

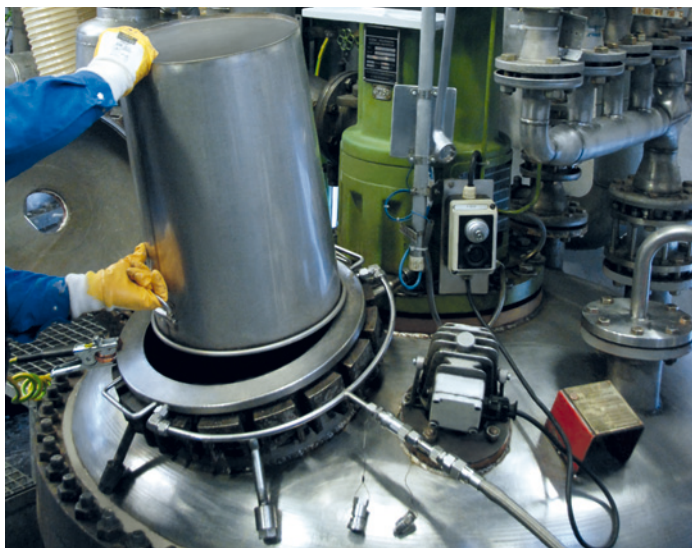
White Paper. Inerting in the chemical industry.

Authors Dr Hans-Jürgen Reinhardt – Kaufbeuren, Germany
Hans-R. Himmen – Unterschleissheim, Germany
Published in Hydrocarbon Processing, April 2010

Contents.

- 03 Introduction
- 04 Survey of applications/Inerting methods
- 07 Properties of gases
- 08 Equipment for inerting
- 10 Software for inerting
- 11 Safety in inerting
- 12 Sample applications
- 15 Inert-gas production and supply/Linde Services

Introduction.



In many processes in the chemical industry, it is necessary to:

- prevent explosions
- eliminate undesired reactions
- keep moisture away from products
- ensure safety when maintenance is being performed

These goals cannot always be achieved through technology and equipment design alone, and so inert gases and the special apparatus needed for their use often come into play. Key goals include holding down the level of oxygen and preventing oxygen and/or moisture from coming into contact with reactive or adsorptive products. The principal technique for these purposes is inerting (inert-gas blanketing) with nitrogen, less frequently with carbon dioxide or in exceptional cases with argon. The most common function of the inert gas is to displace air, which contains oxygen and often moisture as well, or to keep air away from products. Air displacement can be partial or complete.

There are many situations in which inerting is the only way to meet safety standards in processing and maintenance. In other cases, inerting is used to maintain and improve product quality. Fields that make use of inerting include refining, basic chemistry, petrochemistry and the manufacture of speciality and fine chemicals.

Survey of applications.

In line with the variety of substances, technologies and apparatus applied in the chemical industry, there are many options for inerting with nitrogen, carbon dioxide and argon. These include above all:

- Reactors, stirred tanks
- Centrifuges and vacuum filters
- Size-reduction and mixing equipment
- Storage tanks and vessels
- Dryers, silos
- Charging systems
- Oil and fuel pipelines
- Industrial services

Important requirements that favour the use of inert gases include:

1. Prevention of explosive atmosphere formation in apparatus such as reactors
2. Safe startup and shutdown of plants and apparatus
3. Avoidance of explosion risks in storage and transport of combustible substances
4. Protection of products against atmospheric oxygen when oxidation reactions would impair quality
5. Protection against atmospheric moisture, either to maintain product quality or to ensure optimal downstream processing (as for example in grinding)
6. Prevention of safety and health hazards during maintenance of equipment, apparatus and piping

Inerting methods.

Inerting techniques exist for a great variety of tasks:

→ **Purging**

An inert gas is admitted to an apparatus or pipeline in order to displace a process gas from it.

