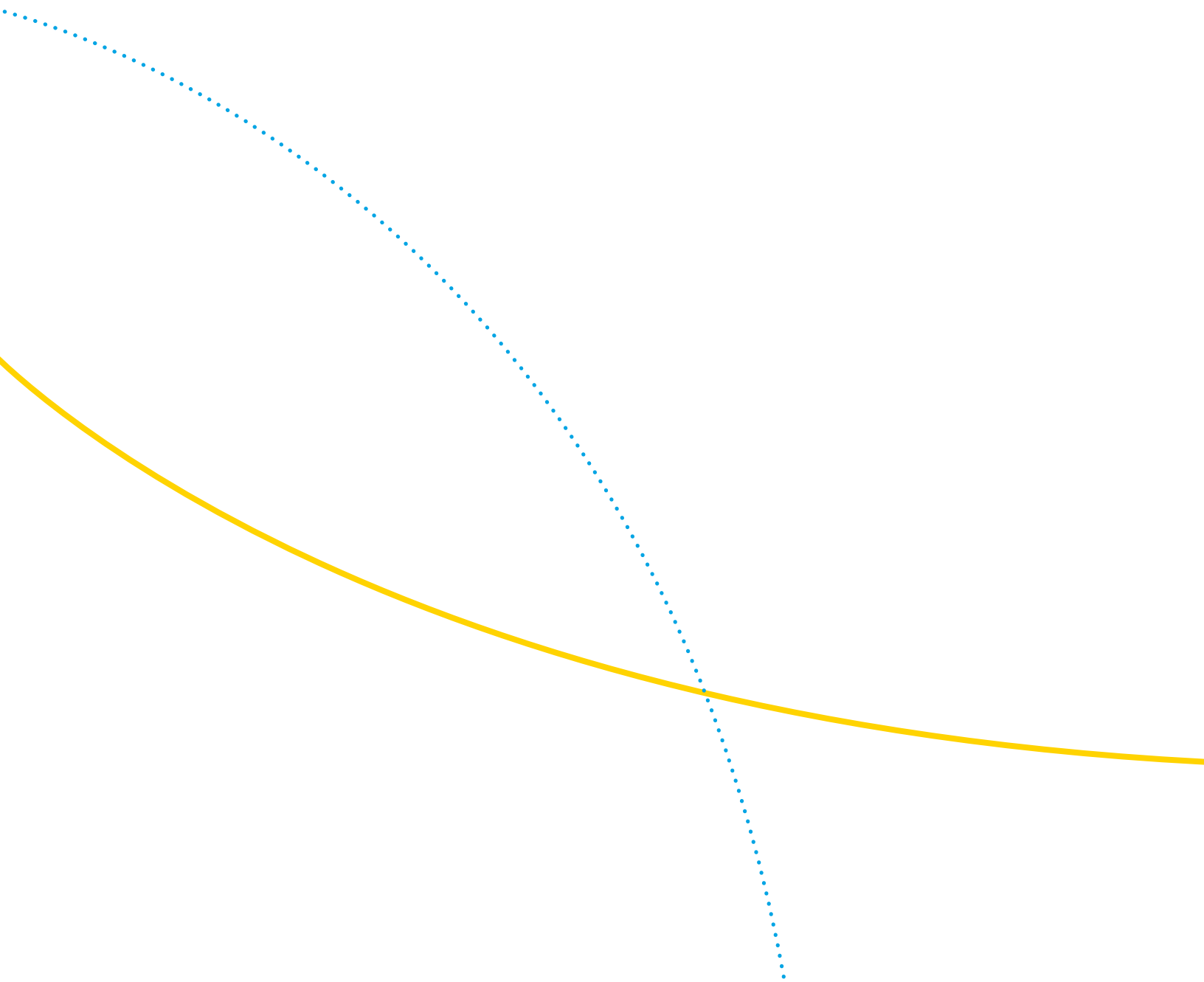


Nitrogen as the Safety Blanket for Your Industrial Process

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Abstract

Although nitrogen blanketing is a simple practice that is widely used in the chemical, pharmaceutical, food processing, and petroleum refining industries, its potential to improve productivity and safety is often overlooked. Blanketing is the process of applying a gas to the vapor space of a container or vessel in order to control its composition. It can be implemented during production, storage, transportation, and final packaging, and can be used in a wide variety of containers ranging in size from storage tanks with capacities of millions of gallons to quart-size or smaller bottles.

