

Focus on

VOC Emissions Reduction Using an Oxygen Based Inerting Control System For Inert Gas Blanketing of Chemical Process Vessels

A guide to reducing VOC Emissions

General

Flammable solvents and highly combustible powders are essential ingredients of many industrial-manufacturing processes. Such combinations of ingredients raise the possibility of flash fires or explosions within those processes.

No flammable process is immune to this threat.

If the oxygen concentration within the combustible mixture is decreased sufficiently, a flame cannot propagate. So a common method of fire or explosion prevention is using an inert gas blanket within the process vessel.

The inert gas blanket will effectively deplete the oxygen concentration in the process and provide an adequate measure of safety.

Consequently, the purging process also impacts the emissions of Volatile Organic Compounds or "VOCs". VOC's consist of the organic solvents used in the process. VOC Emissions are directly proportional to the amount of inert gas introduced to the process vessel.

Using an inert gas control system based on the concentration of oxygen in the process will optimize inert gas usage and minimize VOC emissions.

Inert Gas In = VOC Out

To determine and eventually minimize the amount of VOC emissions, it is important to understand the amount of inert gas that will be required to purge the process.

These calculations are possible using basic guidelines. To begin, it is important to note there are several factors that impact the amount of inert gas that will be consumed:

- Size and shape of process vessel
- Process temperature and pressure
- Inert Gas: N₂, CO₂, Steam
- Leaks or access points to air
- Headspace volume
- Tank loading or unloading rates

Size and Shape: Because of the shape and size of the typical chemical process vessel (centrifuge, mixer, reactor), inerting using a turbulent flow is generally more effective than a laminar flow. A turbulent flow ensures complete mixing and even dilution of the process atmosphere and inert gas.

Temperature and pressure: Cooling of a process containing a hot vapor or liquid can result in condensation of the vapor headspace. Condensation can produce a reduction in headspace pressure and even create a vacuum situation. In situations where the process vessel pressure is lower than the ambient pressure, air may be sucked in through leaks in the system. This will result in the need for more purge gas to lower the oxygen to safe levels. High temperature processes typically run at increased pressures and may result in more VOC emissions.

For outdoor process vessels operating at near atmospheric pressure, the rate of purge gas supply will increase with a drop in temperature. In most cases a typical process vessel will require an additional rate of 1 cubic foot (0.028 cu meter) of purge gas per hour per 40 gallons (151 L) of vessel capacity.

To minimize a back flow of gases from the exhaust vent (and from other process vessels connected to a common exhaust manifold), a slight positive pressure is maintained on the process vessel using a "conservation vent". The vent is spring loaded to maintain a slight pressure of purge gas in the vessel headspace. This aids to minimize leaks of air into the process and to optimize purge control of the process vessel.

Inert Gas Type: Various inert gases can be used to purge oxygen from a vessel. For example N₂, He, H₂O, or CO₂ may be used. The type of purge gas will impact the minimum oxygen required for combustion of various solvents due to their heat capacity. Generally speaking, Nitrogen or Carbon Dioxide is used as the purge gas because they are readily available and are reasonably priced. Carbon Dioxide is heavier than Nitrogen and tends to diffuse less quickly. Thus in some instances, less VOC emissions may occur when using CO₂ as the diluents gas.

Leaks or access points to air: A process vessel that is well sealed will consume less purge gas and ultimately emit less VOCs. Additionally, solvent, product, and wash pipes leading into the process vessel should be equipped with valves to help seal the vessel when additions are not being made. If at all possible, it is best to minimize manual additions through man hole covers or entry doors to the process vessel in order to optimize purge gas usage and reduce VOC emissions.

Headspace Volume: In most cases the process vessel is filled to a suitable level to minimize the volume of headspace. The larger the headspace, the more inert gas will be required and also the more VOC emissions will result. Conversely, over filling the process vessel can lead to product loss or contamination if the product overflows into feed pipes or exhaust vents.

Tank loading and unloading rates: The purge gas must be added at a reduced rate equivalent to the volume being displaced when loading ingredients to the vessel. Conversely, the inert gas must be increased to match the increase of headspace volume as the product is being unloaded.