→ **Blanketing**

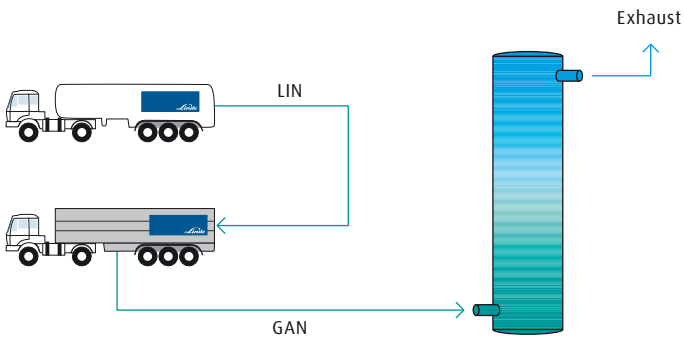
Blanketing is practised when constant inert conditions must be maintained over a product, for example in a vessel, in order to prevent explosions, discolouration, polymerisation and other undesirable changes in quality. The operation is monitored through the flow rate and pressure of the inert-gas stream and/or the oxygen level in the gas exiting the vessel.

→ **Sparging**

Sparging means passing finely dispersed gas through a liquid in the form of bubbles in order to improve mixing and to increase the surface area for gas-liquid mass transfer. The technique finds use in chemical and biological reactions and also in stripping. Nitrogen is used for example to strip oxygen from oil, wastewater and other products.

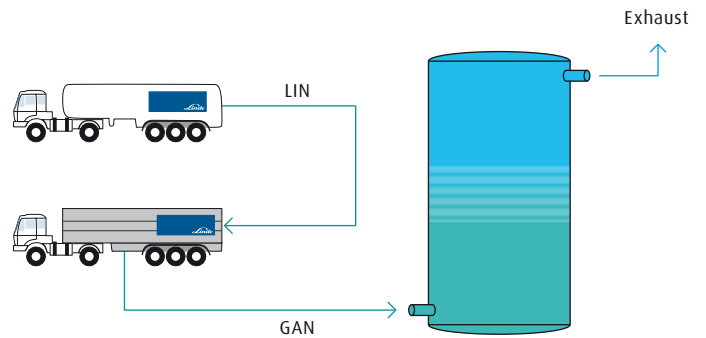
Several methods of purging are applied:

Displacement purging



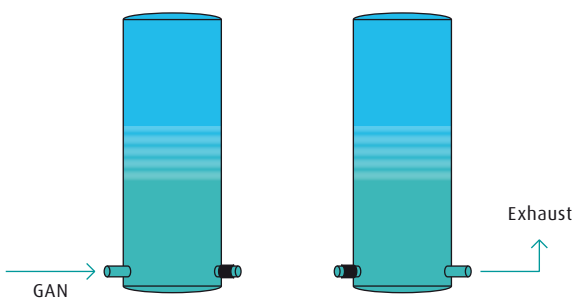
In displacement purging, vaporised nitrogen (gaseous N_2 , GAN) is injected into an open apparatus to displace a dangerous or harmful gas. The method is used primarily where the H/D ratio is large. The quantity of nitrogen required is commonly of the order of 1.2 times the capacity of the vessel.

Dilution purging



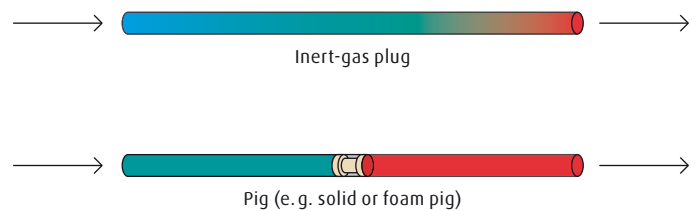
Dilution purging involves the introduction of gaseous nitrogen into an open apparatus to dilute a dangerous or harmful gas, which is then discharged through the exhaust. The method finds use where the H/D ratio is smaller. The nitrogen consumption is roughly 3.5 times the capacity of the vessel.

Pressure-swing purging



In pressure-swing purging, a closed apparatus is pressurised with gaseous nitrogen. The dangerous or harmful gas escapes first when the pressure is released. The four steps closure, injection, opening and release are continued until the desired concentration is achieved. The process can employ overpressure or underpressure. Pressure-swing purging is practised when, for example, the inlet and outlet ports are located close together.

Inerting of pipelines



Two methods are used to expel liquids or gases from a pipeline and to inert the system:

1. The process gas is forced from the pipeline by a plug of inert gas.
2. A "pig" driven by nitrogen pressure displaces the process gas.