Nitrogen is the most commonly used gas for blanketing because it is inert, widely available, and relatively inexpensive on virtually any scale. Other gases, such as carbon dioxide or argon, are also occasionally used; however, carbon dioxide is more reactive, and argon is a less economic solution for inerting at scale.

In this article, Air products will discuss the basics of nitrogen blanketing, elucidate its various value propositions to maximize safety and efficiency, and explain how to practice it effectively and efficiently across a variety of industrial settings.

The Benefits

Nitrogen blanketing can aid in maximizing the safety and operability of plant personnel, facility infrastructure, and product inventory – by reducing the oxygen content in the vapor space of storage tanks and process vessels, nitrogen renders the atmosphere within the equipment inert. This eliminates the possibility of combustion or explosion, ensures product quality by rejecting contaminants, and protects the plant infrastructure from structural corrosive damage instigated by oxygen and moisture.

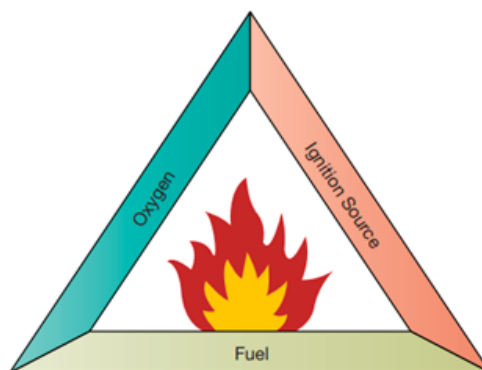
Critical Safety Benefits

Tank blanketing provides the greatest safety benefit in industries where combustible, flammable, or explosive materials are processed, stored, or generated. Blanketing prevents these types of products from coming into direct contact with the oxygen in air, thereby rendering the environment nonflammable as combustion requires the presence of oxygen to occur.

A fire requires three elements (**Figure 1**): fuel, oxygen, and an ignition source. Removing any one of these three elements from the environment eliminates the possibility of fire.

Without the presence of nitrogen, the headspace of a storage tank holding a flammable liquid contains a mixture of air and the vapor of the flammable material being stored (e.g., a solvent). The mixture of solvent vapor and air may ignite and burn if the vapor mixture is within the solvent's flammability limits and an ignition source is present. Even if the storage tank is electrically grounded to reduce the probability of ignition, a static charge can develop within the system or within the solvent itself and act as an ignition source. Since it is practically impossible to completely eliminate sources of static charge, and the fuel itself cannot be removed because it is the material being stored, oxygen is the only leg of the fire triangle that can be controlled.

Figure 1: The fire triangle depicts the three elements needed for a fire: fuel, oxygen, and ignition source



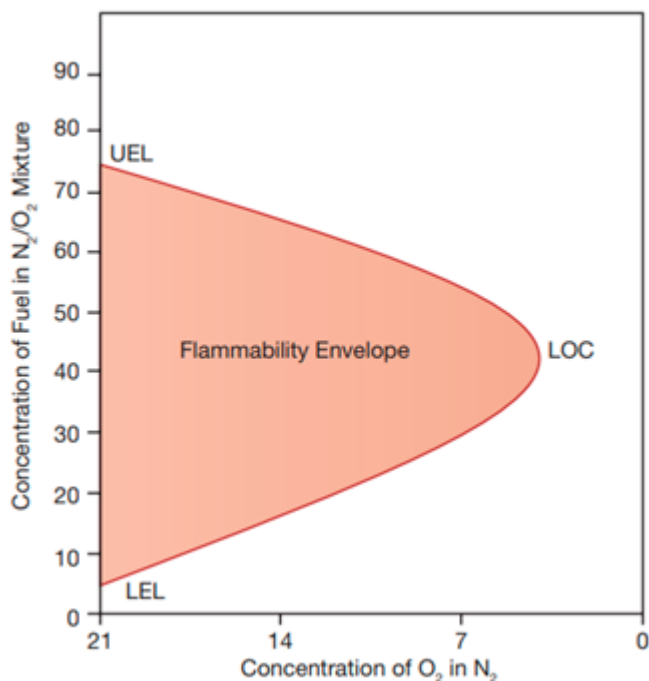
A storage tank can be made inert by:

- reducing the oxygen content of the vapor space to a value that is less than the concentration that will support combustion, i.e., the limiting oxygen concentration (LOC)
- reducing the fuel concentration in the vapor space to a value less than the minimum concentration that can support combustion, i.e., the lower explosive limit (LEL) or lower flammability limit (LFL)
- increasing the fuel concentration in the vapor space to a value greater than the maximum concentration that can support combustion, i.e., the upper explosive limit (UEL) or upper flammability limit (UFL).

