrogen pipes (plus sign with pictogram not visible on picture)

Valves locked

Check valves

Specific nitrogen connectors

Permanent nitrogen connections **required** for safety or process reasons must include a non-return device (for example, check valve) to prevent potential contamination of the nitrogen system.

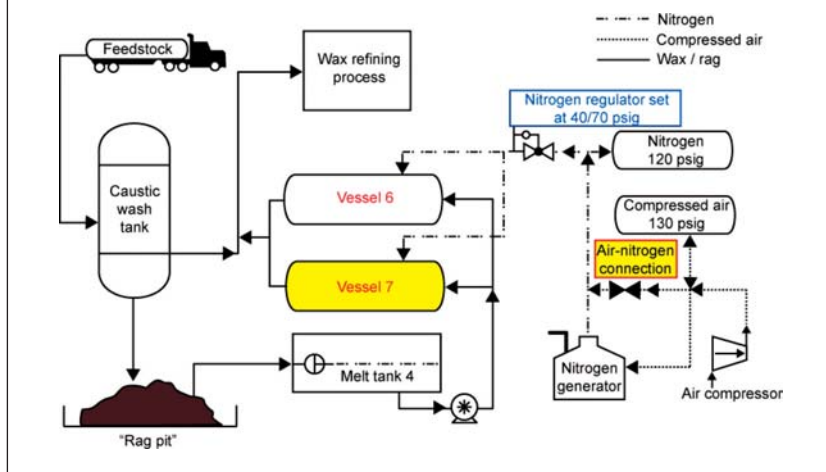
ACCIDENT

A pressure vessel (**not** designed, constructed or modified to internationally accepted standards for pressure vessels) was one of two (vessels 6 and 7) that received molten polyethylene wax for processing (see figure below). It contained steam piping in order to maintain the temperature of the molten wax at 149°C (300°F). Nitrogen was used to pressurise / force the liquid wax to the feed pump for the wax refining process.

The flow from the N₂ generator was sometimes insufficient to maintain the required throughput of wax. As a result, a temporary hose was connected up to bypass the N₂ generator with air to make up the reduced pressure. Later, this temporary modification was replaced by permanent piping. Operators pressurised the vessel with N₂ containing 18% O₂, more than enough to sustain combustion.

Sparks generated from a ruptured patch plate probably ignited the wax and hydrocarbon vapours (the wax had a flashpoint of 110°C / 230°F).

An internal deflagration blew the vessel head into multiple fragments. The blast ignited large fires that burned for several hours, and two firefighters were injured during the emergency response.



Assurance must be provided that supplied nitrogen, as it enters the site, is not contaminated with oxygen, whether via pipeline or vaporisation into the plant distribution system. This assurance can be provided in a variety of ways, (e.g., process analyser, regular laboratory testing, supplier QA/QC procedures, etc.).

Consideration should be given to additional monitoring at individual units or at other key locations in a nitrogen distribution system to ensure non-contamination.

- All personnel required to wear breathing apparatus must be properly trained and 'refresher courses' incorporated into the annual training program.

- Evaluate the use of portable gas detectors that will give off alarms when the oxygen concentration in the vicinity of the vessel drops below a critical level. Typically, normal oxygen level is 21%, and alarm levels on gas detectors are **19.5%** (low O₂ alarm) and **23.5%** (high O₂ alarm).
- If the oxygen content ever goes above 21%, there is something wrong like a leaking oxygen cylinder. Investigate the situation first before allowing personnel in the confined space.

If you see someone lying unconscious on the ground or through the opening of a tank or pipe:

- Call the fire department / rescue team

**NEVER ENTER A CONFINED SPACE OR
AREA ALONE TO GIVE HELP. CALL FOR ASSISTANCE**

For more details on permit to work and confined space entry, refer to BP Process Safety Booklets *Control of Work* and *Confined Space Entry*.

Unacceptable behaviour

- Peeking into a reactor without respiratory protection.
- Working near open manholes of a vessel under nitrogen without wearing adequate breathing apparatus (cartridge or dust masks are unacceptable).

2

Safe handling of catalyst

2.1 Properties of catalysts

Catalysts are substances that increase the rate of reaction in certain processes. Catalysts are available in many forms (e.g. cylinders, tubes, balls, granules, powder) and colours. They are used in a number of processes at refineries that include naphtha hydrotreatment, hydrocracking, resin hydroprocessing, alkylation, fluidized catalytic cracking, sulphur recovery, chloride removal and in absorbers and dryers.



Presulfided CoMo catalyst

Examples of common refining catalysts



FeCr NiMo CoMo CoMo Pa Pt

Some common catalysts used in the refinery and petrochemical plants.

Some catalysts must be handled under a nitrogen atmosphere due to their pyrophoric and self-heating characteristics. Two types of substances distinguished by their spontaneous combustion properties are:

Pyrophoric substances: even in small quantities will ignite within five minutes of coming in contact with air and are liable to spontaneous combustion.

Self-heating substances: substances in contact with air, without energy supply are liable to self-heating; ignite only when in large amounts (kg) and after long periods of time (hours or days) e.g. presulphided new catalyst or used catalysts.

The increasing use of nitrogen in catalyst charging and changeout has no doubt increased the number of fatal nitrogen gassing incidents in the industry reported over recent years. Today, nitrogen is becoming as serious a gassing hazard as H_2S . Therefore, it is vital to fully understand the hazards of catalyst charging and changeout and how it can be carried out safely.

Unregenerated catalyst is normally a self-heating substance and often pyrophoric. On exposure to air, it can rapidly catch fire.

2.2 Fire hazards

HOW????

HOW????

- Caused by reaction of catalyst with oxygen (in the air) if the heat developed is not conducted away rapidly enough to the surroundings.
- Spontaneous combustion occurs when rate of heat production exceeds the rate of heat loss.
- When the auto-ignition temperature is reached.



Good practice

- Storage and transport of self-heating catalyst carried out in accordance with UN/IMO regulations.
- Always securely seal prescribed containers to prevent contact with air.
- Certain conventional methods include storage and transport of catalyst under oil / water cover or nitrogen blanket.
- In case of fire, fire-fighters should wear self-contained breathing apparatus.
- Water is the best extinguishing media, but CO_2 , powder or foam can also be used (refer to the MSDS for each catalyst).
- Safety showers should be available near catalyst unloading manholes to allow total removal of catalyst dust from the surface of protective clothing that could potentially ignite when in contact with the air.
- For extremely pyrophoric catalyst, fire resistant throw-away coveralls should be provided to catalyst handling personnel.

Poor practice

- Never store presulphided new catalyst in bags (except for a very short period of time such as for loading the reactor). Use metallic drums or containers.





Fire from presulphided new catalyst stored in large cardboard boxes.



Reloading of a reactor using 'big bags'



Metallic containers and UN/IMO drums for the transport and storage of preactivated new catalyst or spent catalysts.

Do not reuse the drums.

Wear the correct personal protective equipment and use the correct storage containers when handling catalyst.

INCIDENT

While dumping catalyst from an isomerization reactor (via the bottom dump valve) an uncontrolled release of catalyst occurred and caught fire. The reactor was being dumped under a nitrogen purge. The catalyst contractor had two employees, wearing fall protection and supplied breathing air equipment, stationed on a small scaffold to operate the dump valve, the unloading shoot, and the catalyst bin.