Estimate Inert Gas Usage

Using the following equation, it is possible to calculate the amount of inert gas consumption for the initial purge. Once the initial purge is made to dilute process oxygen from air to the desired concentration, additional inert gas may be required to maintain the desired level.

$$V = 2.34 \times \frac{\log(I-C)}{(F-C)}$$

Where:

V = Vessel volume exchanges required
I = Initial oxygen concentration
C = Purge gas impurity in % O₂
F = Final desired oxygen concentration

Example 1:

From 20.9% O₂ (air) to 5% O₂ in a vessel using pure nitrogen as the purge gas...

$$V = 2.34 \times \frac{\log(20.9 - 0)}{(5 - 0)}$$

V = 1.45 volume exchanges required

Example 2:

From 20.9% O₂ (air) to 5% O₂ in a vessel using 97% N₂ / 3% O₂ as the purge gas...

$$V = 2.34 \times \frac{\log(20.9 - 3)}{(5 - 3)}$$

V = 2.23 volume exchanges required

Chart 1: Final O2 Concentration Vs. Purge Volumes Required

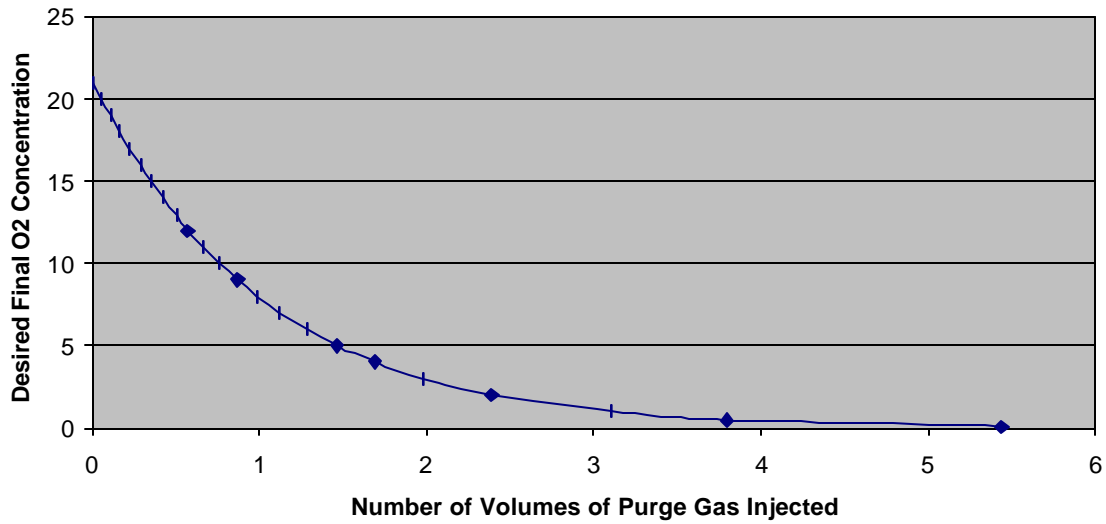


Table 1

$V = 2.34 \times \text{Log}(I/F) = \text{Vessel Volume Exchanges Required}$

Where Volume exchanges = V

I = Initial Oxygen Concentration (21%)

F = Final oxygen concentration after purging

F Final oxygen concentration	I/F	V 2.34*Log(I/F)
21	1.00	0.00
20	1.05	0.05
19	1.11	0.10
18	1.17	0.16
17	1.24	0.21
16	1.31	0.28
15	1.40	0.34
14	1.50	0.41
13	1.62	0.49
12	1.75	0.57
11	1.91	0.66
10	2.10	0.75
9	2.33	0.86
8	2.63	0.98
7	3.00	1.12
6	3.50	1.27
5	4.20	1.46
4	5.25	1.69
3	7.00	1.98
2	10.50	2.39
1	21.00	3.09
0.5	42.00	3.80
0.1	210.00	5.43

So, an example of calculating the initial purge of a 500 cubic foot vessel that is filled with 50% product (50% headspace):
 $50\% \times 500 \text{ cubic feet} = 250 \text{ cubic feet available purge headspace.}$
 To purge from air down to 1% oxygen would require 3.1 volume exchanges or...
 $3.1 \times 250 \text{ cubic feet} = 775 \text{ cubic feet initial purge.}$

Comparison of Purge Methods:

The actual amount of inert gas consumed over an extended period of time is dependent upon the method of purging (oxygen measurement based, timed volume purge, or pressure based).

In the **pressure based method**, a continuous positive pressure is maintained on the process vessel. Since the concentration of oxygen is never determined, the accepted method consists of initially purging to near 0% oxygen to assure a safe atmosphere in the process vessel. Then a positive pressure of inert gas is maintained on the process. This is accomplished using a pressure regulator with pressure sensor for confirmation. The concept assumes that once the vessel has been initially purged of oxygen, a positive pressure will prevent oxygen (in the form of air), from entering the process. This method generally results in maintaining a near 0.01% of oxygen in the vessel (when using pure N2 as the purge gas).