A material's LEL and UEL (**Figure 2**) can be found in the material safety data sheet (MSDS) provided by the manufacturer. LOC values for many chemicals (**e.g., Table 1**) can be found in chemical engineering and chemistry handbooks as well as in the National Fire Protection Association's NFPA 69: Standard on Explosion Prevention Systems (1). Computational methods can be used to determine the flammability limits of mixtures of gases, fuels, and inert substances at elevated temperatures and pressures (2).

The U.S. Chemical Safety Board (USCSB) notes how complex, persistently present and under-communicated flammable and combustible material hazards can

Figure 2: A flammability diagram illustrates the material's flammability envelope, which is bounded by the lower and upper explosive limits (LEL and UEL) and the limiting oxygen concentration (LOC). This diagram is for hydrogen in air at standard temperature and pressure, for which LEL = 4.0%, UEL = 75.0%, and LOC = 5.0%



be. The USCSB points out that standard protections such as bonding and grounding might not prevent accidents in cases involving nonconductive flammable liquids, which include many common materials (**see Table 1**). Inerting practices mitigate these hazards and are a benefit particularly where it is challenging or impractical to eliminate all ignition sources. When executed properly, inerting prevents fires and explosions above and beyond that of normal bonding and grounding, and it can further protect product quality if that is another operational challenge within a manufacturing process.

Table 1: NFPA 69 (1) contains a full table of limiting oxygen concentrations (LOC), such as those listed here for some common materials at ambient temperature and pressure.

Material	LOC, vol. % O ₂
Propylene Oxide	5.8
Methanol	8.0
Ethanol	8.5
Acetone	9.5
Benzene	10.1
Vinyl Chloride	13.4

Quality Protection

When handling sensitive process inputs, especially in the food, pharmaceutical, and nutraceutical industries, quality degradation often becomes a reality when moisture, oxygen, and other atmospheric contaminants permeate the manufacturing process or downstream preservation and packaging. Introducing nitrogen to inert the sequential atmospheres that the product may come in contact with creates a slight positive pressure inside the storage vessels to prevent oxidative degradation and spoilage, with the end result being an increased product shelf life.

One example of this degradation can be seen in the edible oils industry, in which the triglyceride product may react with contaminant water and oxygen to break down into diglycerides and fatty acids if not properly shielded from those common atmospheric components. The exposure reduces the oil's stability and alters its color, flavor, and aroma, which are all critical to end product quality. In this type of process, nitrogen blanketing of the oil storage tanks (both the feed and the output), transfer lines, and distribution equipment can effectively eliminate the exposure to contaminants to prevent oxidation of the core triglycerides, phospholipids, and any free fatty acids – a simple, efficient, and cost effective method to maintain product integrity. Adjacent to, in the pharmaceutical industry, critical active ingredients such as epinephrine, antioxidants, and sterile injectables require inert atmospheres to eliminate the possibility of oxidation during both production and distribution.

Corrosion Prevention

In a similarly simple equation to combustion, corrosion requires a susceptible metal (iron- and magnesium-based metals, in particular), oxygen, and water. Certain acids that may be integral to a facility's process, such as hydrochloric and sulfuric acid, can quickly dissolve a wide range of metals used throughout plant infrastructure. Common waste gases, such as sulfur dioxide, nitrogen dioxide, and hydrogen sulfide can also act as agents in accelerating corrosion.

While corrosion prevention can require a wide array of prevention techniques, nitrogen can help maximize resistance by fulfilling its ideal role in purging atmospheric oxygen from the system, which eliminates one of the critical elements that instigates corrosion. Many metals used in piping and container infrastructure (copper-bearing and certain aluminum alloys) create a passive film lining through initial corrosion that subsequently provides an effective barrier to protect against further corrosion – nitrogen can help improve the formation and stability of this passive film to further enhance the corrosion barrier.