From a safety standpoint, the limiting oxygen concentration (LOC) is a key criterion for inerting. For a specific fuel/air/inert-gas mixture, this parameter is the highest concentration of oxygen at which no explosion takes place. The LOC must be determined by experiment. The table below gives selected examples with nitrogen and carbon dioxide as inerting agents; the LOC values for carbon dioxide can be as much as 25 % higher than for nitrogen.

LOCs for selected fuels

Fuel	LOC, vol. %	
	Nitrogen	Carbon dioxide
Benzene	9.0	11.4
Butadiene	11.0	13.3
Cyclopropane	10.8	13.0
Ethylene	6.9	9.1
Hexane	10.0	12.4

The exhaust gas from purification and inerting must be treated before it can be discharged into the atmosphere. Treatment is often effected or aided by cryocondensation, which utilises the cold of the nitrogen employed for inerting. So N_2 can be used twice.

The time and the amount of nitrogen required for inerting depend not only on the inerting method but also on the degree of mixing (e. g. plug flow, ideal mixing, bypass). Other controlling conditions include the properties of the gas, the geometry of the space being inerted, the inlet and outlet port configuration and, not least important, the flow velocity.

An example of a geometrical parameter is the H/D ratio of the vessel.

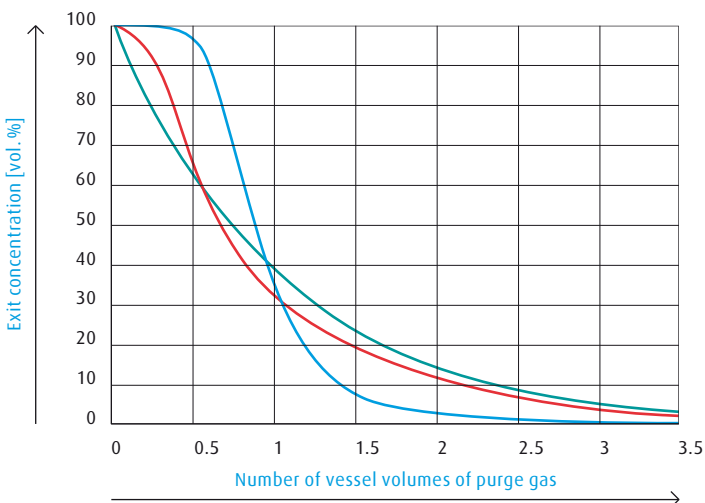
The following is a rule of thumb:

- $H/D < 1$: No plug flow (dilution purging)
- $H/D > 10$: Predominantly plug flow (displacement purging)

If the aim of inerting is to attain a very low oxygen concentration, high-purity nitrogen must be employed.

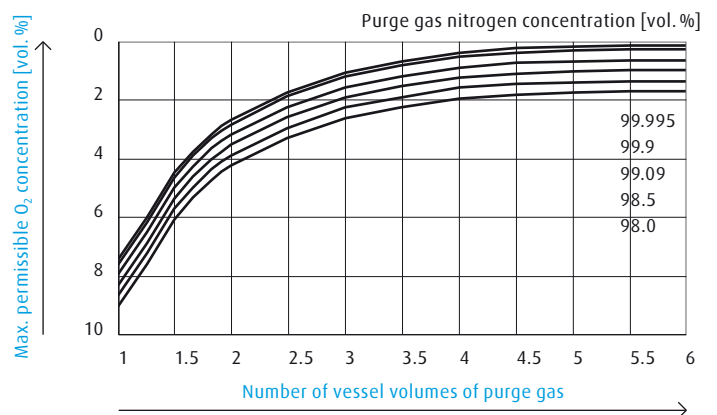
Influence of H/D ratio on purging efficiency

— $H/D = 3$ — $H/D = 1$ — $H/D = 1/3$



As the H/D ratio increases, the flow approaches plug flow and fewer vessel capacity changes are needed. As a consequence, nitrogen consumption and inerting time drop.

Influence of nitrogen concentration in the purging gas



The graph shows that if the maximum permissible oxygen concentration is very low ($< 1\%$), the nitrogen purity must be over 99%. Using a higher purity makes it possible to reduce the number of volume replacements needed.

Properties of gases.