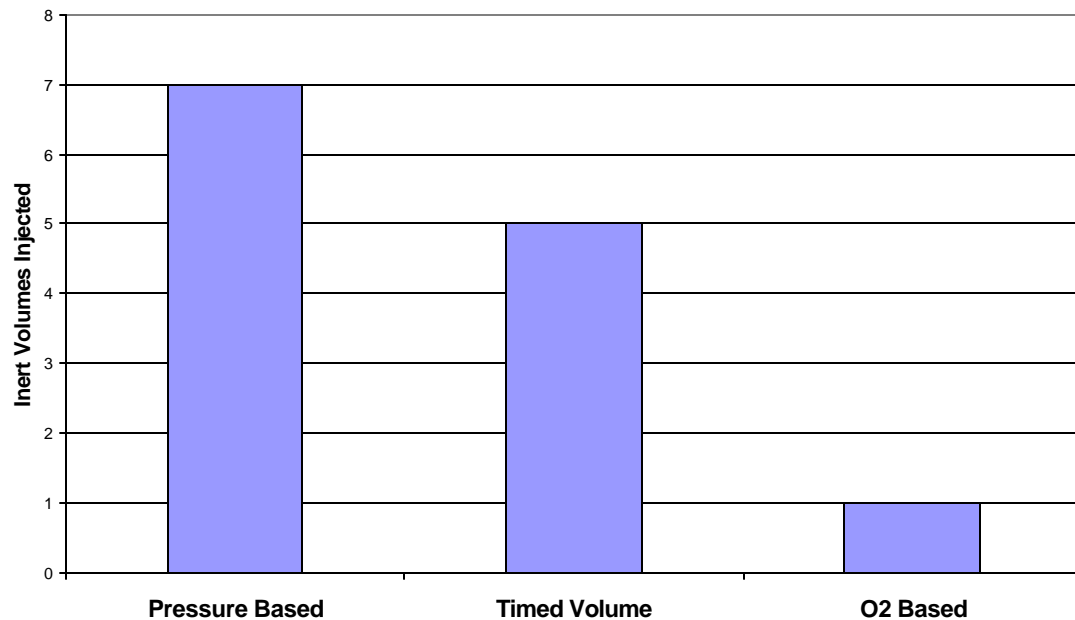
The **Timed Volume Method** is based on volume exchanges to get the oxygen concentration to a safe level. Again, since the concentration of oxygen is never determined, the accepted method consists of initially purging to near 0% oxygen to assure a safe atmosphere in the process vessel. The vessel is completely flushed with inert gas before operation. This initial purge is

designed to bring the oxygen concentration to a safe value. Once completed, additional inert gas is added at a calculated flow rate for the rest of the process. A safe level of oxygen is assumed to be present in the vessel. This continuous purge is usually at a higher flow rate than needed. This technique does not account for the changes that can occur in modern complex manufacturing processes. Actual consumption of nitrogen in a typical process using this method requires approximately 4-5 volume exchanges plus additional nitrogen consumption during manual ingredient additions. The vessel atmosphere will hover around 1% O2 when no manual additions of ingredients are made.

In the **Oxygen measurement and control method**, the appropriate amount of inert gas is automatically added to the vessel to maintain a safe level. This amount is based upon the direct measurement of oxygen... not estimations or calculations. This means inert gas usage is optimized while safety is ensured. This method generally results in maintaining a concentration of oxygen in the range of 5.0 to 7.0 % by volume.

Chart 2

Comparison of Inerting Methods - Dilution Ratio Purge Requirement over time



Note: This table is based on actual field data gathered from installations in pharmaceutical facilities in North America.

Relationship of VOC emissions to Inert Gas Usage:

Most organic solvents are highly volatile: they evaporate quickly to reach equilibrium with the process vessel headspace. The amount of solvent in the vapor headspace is directly related to the vapor pressure of the solvent, and the temperature and pressure of the process. Generally speaking, you can assume solvents reach complete saturation of the headspace vapor for most processes.

If you know the solvent physical characteristics (vapor pressure, molecular weight,...), process temperature & pressure, you can calculate the amount of solvent (VOC) emissions per cubic foot of inert gas consumed.

An example by Dr. Arthur Gow, Ph.D. Resident Chemist at Neutronics Inc:

For a system in which the total pressure is P_T atm and the process headspace, nitrogen, is saturated with solvent at temperature $T^\circ\text{K}$:

$$\text{Moles } N_2 \text{ in headspace, } V_H = \frac{P_T - P_s}{RT} V_H$$

$$\text{Moles Solvent in headspace} = \frac{P_s V_H}{m RT}$$

$$\frac{\text{moles solvent}}{\text{moles } N_2} = \frac{P_s}{m (P_T - P_s)} \quad (1)$$

Where P_s is the vapor pressure of solvent at $T^\circ\text{C}$ and μ is the compressibility factor of the saturated vapor.

Although the inerting gas in the headspace may contain oxygen, the mixture can be considered pure nitrogen.