The catalyst contractor's plan identified the bottom dump valve as the reactor nitrogen purge vent to avoid excessive pressure buildup within the reactor. Just prior to the release of catalyst, the employee at the bin told his foreman there was excessive nitrogen blowing past the closed dump valve and to reduce the nitrogen flow into the reactor. However before the nitrogen flow to the reactor was reduced the other employee began opening the dump valve. A pressurized cloud of catalyst dust and catalyst blew out and overflowed the bin. Both employees moved quickly to a safe location. After a few minutes the catalyst pile ignited. The refinery fire department secured the slide valve, and extinguished the fire, with some difficulty using foam.

The investigation report recommended to:

- install a regulator on the nitrogen supply;
- install a low range pressure gauge on the reactor;
- install a vent and relief system on the reactor."

Exothermic reactions

- The risk of an exothermic reaction usually occurs during plant operations (not during loading or unloading of catalyst).

- When catalyst is exposed to abnormal chemicals, water or abnormal temperature/pressure conditions (such as during start-up or shutdown), exothermic reactions may develop.
- Kinetics of reaction may be very fast, with risk of metal overheating and over pressuring.



ACCIDENT

CoMo catalyst in its oxide form, not in its sulphided form, was loaded into the hydrodesulphurization (HDS) reactor. Due to the incorrect catalyst used in the reactor, a runaway temperature reaction (hydrocracking) took place and deformed/bulged the bottom head of the HDS reactor and the top head of a downstream vessel, indicating direct exposure to operating temperatures over 620°C. The HDS reactor also suffered a leak on a flanged joint at the reactor outlet. The resultant fire at the flange damaged instrument cabling in the vicinity of the reactor, causing an emergency shutdown of the unit.



The deformed / bulged section of the overheated reactor from a runaway reaction.

Reaction with water

Catalysts may react violently with water, where penetration into the catalyst pores causes an exothermic process. This may lead to violent expulsion of both the boiling water and catalyst. The smaller the pores, the more exothermic the reaction, particularly with catalysts used in dryers as desiccants or adsorbents.

Good practice

- Adequate start-up procedures, planning, control and supervision during commissioning of catalyst loaded reactors.
- Process Hazards Analysis (PHA) must cover the potential failure of critical operating systems, such as temperature indicators and emergency operating systems.
- Backup systems should be available so that reactors can be operated safely in cases of instrument malfunction especially during a temperature runaway. Instrumentation should maintain equipment integrity and discontinue operation if conditions go outside the stipulated safe operating envelope. Critical safety devices should be tested regularly.
- Operators should receive regular training on unit process operations and chemistry (including reaction kinetics and the causes and control of temperature excursions). Operators must be familiar with the use of emergency procedures when required. Emergency drills should be practiced regularly.

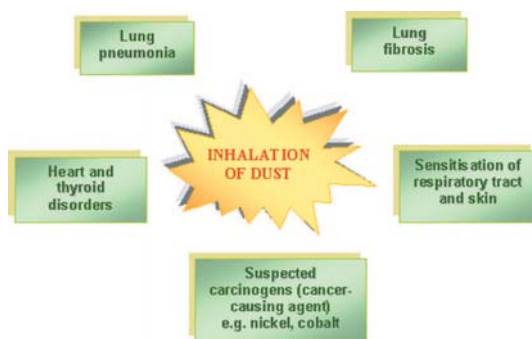
ACCIDENT

Natural gas liquids are passed through molecular sieves in a dryer vessel to remove water prior to a cryogenic process. After 3–4 years the adsorbent is used up and has to be replaced. The renewal process involves purging of the molecular sieve with hot residue gas (containing approximately 830 ppm H_2S), followed by cooling with nitrogen. For disposal, the adsorbent material is removed from the dryer into a high-sided tipper truck via a chute. The spent adsorbent is kept wetted in the truck to avoid pyrophoric activity and generation of dust.

On this occasion, a mound of spent adsorbent was formed at one end of the truck. A contract employee climbed into the truck to level the mound using a shovel. He was later assisted by two additional contract employees. Ten minutes later, all three became unconscious and died. The spent adsorbent contained adsorbed and trapped H_2S that was released to atmosphere into the semi-confined space provided by the high-sided truck. The spent adsorbent had a far greater affinity for water than for H_2S . H_2S is only slightly soluble in water and was released into the semi-confined space killing the contractors.

2.3 Health hazards

- Health hazards are mainly associated with *metallic dusts* that are toxic when inhaled.
- Exposure occurs during the handling of catalyst at site during loading and unloading of reactors.
- Catalysts can enter the body by a number of routes including skin absorption. Long-term exposures to low concentrations can cause serious chronic illnesses.



Catalyst dusts are a hazard to health—wear the stipulated respirator that provides the appropriate level of protection.

2.4 Spent catalyst

- Spent catalyst exhibits the same hazards as new catalysts as well as other hazards associated with the products they come into contact with. For example, steam cracker gasoline hydrogenation catalysts may contain high

concentrations of benzene. Therefore, more extensive precautions should be exercised when handling spent catalysts.

- Typical catalyst used in hydrogenation units contains between 4 to 21% carbon and 5 to 10% sulphur. Reprocessed or regenerated catalyst is considered spent catalyst and not new catalyst, as trapped products may be released during handling. Beware that *hydrocarbon vapours* can be released in very high concentrations when handling the spent catalyst.



Example of protecting workers at bottom of reactor from catalyst dust using full life support system that is designed for entry into inert gas atmosphere.

Another good example is to use hoods pressurised with a fresh air supply (not a dust mask).

ACCIDENT

Reprocessed catalyst was being loaded into a reactor. After each bed loading, an inspector went in to check the partition of the catalyst. He was protected only by a dust mask, and was overcome by hydrocarbon vapours and collapsed. Fortunately, he was quickly rescued and fully recovered.

When stipulating precautionary measures, the hazards to be considered are not limited to skin absorption of catalyst but must include the flammability, reactivity, corrosiveness and toxicity of the hydrocarbons present.