The gases typically used are nitrogen and carbon dioxide. In some few cases, argon is also applied. The table below describes selected properties of these three gases.

Selected properties of gases used for inerting

Property	Nitrogen	Carbon dioxide	Argon
Detectability by senses	Colourless, odourless	Colourless, odourless	Colourless, odourless
Reactivity	Unreactive because of N≡N	Unreactive because of O=C=O	Chemically inert
Fire hazard	Not combustible	Not combustible; extinguishes combustion	Not combustible
Molar mass	28 g/mol	44 g/mol	39.948 g/mol
Max. allowable workplace concentration	–	5,000 ppm	–
Density at 1 bar, 0 °C	1.250 kg/m ³ ; relative density in gas form (air = 1): 0.97	1.977 kg/m ³ , relative density in gas form (air = 1): 1.52	Relative density in gas form (air = 1): 1.380
Boiling point at 1 bar	-195.8 °C	–	-185.86 °C
Melting point at 1 bar	-209.86 °C	-56.6 °C (triple point)	-189 °C
Sublimation point at 1 bar	Not applicable	-78.5 °C	Not applicable
Critical point	-146.95 °C (33.94 bar, 314 kg/m ³)	-31.21 °C (73.83 bar, 466 kg/m ³)	-122.4 °C
Solubility in liquids	In water: 20 mg/l	In water: 2,000 mg/l	In water: 61 mg/l
Health relevance	Suffocating at high concentrations	Hazardous to health at higher concentrations; lethal at > 8 vol. %	Suffocating at high concentrations
Delivery forms	<ul style="list-style-type: none"> → Compressed, up to 300 bar → Cryogenically liquefied, down to -196 °C 	<ul style="list-style-type: none"> → Liquefied under pressure, about 55 bar, ambient temperature → Cryogenically liquefied, 20 bar, -20 °C → Solid (dry ice), -78.5 °C 	<ul style="list-style-type: none"> → Compressed, up to 300 bar → Cryogenically liquefied, down to -183 °C

The properties of carbon dioxide permit its use not only for inerting but also for extinguishing fires in municipal waste bunkers and silos containing biomaterials. A special nozzle has been developed for this purpose.



The expansion nozzle shown at left ensures that the carbon dioxide is completely vaporised while remaining as cold as possible. In particular, it prevents the formation of CO₂ snow. The gas issues from the nozzle at a low velocity so that a stable layer can form above the bulk material.

In certain cases, as in the production of food supplements, argon replaces nitrogen as inerting agent. The principal reason is that argon, being heavier than air, remains in the vessel when it is opened. The use of argon greatly improves the exclusion of oxygen from product contact.

Equipment for inerting.

In line with the needs of the chemical industry, special equipment has been designed, built and successfully employed for inerting:

Inert-gas control units



A measuring and metering station for the inerting of mixers or reactors

Inert-gas locks

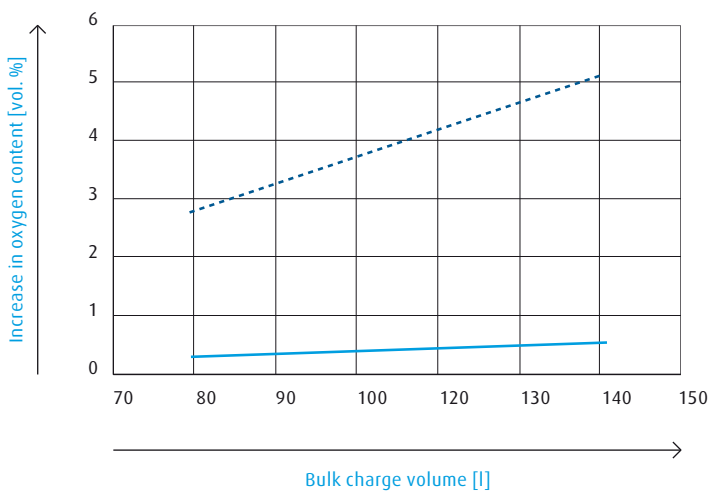
In fine and speciality chemicals manufacturing, some process stages – such as reactions in stirred tanks – involve not only liquids and gases but also solids. Inert-gas locks have been developed to ensure safe handling of solids and to suppress side reactions such as oxidation due to the admission of oxygen when solids are charged into reactors and vessels. These devices also reduce emissions and provide protection against moisture. Among their advantages are:

- Admission of very little oxygen when the vessel is opened and charged
- Low nitrogen consumption
- Ease of installation in the charging ports of existing vessels
- Simplicity of routine operation
- Low investment and operating costs
- Design versatility allowing adaptation to specific applications

The following illustrates an example and the effects that can be achieved.