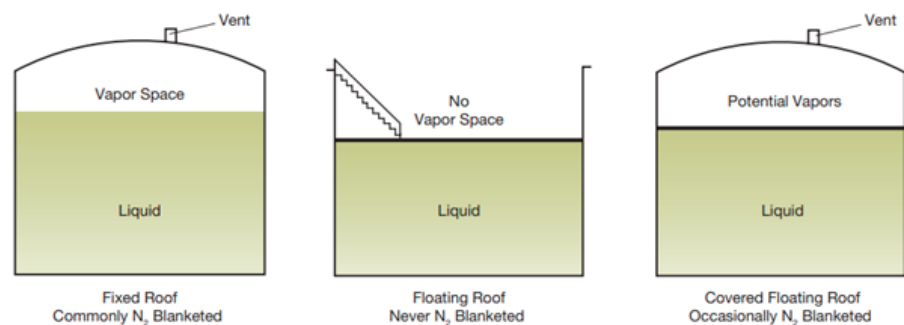
Types of vessels

When considering a new blanketing design or an upgrade to an existing installation, the first factor to consider is the type of vessel. This will determine whether blanketing is needed and, if so, the appropriate means of control (pressure or concentration).

The most common type of tank (**Figure 3**) is the fixed-roof tank. When flammable or sensitive materials are stored in fixed-roof tanks, nitrogen blanketing is highly recommended. Floating-roof tanks usually are not blanketed because there is no headspace where vapor could build up. The headspace above the internal roof of a covered floating-roof tank (or internal-floating-roof tank) is occasionally blanketed.

Some enclosed spaces that do not hold pressure, such as pneumatic conveyors, hoppers that contain powders and dust, or controlled-atmosphere containers, may also require blanketing. Nitrogen blanketing systems are essential in spaces that are not sealed tight enough to hold a slight positive pressure.

Figure 3: The type of vessel is an important consideration when designing a new or retrofit tank blanketing system



Nitrogen control by continuous purge

Three methods are commonly used for nitrogen control: continuous purge, pressure control, and concentration control.

Continuous Purge

Continuous purge systems employ a constant flow of nitrogen. This approach, while simple, has several disadvantages. First, its nitrogen consumption rate is high. In addition, the flowing nitrogen may strip the vapors in the headspace and place an additional load on the plant's air-emission control system; and, air can infiltrate the headspace if the tank discharges too quickly and the liquid level drops too fast. Despite these shortcomings, however, continuous purge systems remain in use because they can be implemented quickly and easily. Retrofitting existing continuous-purge blanketing systems with pressure or concentration controls (discussed in the next two sections) will usually reduce costs.

Pressure Control

Pressure-control systems are employed for sealed tanks, which hold pressure. A valve senses the pressure in the headspace of the tank and delivers nitrogen accordingly. The headspace pressure can be set quite low-less than 1 in. w.c. is sufficient. As the tank discharges, the liquid level falls, the pressure drops, and nitrogen is added; as the tank is filling, the pressure rises, and nitrogen exits through a vent valve (Figure 4). Several pressure-control systems are available in the marketplace.

The amount of nitrogen required to blanket a tank under pressure control is the sum of the nitrogen required based on the tank's working throughput (N₁) and the nitrogen required by thermal breathing, i.e., the rise and fall of the liquid level due to the external temperature changes (NT). The total volume of nitrogen needed can be calculated by the following simplified equations:

Equation 1

$$N_T = N_w + N_{TB}$$

Equation 2

$$N_w = \frac{V_T}{7.48}$$

Equation 3

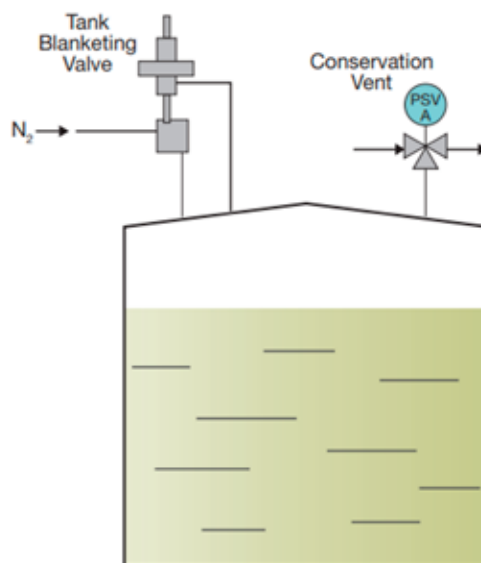
$$N_{TB} = V_{HS} + \left(\frac{T_{max} - T_{min}}{555} \right) \left(\frac{1}{7.48} \right) F$$