Good practice

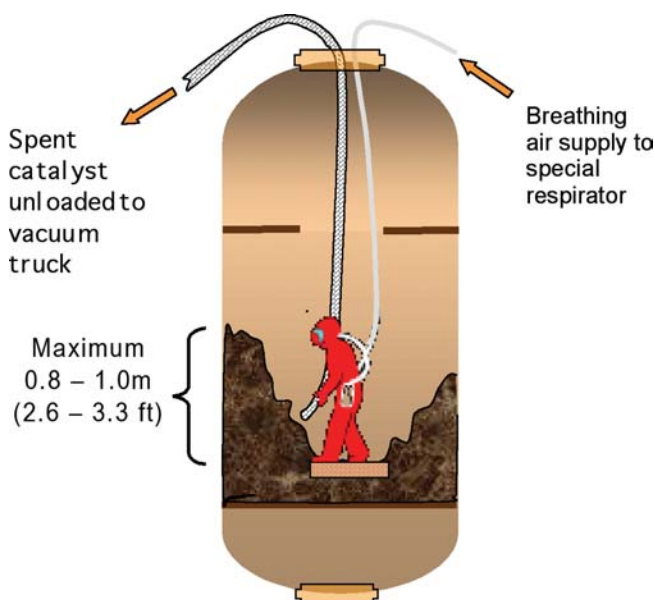
- An occupational health risk assessment must be undertaken using MSDS and other information available from the suppliers / manufacturers of the catalyst and licensor of the process technology to prevent harmful effects.
- Undertake airborne monitoring of the atmosphere and regularly carry out a medical evaluation of the technicians.
- Clean full-body clothing should be provided at the beginning of each shift and removed prior to breaks/meals.
- Contaminated clothing must not be taken home. It must be discarded into properly labelled drums for disposal or laundered on site under special instructions.
- A person entering the exclusion zone must wear the appropriate approved respirators.
- All personnel wearing respiratory protection must conform with the site's safety requirements and be instructed in its proper use and limitations as part of any statutory written program on respirators.
- Personnel entering vessels must conform with the minimum precautionary measures stipulated under the site's safety standards.
- All personnel should be trained on the hazards of the dust and operations according to the local statutory hazard communication standard.
- If in doubt, overprotect the workers, for example, use air-line respirators that provide a higher protection factor than air purifying respirators.

2.5 Nickel carbonyl

Nickel carbonyl [$\text{Ni}(\text{CO})_4$] is used as a catalyst in some plastic, rubber and petroleum industries. Nickel carbonyl vapour may also be formed inadvertently in refining cracking processes that use nickel as a catalyst. Nickel carbonyl is highly irritating to the lungs and can produce asphyxia by decomposing to liberate carbon monoxide. Lethal human exposures have been estimated as 30 ppm for 30 minutes inhalation, and 50 to 500 mg/kg if ingested. Initial symptoms include headache, dizziness, nausea and vomiting, which disappear when exposure ends. Vapour also irritates the eyes, nose and throat. Nickel contact dermatitis is the most common skin reaction to nickel carbonyl, often referred to as 'nickel itch.' It is also a suspected carcinogen (cancer-causing agent).

Carry out an occupational health risk assessment before undertaking any work associated with the handling of catalysts.

2.6 Crushing hazards



When digging through catalyst, specialist contractors must take care that no high 'wall' of catalyst is left in place, ready to cave in if disturbed.

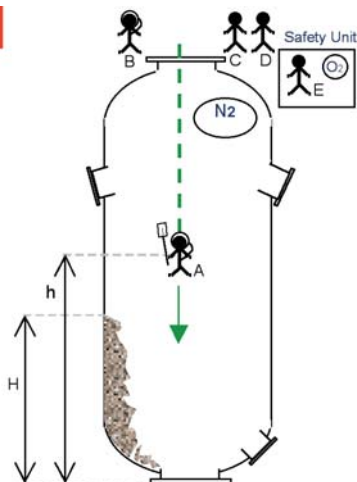
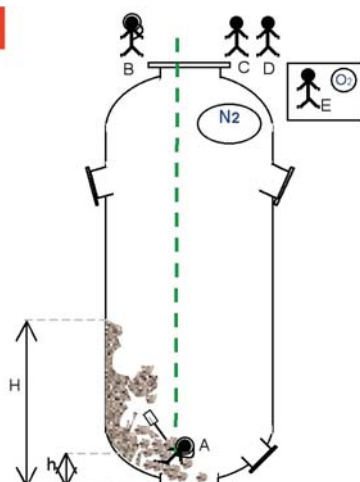
A recommended maximum height is 0.8 to 1.0 m (2.6–3.3 ft).

- Entry personnel should be properly trained on this issue and a good control of the work by both the specialist contractor and the refinery team is essential.

- Specialist contractors are responsible for the rescue of personnel from a confined space that is knowingly under 100% nitrogen.
- The specialist contractor's emergency response team must always be well equipped and ready to enter the reactor in case of an incident.

ACCIDENT

A nitrogen entry specialist contractor was buried under hot catalyst while carrying out catalyst unloading work in a nitrogen purged reactor at a refinery. This work was carried out despite a clear recommendation on the permit that any 'inert entry diver must never come under the catalyst level'.

1**2**

The worker was successfully rescued by his partner who was fully equipped, suited and on stand-by. The victim suffered burns to his neck. Local catalyst self ignition was made possible because of air leakage from a damaged supply hose (and also maybe because of the atmosphere disturbance when the catalyst wall fell). This successful rescue was possible due to a recent change of procedure requiring a stand-by person to be available at all times and prepared during any vessel entry under nitrogen purge.



Severe burns to
safety harness and
damaged air hose



2.7 Other hazards associated with catalyst handling

It is worth noting that other 'more conventional' incidents frequently occur during catalyst loading and unloading operations, for example:

- A fork-lift truck overturned and crushed the operator while transporting catalyst on pallets.
- An operator fell while handling catalyst at height (the use of a rope ladder in a 30-metre (100 ft) high reactor is unacceptable).
- The weak internal structure of a reactor collapsed under the weight of an operator.
- Dropped object during lifting of equipment of catalyst (in containers or big bags).

Provide an exclusion zone around catalyst handling areas. Conditions for entry shall be stipulated on work permit and procedures.

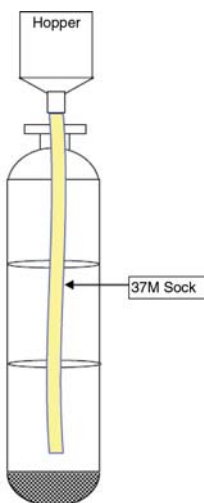
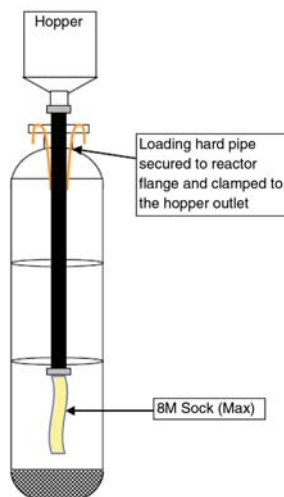
ACCIDENT A forklift truck was moving catalyst drums to the hydrofiner loading area. It collided with a lamp-post and knocked it down. The driver was thrown out and the vehicle overturned trapping him underneath. The driver died from the injuries he received during this incident.