Change in O₂ concentration in vessel versus bulk charge volume with and without active lock

--- Lock inactive — Lock active



Using an inert-gas lock when charging a vessel makes it possible to keep the oxygen concentration in the vessel at the desired low value.



N2LOCK® inert-gas lock integrated into the charging port of a mixer



The nozzles shown in the photograph are used for injecting liquid nitrogen into a stream of gas flowing in a pipe to a reactor or other apparatus.

Nozzles for injecting liquid nitrogen into a gas stream

With special nozzles, liquid nitrogen can be distributed in piping – over a wide range of flow rates – in such a way that the mixing zone is short and virtually no liquid nitrogen reaches the pipe wall or downstream apparatus. The danger of embrittling the material of the pipeline or apparatus is greatly reduced as a consequence.

Software for inerting.

With the aim of improved customer support, a wide variety of experience has been embodied in programs for calculating explosion limits, the quantity of nitrogen required and also the inerting time. Two software packages in particular have been applied with success to many inerting tasks:

Linde Safety System

Safety system – safety triangle (screenshot)

AT 25.0 °C AND 1.0 BAR (a) FOR MIXTURE (FUEL)

(L) LOWER FLAMMABILITY LIMIT 3.3 vol% FUEL

(U) UPPER FLAMMABILITY LIMIT 14.8 vol% FUEL

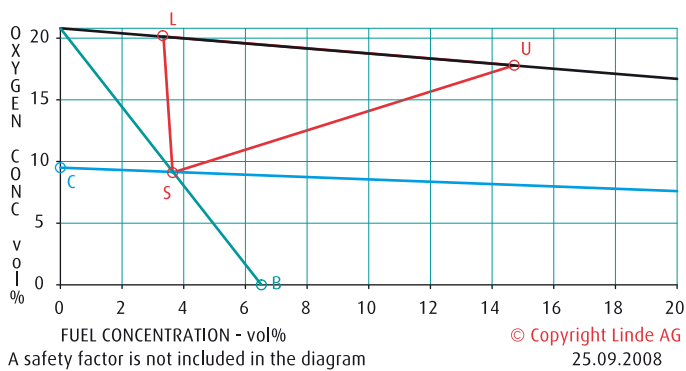
(S) MIN O₂ FOR FLAMMABILITY 9.2 vol% OXYGEN (3.7 vol% FUEL)

(C) START UP = MAX 9.5 vol% OXYGEN

(B) SHUT DOWN = MAX 6.5 vol% FUEL

Inert gas Nitrogen

FUEL MIXTURE	vol%
METHANE	75.0
PROPANE	15.0
ISOBUTANE	10.0



- A computer program for calculating and plotting explosion limits at standard pressure
- Applicable to gas mixtures of up to 99 components and to a range of temperatures as well as many inert gases
- Accesses data for 1,800 substances
- Principal data source: Design Institute for Physical Property Data (DIPPR)

PAM, Process Application Management

- Compounds	LFL vol %	UFL vol %	Min O ₂ vol %	Fuel vol %	Notes
n-HEXANE	1.1	7.7	10.0	1.2	2593/2593
2-METHYLPENTANE	1.2	7.0	11.4	1.8	2384/2384
3-METHYLPENTANE	1.2	7.7	11.4	1.8	2384/2384
2,2-DIMETHYLBUTANE	1.2	7.0	11.4	1.8	2384/2384
2,3-DIMETHYLBUTANE	1.2	7.0	11.4	1.8	2384/2384
METHYLCYCLOPENTANE	1.2	8.8	10.8	1.9	2384/2384

PAM calculates, among other parameters, the quantity of nitrogen required and the purging time. It also allows for comparisons between methods.

Safety in inerting.