where NT = total volume of nitrogen required per month, ft³; N_w, nitrogen required by the material flow through the tank, ft³; N_{TB} = nitrogen required by thermal breathing, ft³; V_T = total volume of material discharged from the tank per month, gal; V_{HS} =

average empty headspace, gal; T_{max}= maximum temperature in the tank, °F; T_{min} = minimum temperature in the tank, °F; F = estimated number of temperature swings per month; 7.48 is the factor to convert gallons to cubic feet; and 555 is a constant related to the vapor space expansion factor, °R.

The working-throughput component, N_w, can be calculated easily from the total volume of liquid discharged from each tank per month. The thermal breathing component, N_{TB}, is a function of the size of the tank, the average liquid level in the tank, and atmospheric conditions affecting the temperature in the tank (which vary due to changing weather). Furthermore, the actual temperature in the headspace of the tank is not always the same as the ambient air temperature – on sunny days, it is much higher, which in turn causes larger temperature swings and increases nitrogen consumption. But because thermal breathing is usually much smaller than the working throughput, the uncertainties associated with calculating N_{TB} result in relatively small errors in estimating total nitrogen usage per month.

Figure 4: A tank equipped with pressure-controlled blanketing adds nitrogen via the tank blanketing valve when the liquid level drops, and vents nitrogen through the conservation vent when the liquid level rises.



The peak nitrogen usage, however, can be surprisingly large due to rapid temperature changes. The peak nitrogen requirement and its frequency of occurrence are important for selecting and sizing the nitrogen supply system. The peak usage can be estimated by the following simplified equations:

Equation 4

$$N_{max} = 8.021P + 0.02382C \text{ for tanks up to } 840,000 \text{ gal}$$

Equation 5

$$N_{max} = 8.021P + G \text{ for tanks larger than } 840,000 \text{ gal}$$

where Nmax = maximum nitrogen flowrate, scfh; P = pump-out rate, gpm; C = total tank capacity, gal; 8.021 is the factor to convert from gpm to scfh; 0.02382 is a factor based on cooling

an empty tank from a high of 120°F at rate of change of 100°R/h; and G is the nitrogen breathing requirement, scfh, obtained from **Table 2**.

Concentration Control

Concentration control is suitable for unsealed tanks, which cannot hold pressure. It is very efficient – nitrogen usage is optimized because it is only added when it is needed. An oxygen analyzer (**Figure 5**) directly measures the actual oxygen concentration in the headspace vapor and uses it to control the flow of nitrogen to the tank. The conditions of most processes are much too harsh to permit the use of an in situ oxygen sensor. Thus, the sample-conditioning equipment is an integral part of the analyzer system. A properly designed

sample-conditioning system allows the analyzer to measure reliably over a wide range of process conditions, including extremes in pressure, vacuum, and temperature, as well as in heavy- particulate and high-moisture environments.

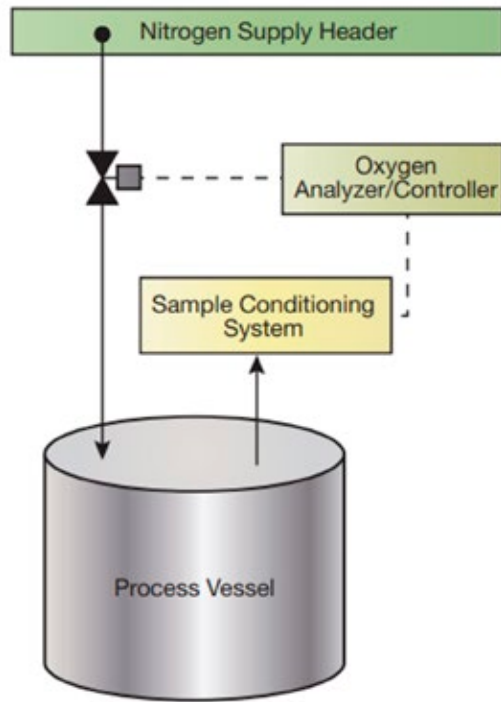
The advantage of continuous concentration monitoring and control is that it conserves nitrogen by optimizing nitrogen usage. The savings can provide an accelerated payback on the cost of the monitoring and control equipment. Several commercially available systems are on the market, with varying degrees of complexity and in various price ranges.