ACCIDENT

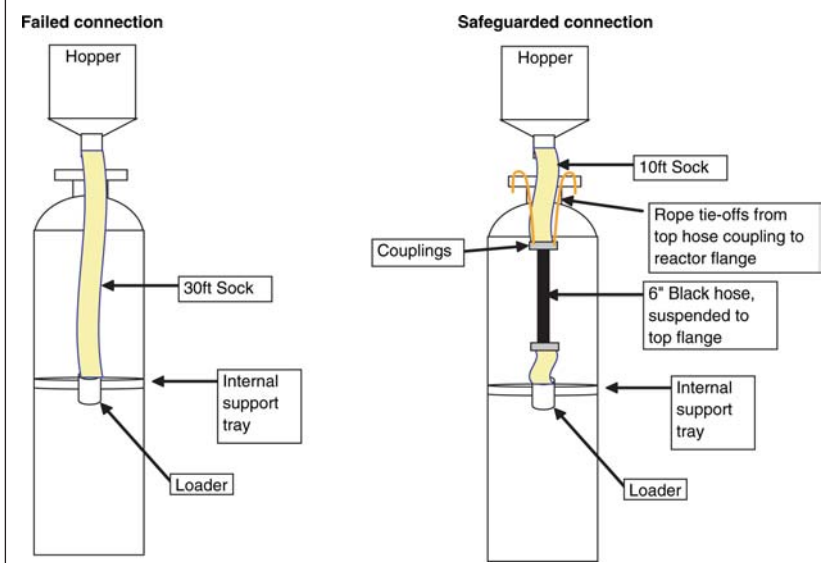
During the loading phase under air of a catalyst change out of hydrodesulfurizer (3 beds) reactor, a technician entered the reactor to commence sock loading of catalyst in the bottom bed. Loading of the required layers of ceramic balls had previously been completed and the target was to load 4 m³ (141 cu ft) of catalyst to bring the level up to the first thermocouple. A short time after loading of the catalyst was underway the flexible loading sock that was being used to convey the catalyst from the loading hopper to the bottom of the third bed became detached from the loading hopper. The loading sock had become overfilled with catalyst and a large portion of it fell to the bottom of bed number three where the technician was working. The loading sock struck the technician on the back of his neck. Whilst being restrained by his umbilical line and unable to roll with the blow, the force of the loading sock broke his neck resulting in a fatal injury.

The catalyst sock (approximately 37m (120 ft) in length) far exceeded the recommended maximum length and was unable to support the weight of the catalyst.

**Detached sock in reactor****Loading hopper valve****Incident configuration****Configuration recommended by investigation team.**

ACCIDENT

A similar incident occurred in another refinery whilst the catalyst loading was being performed under nitrogen atmosphere. Two contractors were hit by a catalyst loading sock that separated from the loading hopper, right above the reactor top flange. There was the potential for two fatalities, if dropping of the sock had damaged the air supply of the two contractors working in the vessel under inert entry, or potential for serious physical injury due to the 320 kg (700 lb) weight of the catalyst sock (appx. 30m (98ft) long).

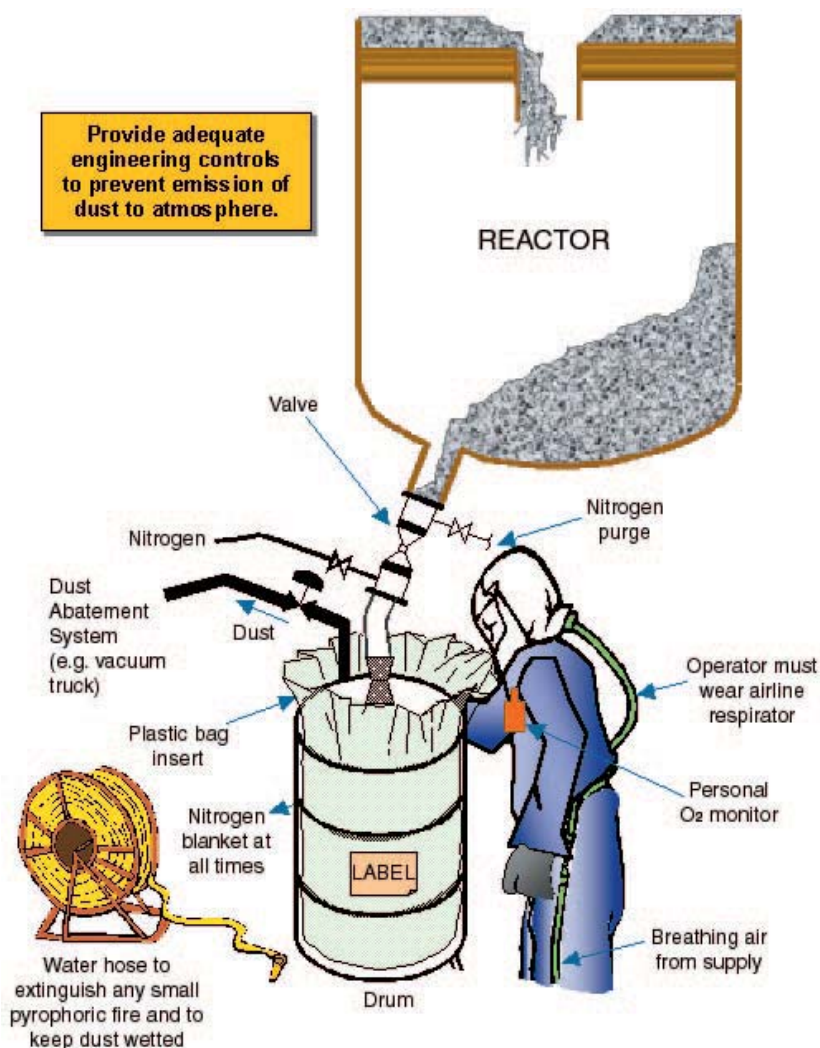


The risk analysis for these operations should consider the following issues:

- Is there a real need to load catalyst under inert atmosphere? Could it be done under air (using a different catalyst or using filtering masks)?
- Do the workers need to be in the vessel every time a big bag is emptied? Could they enter only after the big bag is emptied?
- Are the air hoses protected and entering by another manhole? What if the big bag is dropped on the funnel, jamming the manhole and severing the air hoses?

2.8 Catalyst unloading

Typical discharge of unregenerated catalyst to prevent pyrophoric activity.



2.9 Catalyst labelling

Drums of spent or unregenerated catalyst must be properly labelled. For example:

- Danger
- contains nickel
 - pyrophoric; will catch fire on exposure to air
 - avoid dust inhalation and skin contact
 - cancer suspect agent



2.10 Catalyst disposal

The final word is for the protection of the environment. Unregenerated catalysts and used catalysts must be sent to an approved recovery plant through a reputable contractor meeting all statutory requirements for shipment and handling.