Safety is of major importance for inerting, and so the following hazards must be addressed in a timely manner when nitrogen is to be employed:

→ Asphyxiation: When it is necessary for personnel to work in a partly inerted environment, for example during cleaning, the oxygen level must be kept at a minimum of 15%. The table below gives further details.

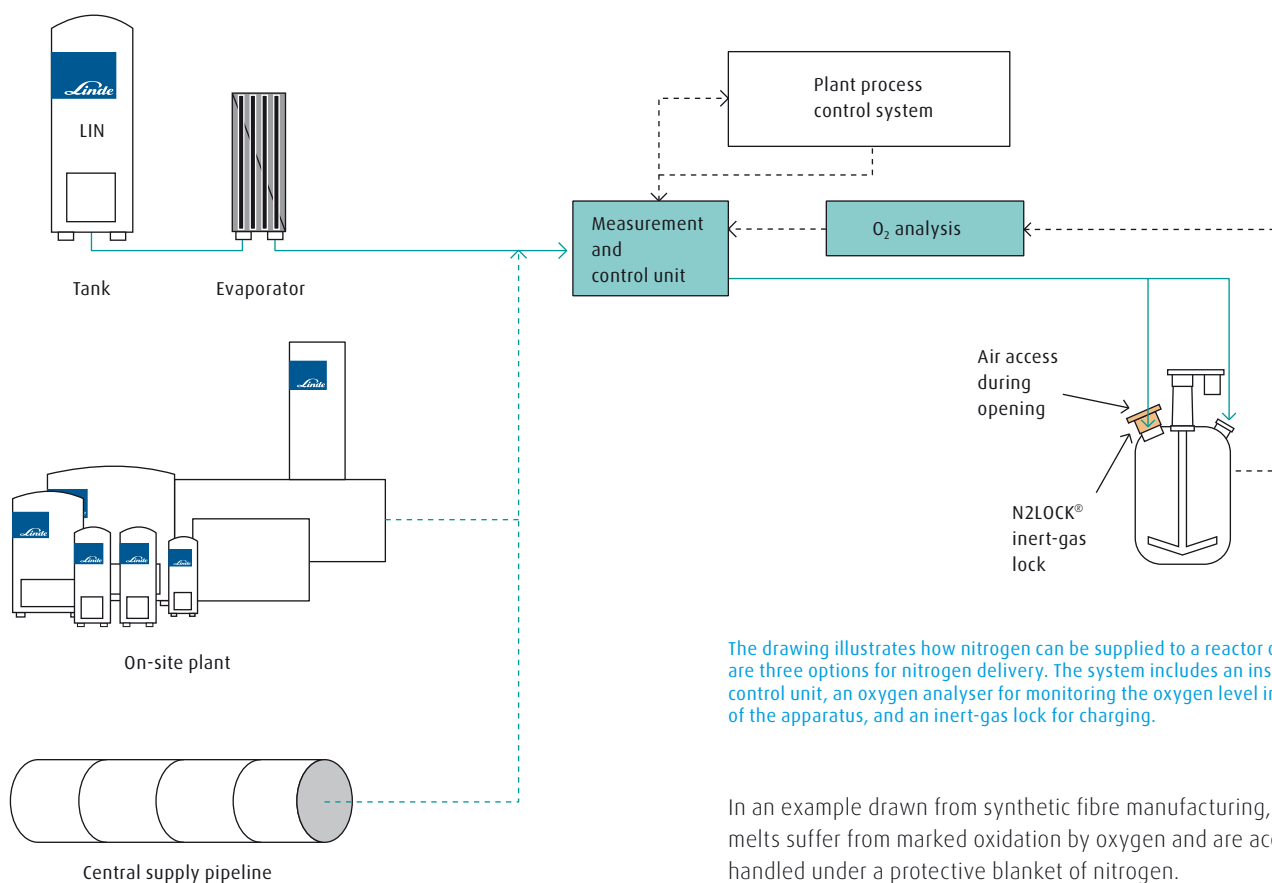
- Contact with cryogenic liquid nitrogen leads to cold burns and freezing.
- In light of the low temperatures involved, liquid nitrogen (LIN) can diminish the ultimate elongation and toughness of some materials so that they become embrittled and may fracture. Suitable materials include stainless steel, copper and aluminium.