For acetone as the solvent in a process operating at essentially 1 atmosphere pressure and 23°C :

$$P_s = 211.8 \text{ mm Hg} = 0,279 \text{ atm (data from Table 5.9 Lang handbook of chemistry, 14 th edition, 1992)}$$

$$m = 0.94 \text{ (data from Table 3-157 and Fig. 3-52a Chemical Engineers Handbook, 5}^{th} \text{ edition, 1973)}$$

From EQ (1):

$$\frac{\text{moles acetone}}{\text{moles } N_2} = \frac{0.279}{0.94 \times 0.721} = \frac{0.412 \text{ mole acetone}}{\text{moles } N_2}$$

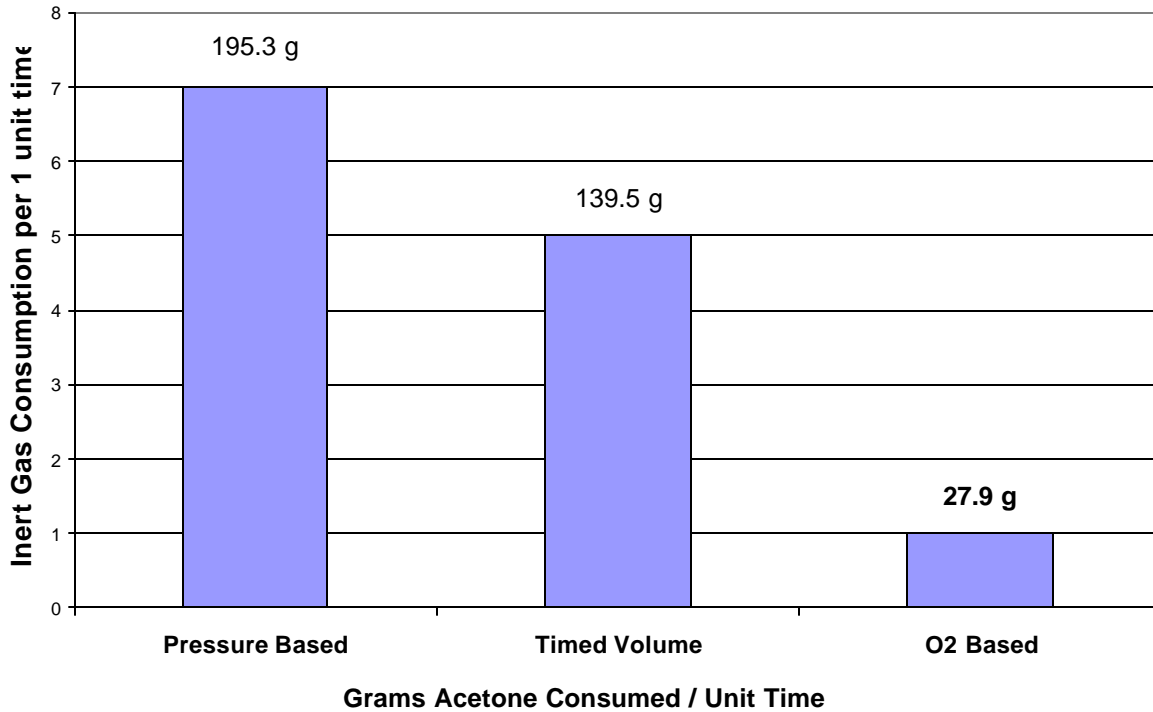
$$\frac{\text{grams acetone}}{\text{SCF } N_2} = \frac{0.412 \text{ lb/mole acetone}}{\text{lb/mole } N_2} \times \frac{58.08 \text{ lb}}{\text{lb/mole acetone}} \times \frac{453.6 \text{ gram}}{\text{lb}} \times \frac{1 \text{ lb / mole } N_2}{359 \text{ SCF } N_2}$$

$$= \frac{0.412 \times 58.08 \times 453.6 \text{ grams}}{359 \text{ SCF } N_2} = \frac{30.2 \text{ grams acetone (@ } 0^\circ\text{C)}}{1 \text{ SCF } N_2}$$

$$= \frac{27.9 \text{ grams acetone}}{1 \text{ CFN}_2 \text{ at 1 atmosphere @ } 23^\circ\text{C}}$$

So, in general, you can compare the three methods of inerting control Vs VOC emissions:

**Chart 3: Comparison of Inerting Methods
VOC Emissions Vs Typical Inert Gas Usage Rates**



References:

ANSI / NFPA 69, 1998 Explosion Prevention Systems

Industrial Explosion Prevention and Protection, Frank Bodurtha 1980

Lang handbook of chemistry, 14 th edition, 1992

Chemical Engineers Handbook, 5th edition, 1973