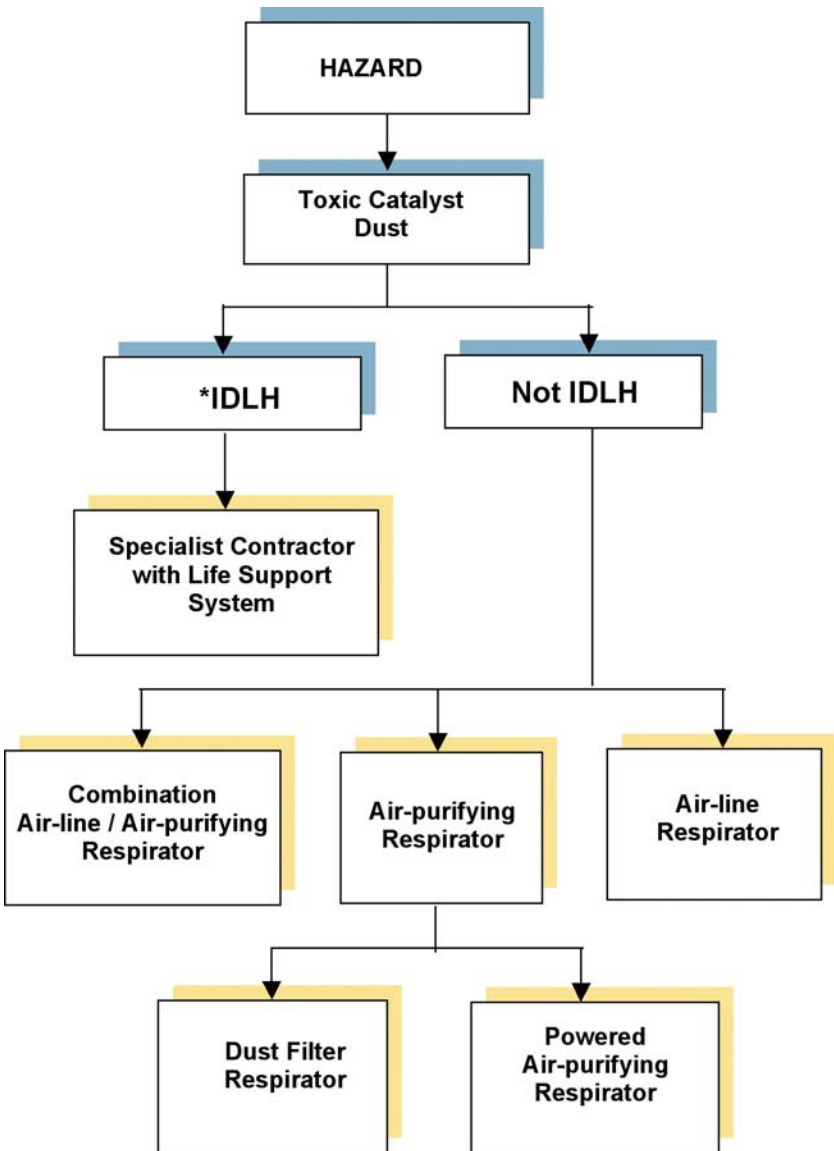
*Wrong way to dispose
of spent catalyst*



*Melted metals recovered
from used catalysts*

Unregenerated catalysts shall only be sent off site in high integrity containers correctly labelled to approved reprocessing plants.

2.11 Respiratory and protective equipment requirements



Guide to respirator selection *(IDLH = Immediately Dangerous to Life & Health)



Air-purifying Respirators have filters, cartridges, or canisters that remove contaminants from the air by passing the ambient air through the air-purifying element before it reaches the user. E.g. dust mask, gas mask.



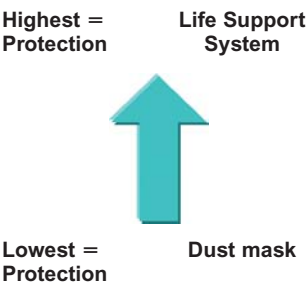
Combination Respirators Continuous flow air-line/air-purifying respirator with full facepiece. Filters are facepiece-mounted.



Air-line Respirators supply clean air directly to the user from a source other than the air surrounding the user. E.g. air-line respirator, self-contained breathing apparatus (SCBA).

Respirator assigned protection factor

The assigned protection factor of a respirator reflects the minimum level of protection that a properly functioning respirator would be expected to provide to a properly fitted and trained user. For example, a protection factor of 10 for a respirator means that a user could expect to inhale no more than one tenth of the airborne contaminant present.



Permitted maximum airborne concentration of catalyst dust around technicians	<	Protection Factor of Respirator*	×	Maximum permissible exposure limit for the particulate/contaminant*
Note: < = Less Than				

* Refer to manufacturers literature, national standards and NIOSH Pocket Guide to Chemical Hazards for further information. Visit NIOSH web pages <http://www.cdc.gov/niosh/homepage.html> for details.

TASK TYPES OF RESPIRATORS	Entry into barriered off area	Inside Inerted reactor	Standby attendant adjacent to top manhole	Working adjacent to unregulated catalyst drum filling	Catalyst drum handling outside barriered off area	Refilling reactor with catalyst in air (normal atmosphere)	Refilling reactor under nitrogen	Rescue Team (specialist contractors only)
Dust mask	✖	✖	✖	✖	✖	✖	✖	✖
Air purifying respirator with full face piece	✖	✖	✖	✖	✔	✖	✖	✖
Air line respirator with full face piece	✔	✖	✖	✔	✔	✔	✖	✖
Positive pressure demand Self Contained Breathing Apparatus (SCBA)	✔	✖	✖	✔	✔	✔	✖	✖
Full life support system	✔	✔	✔	✔	✔	✔	✔	✔

Respirator selection for various tasks involving use of nitrogen and catalyst handling.

Besides wearing the correct respirator when handling catalyst, it is also important to avoid skin contact with the catalyst by wearing appropriate dust proof coveralls. Ensure that coveralls are removed and properly disposed of at the end of each shift/work period.



Ensure that workers are informed of the risks of not wearing the correct personal protective equipment (PPE) and are trained in the proper use (including 'fit test') of the appropriate respirator.

ACCIDENT

A contract labourer was asphyxiated as a result of working in an oxygen deficient atmosphere whilst wearing a dust mask. Prompt action by operating staff in rescue and resuscitation saved this man's life. A 'Confined Space Entry Permit' was issued to allow entry to the reactor, which clearly stated that the vessel was: (a) under a nitrogen purge; (b) deficient in oxygen; and (c) that breathing apparatus must be worn. However, conditions were not explained to the person in charge of the job, and the man carrying out the work was not informed that the vessel was under a nitrogen purge and the atmosphere was deficient in oxygen. Previously the workman had worked inside a similar vessel near the one where the incident occurred. The previous vessel had been gas freed and its oxygen content was acceptable so the men assumed that the conditions were the same and worked inside wearing only dust masks.

Good practice

- Personnel must be trained to realise that each vessel entry is a separate job covered by a separate confined space entry permit with different conditions and precautionary measures. Working conditions differ from vessel to vessel and from day to day.

Air-line respirators

Air-line respirators are available in many types of configuration. Each type has specific limitations that must be considered. One major advantage is that air-line respirators can protect against both gases and dusts, and its use is not limited by filter loading or cartridge capabilities (except for combination air-purifying and air-line respirators). These devices tend to consist of more components than air-purifying respirators, perhaps making them more complex. Care must be taken to provide the following:

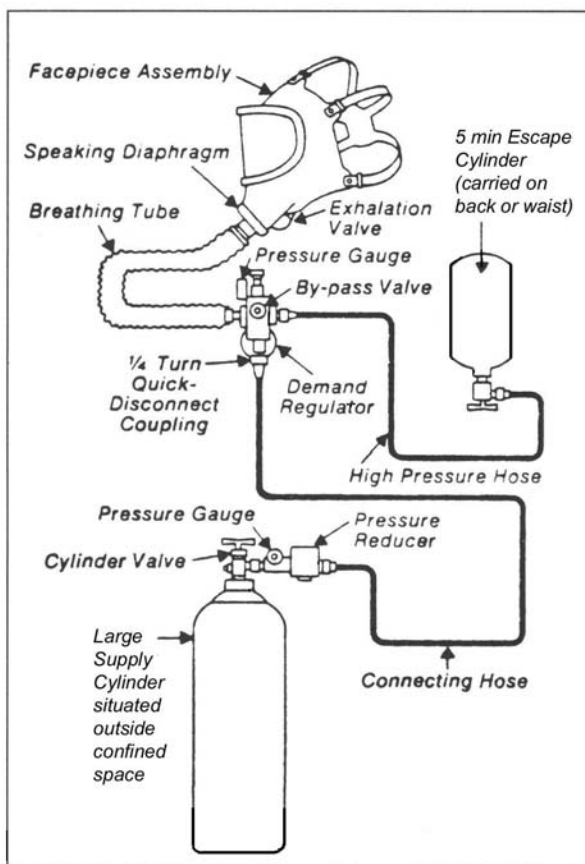
- Good quality air for breathing to a recognized standard.
- Sufficient quantity of air to meet the respirator's operating requirements (as indicated on the approval label) and use duration.
- A vortex fitted to the air supply to provide cool air to prevent heat stress in hot climates. This requires a much bigger air flow rate. The cool air must not be so cold that condensation occurs on the mask and impairs vision.