Effects of reduced oxygen atmosphere

Oxygen level in apparatus, vol. %	Effects on human beings	Effects on inflammability of materials
8	Danger of death	Not inflammable
10	Impaired judgement and pain sensitivity	Not inflammable
12	Fatigue, increased respiratory volume, elevated pulse	Hardly inflammable
15	None	Hardly inflammable
21	None	None

Sample applications.

Supply of nitrogen to a reactor for solids charging



The drawing illustrates how nitrogen can be supplied to a reactor or mixer. There are three options for nitrogen delivery. The system includes an instrumentation and control unit, an oxygen analyser for monitoring the oxygen level in the head space of the apparatus, and an inert-gas lock for charging.

In an example drawn from synthetic fibre manufacturing, polyamide melts suffer from marked oxidation by oxygen and are accordingly handled under a protective blanket of nitrogen.

Industrial services

The preparation and execution of many shutdowns in the chemical industry call for large amounts of nitrogen to be used in a variety of steps.

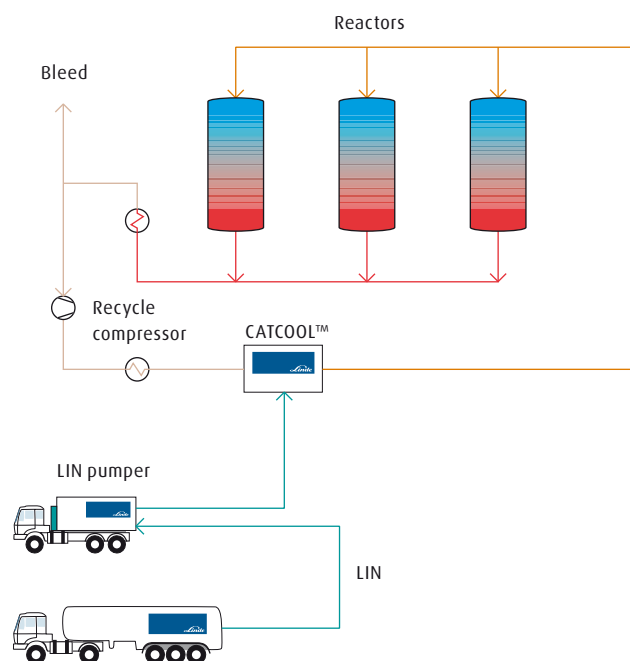
Nitrogen is used to inert the system during shutdown and cooling, in pressure testing, in drying (of the catalyst in particular) and in preheating under inert conditions preparatory to startup. An example is the shutdown of an ethylene cracker, where the following conditions were needed:

- Nitrogen consumption: 1,000–12,000 Nm³/h
- Pressure: 9 bar, 40 bar
- Temperature: ambient, +200 °C