Table 2: For nonrefrigerated, uninsulated above ground tanks larger than 840,000 gal, peak nitrogen requirements due to thermal breathing are specified in API Standard 2000 (3) and ISO 28300 (4)

Tank Capacity		N ₂ Inbreathing Requirement, scfh
bbbl	gal	
20,000	840,000	20,000
25,000	1,050,000	24,000
30,000	1,260,000	28,000
35,000	1,470,000	31,000
40,000	1,690,000	34,000
45,000	1,890,000	37,000
50,000	2,100,000	40,000
60,000	2,520,000	44,000
70,000	2,940,000	48,000
80,000	3,360,000	52,000
90,000	3,790,000	56,000
100,000	4,200,000	60,000
120,000	5,040,000	68,000
140,000	5,880,000	75,000
160,000	6,720,000	82,000
180,000	7,560,000	90,000

Note: API 2000 includes tanks smaller than 20,000 bbl (840,000 gal). The absence of such tanks here does not imply that smaller tanks do not experience thermal breathing. Rather, for smaller tanks, the nitrogen blanketing requirements due to thermal breathing are calculated using Eq. 4, which does not include the G term of Eq. 5.

Figure 5: A concentration-control system directly measures the oxygen in the headspace and meters nitrogen to the tank to maintain the desired setpoint



Nitrogen Supply & Optimization with Air Products Smart Technology

Nitrogen supply options include delivered liquid nitrogen stored in bulk or microbulk tanks or dewars, as well as delivered gaseous nitrogen stored in large tubes, cylinder banks, or cylinders. In addition, nitrogen can be generated onsite by a cryogenic plant, or by pressure-swing adsorption (PSA) or membrane units.

The choice of delivery method depends on the application's requirements for purity, usage pattern, volume, portability, footprint, and local power cost. New blanketing applications require calculations of nitrogen consumption based on tank volumes and throughputs, as discussed previously. Optimizing

blanketing operations to maximize safety, quality, and operability is more accessible than ever before with Air Products Smart Technology, with enhanced tank monitoring and supply chain insights. Air Products Smart Technology is a fully automated and integrated service that allows our customers to control and monitor their operations anytime, anywhere. Specifically, the industry-leading platform provides consistent, up-to-date information for the following:

- Nitrogen delivery schedule and progress
- Nitrogen usage alerts for high-usage events or abnormal process variables
- Integration of nitrogen supply data with process data for optimization
- Real-time monitoring of nitrogen atmosphere concentration and pressure

- Logging of historical data for quality assurance
- Remote data access for both current operations and historical record
- Simplified KPI calculations for your nitrogen utilization

The adaptation of Smart Technology systems reduces safety risk due to physical personnel provide early insights into maintenance needs to prevent unplanned outages

Usage pattern is another important parameter that determines the appropriate delivery method and be integrated with a customized Air Products Smart Technology interface. A plant's usage pattern can be determined by measuring the nitrogen flowrate over time, typically one week. There are three basic usage patterns:

- **Constant baseline** - the flow is constant, such as the blanketing of a large tank farm. Onsite generation is an excellent choice for this pattern.
- **Erratic** - the flows are inconsistent and unpredictable, often due to transfer or purging. Liquid nitrogen is often preferred to match the variable flow requirements.
- **Periodic**-nitrogen consumption is predictable, but not constant. A gas-generation plant backed up by liquid nitrogen may be optimal.

Closing Thoughts

Nitrogen blanketing offers significant benefits in terms of product quality and process safety, and when implemented properly, pays dividends in terms of efficiency, effectiveness, and cost. Choosing the appropriate method of nitrogen supply and nitrogen control system based on the vessel design and the application can maximize the desired safety and quality results while minimizing capital and operating expenses. Implementing state of the art monitoring systems can also go a long way in ensuring product quality and safety, while also potentially improving nitrogen utilization to reduce costs from inefficiencies over time.

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