Air-line respirator and SCBA are *not* life support systems suitable for work inside a nitrogen atmosphere.

Continuous flow air-line respirator with vortex for airflow control valve. Vortex provides cooler air to worker. Note the filter and regulator panel in upper right-hand corner.

NOTE: This is not a full life support system





Schematic diagram of a typical air-line respirator with auxiliary escape air supply worn on the waist.

ACCIDENT

Two men were found dead inside the CO converter in an ammonia plant during the removal of catalyst from the converter under nitrogen cover. One operator was working inside the CO converter which was under a nitrogen blanket wearing *conventional* compressed air breathing apparatus; the air was supplied from bottles situated outside the vessel. He was also equipped with a separate emergency air supply from a small bottle attached to his waist but he had made no attempt to switch it on. The other man remained outside the vessel to act as a 'safety look out'.

Investigations concluded that the man working inside the vessel had a poor seal around the face mask with a faulty air-line and was unaware that the air he was breathing was slowly becoming deficient in oxygen (the symptoms of asphyxiation in the early stages can be loss of judgment and loss of ability to think clearly). The 'look out' man was found inside the vessel without breathing apparatus and it was assumed that he must have gone inside the vessel to rescue his fellow worker.



Lockable helmet connected to Specialist Full Life Support System (refer to figures at the end of this section for details)



*Poor face seal
(see respirator
selection matrix
in section 2.11).*

SPECIALIST LIFE SUPPORT SYSTEM

Unlike the Specialist Life Support System, breathing apparatus normally available at refineries and chemical plants does not provide an adequate safeguard to cover the risks associated with work in an inert gas or nitrogen atmosphere. This work can *only* be carried out by specialist contractors.

The precautions for work in an inert atmosphere must reflect the possibility and seriousness of an incident occurring and therefore requires the use of very sophisticated equipment and experienced personnel not normally available at refineries. This equipment and the expertise that goes with it is only available from outside specialist contractors.

2.12 Catalyst specialist contractors for inert gas/nitrogen reactors

Management must thoroughly scrutinize the management systems and associated procedures employed by inert gas 'specialist' contractors prior to the award of contract.

In view of the restricted space inside reactors and the limited time available to save an 'unprotected' operative inside an nitrogen atmosphere, 'specialist' contractors must prove that they have the required back-up respiratory and other emergency/rescue equipment to handle the range of potential failures.

Due to the hazards of working in nitrogen atmospheres, alternative processes not requiring entry into an inert atmosphere must be considered and, when appropriate, become the preferred alternative.

Pre-contractual arrangements

- Prior discussions involving site safety advisor, maintenance and operations personnel, specialist contractor's project leader. Final approval of procedures by Site Manager.
- Precautionary measures must be agreed and responsibilities assigned.
- Emergency response/egress procedures to be agreed. Trial rescue must be carried out before work commences.
- Visit a site to witness similar work being carried out by proposed specialist contractor.
- Formal appointment of site representative to manage the project.



Pre-requisite for specialist contractors

- Effective safety management system including a drug / alcohol abuse policy.
- Certified life support equipment.
- Safety and operations manual covering procedures to undertake such hazardous work.
- Inert gas confined space training document/certificate for each potential entrant.
- Proven medical fitness of personnel (current certificate).
- Detailed emergency rescue plan.
- Written reports of past similar works undertaken.

Typical specialist contractor's equipment

- Proven certified safety helmets that are lockable providing head protection, primary and secondary regulators and communication system.
- Certified compressed air breathing cylinders.
- Emergency Air Egress bottles connected to each contractor providing an individual independent emergency escape supply.
- An independent backup emergency supply of air available inside the reactor.
- A monitoring station equipped with the following and positioned close to job site:

- a primary air pressure monitor for each individual wearing helmet with audible and visual alarms to indicate low primary supply and regulated pressure;
 - a secondary air pressure monitor for each individual wearing a helmet, including an alarm indicating the cut-in of the secondary supply to any of the helmets and to alarm to indicate a low supply pressure;
 - a battery-fed power supply to cut in automatically on failure of the electrical supply to the monitoring station;
 - an open line communications link between entry personnel and persons supervising the entry. A communications link should also be established between those supervising the entry and emergency standby personnel;
 - communication system between entry person, supervisor and emergency standby attendant.
- Armored umbilical cords for each entry man.
 - Safety harnesses should be of the parachute type.
 - Sufficient instruments to continuously monitor O₂ level together and other contaminants.
 - Portable O₂ meter for the outside atmosphere.
 - Winch for swift removal of personnel from reactor.
 - O₂ resuscitator and at least one entry-monitoring team certified for cardio-pulmonary resuscitation.

Typical procedures

A detailed written procedure to include the following:

- a vessel diagram showing:
 - ◆ isolation points
 - ◆ N₂ purging inlets
 - ◆ O₂ monitoring points
 - ◆ entry point
 - ◆ internal fittings
- safety / procedure check list;
- all remaining potential hazards;
- details of equipment to be used;
- all precautionary measures;
- details of type of Work Permit required for each stage of the operation;
- emergency Rescue Plan for the specific vessel;
- briefing of site personnel on the above requirements prior to commencement of work.