Ethylene cracker

CATCOOL™ – accelerated catalyst reactor cool-down

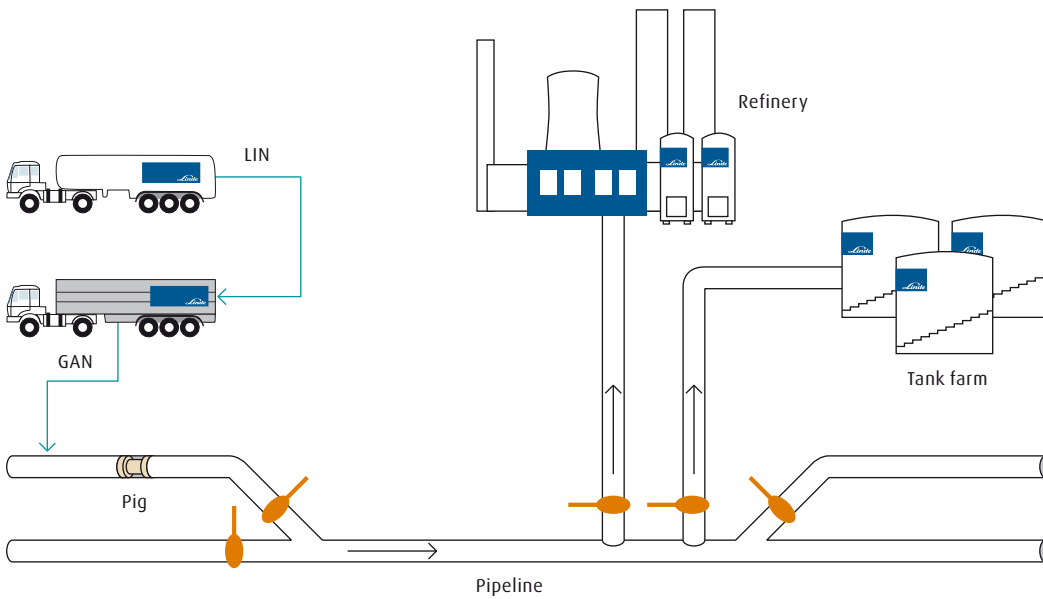


Inerting and accelerated cool-down of fixed-bed reactors by liquid nitrogen injection leads to:

- Inerting of the catalyst
- Shorter cool-down time
- Saving in cost because piping does not have to be reconfigured

Pigging and other pipeline maintenance operations are often carried out under nitrogen inerting.

Pipeline pigging



Nitrogen pressure pushes a pig through a pipeline or piping system. Advantages of using nitrogen to move the pig include:

- Inerting
- Anti-corrosion action of dry gas
- Wide range of volume flow rates, pressures and temperatures

Exhaust gases from inerting and cleaning operations are often contaminated with hydrocarbons, which can be removed by a step such as cryocondensation. This choice is especially advantageous because the cold of the nitrogen – used for inerting – is utilised. Cryocondensation is practised above all for recovering chlorinated hydrocarbons from the inert gas.



Installation of the mobile CRYCON® test unit at customer's site. Convincing test results led to an order of a customised cryocondensation unit.

Inert-gas production and supply.

Several air-separation techniques are used to produce nitrogen:

Cryogenic air separation:

- 100–7,000 m³/h
- < ppm O₂

Adsorptive air separation:

- 10–5,000 m³/h
- 98–99.99 %

Membrane methods:

- 10–1,000 m³/h
- 90–99.5 %

Nitrogen is supplied as:

- Gas in cylinders or cylinder bundles (10 l, 50 l; 200 (300) bar); purities: 4.6, 5.0, 5.3, 5.6, 6.0, 7.0
- Blends of nitrogen with other gases, e.g. synthetic air (20 % O₂, 80 % N₂)
- Liquid (LIN) in bulk tanks (3,000 to 80,000 l); purity commonly 99.995 vol. % nitrogen
- For flow rates up to 3,000 m³/h and pressures up to 600 bar, nitrogen can also be delivered in mobile tanks with evaporators
- Nitrogen gas (GAN) via pipelines or from on-site systems

For larger inerting spot jobs that require large amounts of nitrogen, e.g. in revamps, high-capacity mobile systems can deliver a stable supply of the gas.

The following parameters are feasible:

- Pressures up to 700 bar
- Volume flow rates up to 25,000 Nm³/h
- Temperatures up to 400 °C

Linde Services.

- Application-specific support (optimal supply mode, safety, hardware specifications)
- Performance of safety and economic studies
- Tests at customer's site or Linde pilot plant (e.g. effectiveness of inert-gas locks)
- Leasing or fabrication and delivery of hardware needed for inerting
- Supply of appropriate quantities of inert gas

Getting ahead through innovation.

With its innovative concepts, Linde is playing a pioneering role in the global market. As a technology leader, it is our task to constantly raise the bar. Traditionally driven by entrepreneurship, we are working steadily on new high-quality products and innovative processes.

Linde offers more. We create added value, clearly discernible competitive advantages and greater profitability. Each concept is tailored specifically to meet our customers' requirements – offering standardised as well as customised solutions. This applies to all industries and all companies regardless of their size.

If you want to keep pace with tomorrow's competition, you need a partner by your side for whom top quality, process optimisation and enhanced productivity are part of daily business. However, we define partnership not merely as being there for you but being with you. After all, joint activities form the core of commercial success.

Linde – ideas become solutions.

Linde AG

Linde Gases Division, Seitnerstrasse 70, 82049 Pullach, Germany
Phone +49.89.7446-0, Fax +49.89.7446-1230, www.linde-gas.com