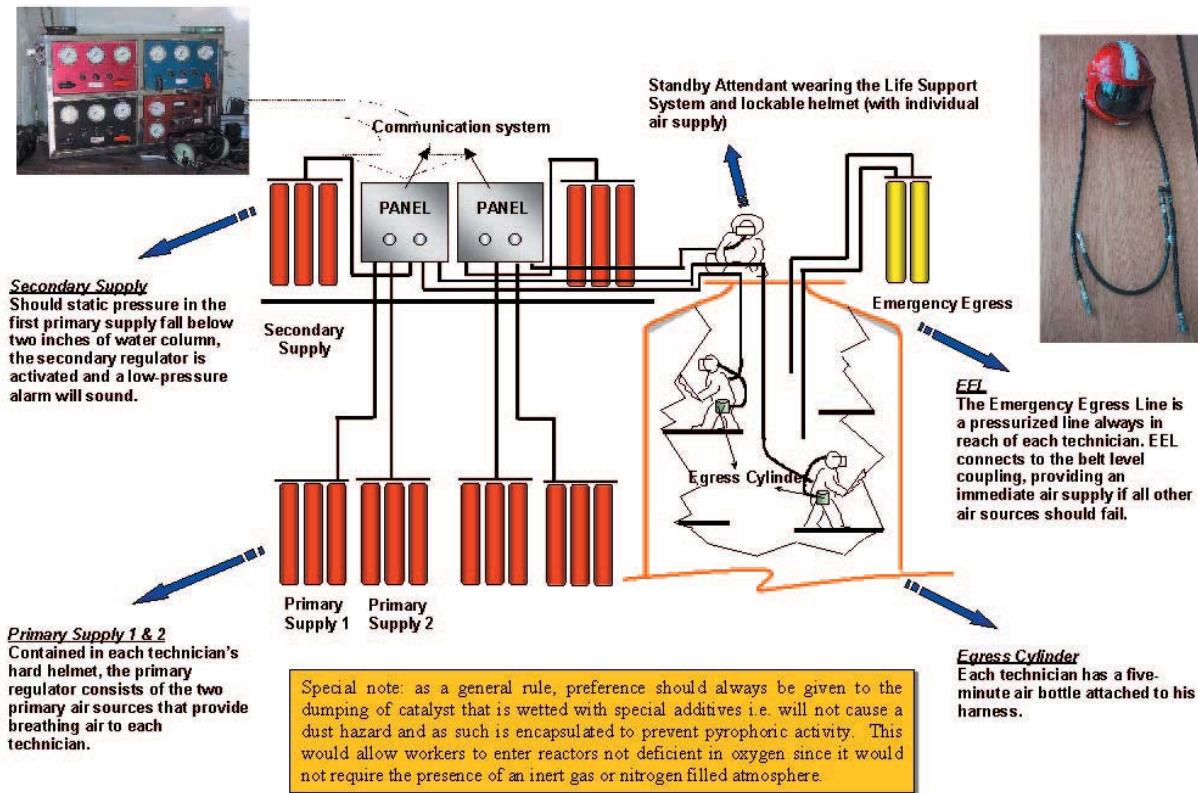
Specialist contractors including their safety management system, equipment, working methods and previous work experience must be thoroughly reviewed before being awarded a contract to remove catalyst from an IDLH atmosphere.

Areas of responsibilities (should be clearly defined in writing)

Site Owner / Representative	Specialist Contractor
- Specify all hazards to contractors and own staff - Enforce Permit to Work System and agreed procedures - Isolate equipment for entry - Minimise presence of other contaminants during the shutdown and purging operations - Provide reliable N₂ supply, if supplied by site - Provide safe access to place of work - Prevent unauthorized access to the area - Provide continuous supervision of work; monitor N₂ purge and provide standby fireman - Provide FM radio sets for communication between site representative and contractor's supervisor - Monitor outside barricaded area for O₂, toxics and flammables.	- Responsible for the safety of personnel - Compliance to agreed protective equipment requirements. - Ensure adequate number of qualified, experienced and properly equipped personnel - Brief employees of any additional hazards and take appropriate measures - Monitor local working environment and arrange precautions if additional necessary e.g. oxygen and flammable gas detectors. - Ensure Emergency Response / Egress Plan in place and ready - Comply to site safety rules and procedures - Ensure any change to agreed procedures is authorized through the site's Management of Change procedure

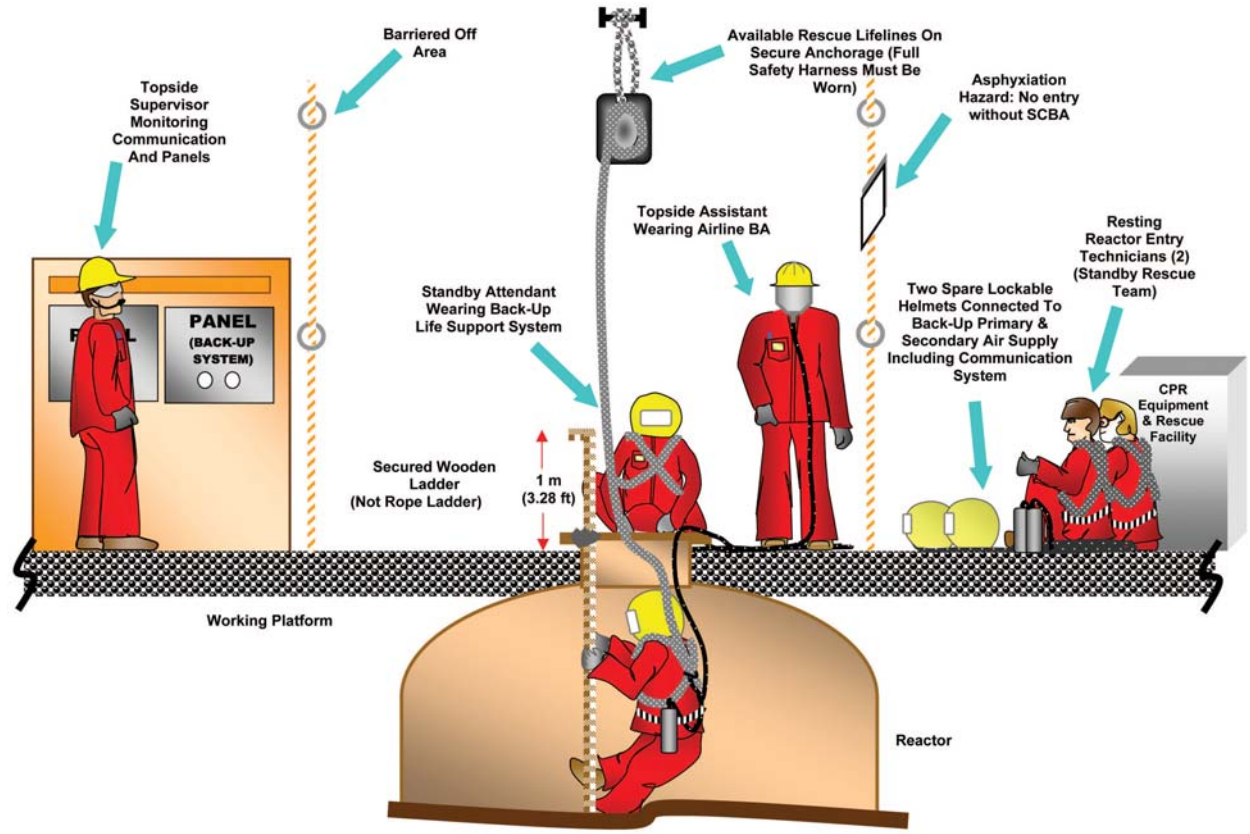
Joint Responsibilities
- To ensure O₂ level is kept down to a safe level (below 2 % v/v) inside reactor - Number of N₂ injection points - Purge position and monitoring of N₂ supply - Number and position of sampling heads for O₂ meters/alarms and person to calibrate and monitor this equipment. Both inside and outside reactor. - Minimum N₂ flow and daily consumption - Continuous temperature monitoring within the vessel

To read more on work in inert atmospheres, refer to API Publication 2217A *Guidelines for Work in Inert Confined Spaces in the Petroleum Industry*.



Example of a high integrity life support system used by a specialist contractor

Typical personnel arrangements at top of reactor



3

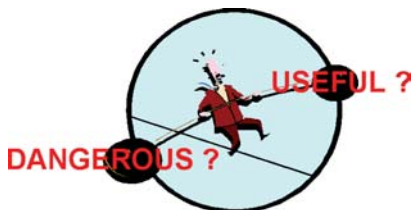
Some points to remember

1. Moving affected and unconscious persons from a nitrogen atmosphere into fresh air is not enough to promote recovery. The patient has to be physically resuscitated in order to restore the oxygen supply to the brain.



2. Nitrogen (N_2) is a very common and extremely dangerous gas that you may be exposed to at a refinery or chemical plant. You must always be on your guard.

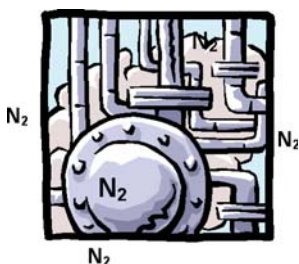
3. Most useful or most dangerous gas???



4. An asphyxiant is a chemical (gas or vapour) that can cause death or unconsciousness by suffocation. Simple asphyxiants such as nitrogen, displace oxygen in air. They become especially dangerous in confined or enclosed spaces. Chemical asphyxiants, such as carbon monoxide and hydrogen sulphide, interfere with the body's ability to absorb or transport oxygen to the tissues.

5. An Oxygen Deficient Atmosphere is an atmosphere with oxygen content below 19.5% by volume. (OSHA Definition)





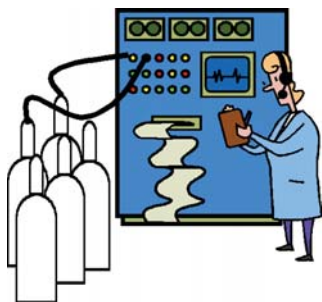
6. Nitrogen can create an oxygen deficient atmosphere outside the vessel/piping that is being purged with this medium.

7. You are asphyxiated with only your head inside an oxygen deficient atmosphere—not your whole body.



8. Keep technicians away from areas outside manholes that could be deficient in oxygen (unless authorized through a Confined Space Entry Permit).

9. Do not confuse N_2 with air !!!



10. A mobile, self-contained, high pressure cylinder storage system undoubtedly provides the highest integrity, freedom of operation and safety when using air-line breathing apparatus. Most sites prefer to either use bottled air, supplied from a trolley set (wheeled trolley with air bottles on it) or from a bank of dedicated air bottles located on the plant. There is a requirement to ensure that the quality of air in supply bottles is correct, whether they are refinery filled or otherwise by a respectable external company.

11. Always check the oxygen level first before carrying out a flammable gas test using an explosimeter in preparation for hot work or confined space entry.



12. If you see someone lying unconscious on the ground or through the opening of a tank or pipe. Call the fire department / rescue team. Never enter a confined space or area alone to give help. Call for assistance.



13. Unregenerated catalyst is normally a self-heating substance and often pyrophoric. On exposure to air, it can rapidly catch fire.



14. Wear the correct personal protective equipment and use the correct storage containers when handling catalyst.

15. Catalyst dusts are a hazard to health—wear the stipulated respirator that provides the appropriate level of protection.

16. Provide an exclusion zone around catalyst handling areas. Conditions for entry shall be stipulated on work permit and procedures.





17. Carry out an occupational health risk assessment before undertaking any work associated with the handling of catalysts.

18. Unregenerated catalysts shall only be sent off site in high integrity containers correctly labelled to approved reprocessing plants.



19. Provide adequate engineering controls to prevent emission of dust to atmosphere.

20. Specialist contractors including their safety management system, equipment, working methods and previous work experience must be thoroughly reviewed before being awarded a contract to remove catalyst from an IDLH atmosphere.



21. Unlike the Specialist Life Support System, breathing apparatus normally available at refineries and chemical plants does not provide an adequate safeguard to cover the risks associated with work in an inert gas or nitrogen atmosphere.

22. Preference should always be given to the dumping of catalyst that is wetted with special additives i.e. will not cause a dust hazard and as such is encapsulated to prevent pyrophoric activity. This would allow workers to enter reactors not deficient in oxygen since it would not require the presence of an inert gas or nitrogen filled atmosphere.

23. Due to the hazards of working in nitrogen atmospheres, alternative processes not requiring entry into an inert atmosphere must be considered and, when appropriate, become the preferred alternative.



**If you have any doubts,
please consult the safety procedures,
Do not hesitate to ask your Safety Department
for more information.**



4

Test yourself!

1. Whatever its state, the only risk related to nitrogen is suffocation.
True ☐ False ☐
2. The smell of nitrogen immediately identifies an oxygen deficient environment.
True ☐ False ☐
3. Testing for flammable gases in pipes purged with nitrogen does not pose any problems with explosimeters.
True ☐ False ☐
4. There is no risk in leaving a bottle of nitrogen in a small room.
True ☐ False ☐
5. An air-purifying respirator will adequately protect me in an oxygen deficient atmosphere.
True ☐ False ☐
6. It is safe to pour liquid nitrogen on myself.
True ☐ False ☐
7. Even if I inhale pure nitrogen, I will be safe for a few minutes thanks to the oxygen stored in my blood.
True ☐ False ☐
8. Nitrogen is not the only gas that can cause suffocation.
True ☐ False ☐
9. Nitrogen is only used on the site for preparing equipment for maintenance (never for other purposes or in the tank farms)
True ☐ False ☐
10. Unregenerated catalyst can be pyrophoric.
True ☐ False ☐
11. Handling, unloading, storage and shipment of unregenerated catalysts is normally carried out under nitrogen cover.
True ☐ False ☐

12. Catalyst dust is not a threat to our health and therefore air-line respirators are not required.

True ☐

False ☐

13. Dust masks always provide adequate protection to prevent inhalation of catalyst particles.

True ☐

False ☐

14. Specialist contractors for inert gas confined space entry projects use conventional SCBA because they are trained underwater divers.

True ☐

False ☐

15. Providing the atmosphere is between 19.5% and 23.5% oxygen, it is always safe to enter the confined space.

True ☐

False ☐

16. Open manholes are dangerous because technicians are likely to put their heads inside.

True ☐

False ☐

17. Oxygen deficient atmospheres can be created outside a confined space.

True ☐

False ☐

18. An occupational health risk assessment is required prior to any possible exposure to catalyst, to protect the technicians and the environment from harmful effects.

True ☐

False ☐

19. Conventional breathing apparatus normally found in refineries provides adequate protection for working in an inert / nitrogen-filled confined space.

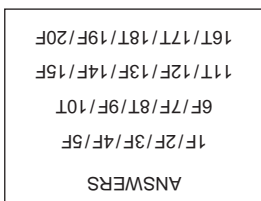
True ☐

False ☐

20. All air compressors provide the quality of air necessary for breathing apparatus.

True ☐

False ☐



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- *Confined Space Entry*, ISBN 978 0 85295 479 4.

Your notes

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- John Bond, IChemE Loss Prevention Panel member

Note: BP also published:

- in 2003 a comprehensive 'Nitrogen Information Package' (including video, CDrom, slides, quiz, leaflet, poster, good practice documents). Some pictures from this video have been included to illustrate incidents described in this booklet.
- and in 2005 a specific Computer Based Training module.