White Paper

Measurement of Oxygen Concentration
in Blanketing and Inerting Operations

Gaseous oxygen measurement with amperometric sensors is the most direct and easy solution for oxydation protection and explosion protection.

Unwelcome oxygen

Tank blanketing is the process of filling the headspace in storage vessels and reactors with an inert gas, usually to protect its contents from exploding, degradation or polymerization due to the presence of oxidation but also to protect equipment from corrosion. A blanketing system is normally designed such that it operates under higher than atmospheric pressures, therefore preventing outside air from entering the vessel. As oxygen and moisture in the air can be undesired in numerous processes and applications, blanketing is done in a wide range of industries, varying from (petro)chemical- to food and beverage-, pharmaceutical- to pure water- and so on.

Inerting is done for similar reasons but is not limited to storage tanks and reactors only. Any confined space can be sparged with an inert gas to create the desired atmosphere. This ranges from packing food under protective atmosphere to increase shelf life to lowering the oxygen concentration in rooms where welding takes place to reduce risk of fire. Very typical also is complete or partial inertization in process equipment and unit operations such as:

- Centrifuges;
- Mills;
- Mixers;
- Fluid bed dryers;
- Silos;
- Pneumatic transport;
- Incinerator / flare feedstock supply.

The most common type of inert gas used is nitrogen for economic reasons and because of its availability.

The blanketing process

The simplest way to protect a vessel, for example a storage tank, against either overpressure or negative pressure is to have an opening at the top of the tank. In that case any excess air or gas can freely leave the tank when product is pumped into the tank and, the other way around; air can flow into the tank when product is drained. Such a system also allows "breathing" of the tank due to temperature fluctuations that normally can lead to significant volume changes.

For obvious reasons this method is unfortunately not suitable for all products. Air entering the tank might contaminate the product and especially when storing organic solvents and hydrocarbons an explosive gas/air mixture will form above the product. Also undesired gases and vapors may be emitted into the atmosphere. As these situations must be avoided the tank needs to be sealed. The tank does however need to be kept under constant pressure in order to avoid overpressure when it is filled or when temperature rises, and much more dangerous, to avoid vacuum when product is drained. Especially large storage tanks do not handle low pressures well.

The blanketing system is there to guarantee that the tank headspace is kept both under inert atmosphere and at constant pressure. One way of achieving this is through continuous purging with nitrogen which is a relatively easy and safe alternative. Though this method requires low capital investment, it involves high operating costs as it consumes nitrogen continuously.

Slightly more sophisticated is pressure based blanketing. In a traditional set-up, such a blanketing system consists of:

- A blanketing valve or regulator allowing the inert gas to enter the tank whenever required;
- A breather valve or vapor recovery valve to allow headspace gas to escape from the tank;
- A safety pressure/vacuum relief valve to prevent tank overpressure or vacuum which could lead to imploding of the tank. A risk that grows with tank size;
- (and of course piping and inert gas supply.)

In this operation the breathing valve opens when the headspace volume decreases and lets headspace gases leave the tank. In case the product is pumped out of the tank or when temperature decreases, the blanketing regulator shall open and fill the tank headspace with nitrogen, avoiding vacuum. Maintaining a constant gauge pressure makes sure that air, and thus oxygen, does not enter the tank. Day and night, sun and weather make that the tank breaths continuously.

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Risks

Wrongly engineered or poorly maintained blanketing systems may lead to serious incidents. The statement that all blanketing systems leak one way or another is probably true. Its complexity, valves with moving parts, packings and sealings etc. are prone to failure. A malfunctioning pressure transmitter may register the wrong headspace pressure causing too high nitrogen consumption. When a blanketing valve does not open far enough the nitrogen flow is too low which may result in too low a headspace pressure which may cause the tank to implode or causes the leaking of air into the tank, which, as mentioned, can have consequences with regard to product quality and, depending on the stored product, can seriously increase risk of explosion.

Nitrogen

Increased focus on both safety and quality has led to an increase in the use of blanketing operations worldwide and consequently in the use of nitrogen. For various reasons the demand for nitrogen has globally increased to such an extend that nitrogen no longer has the status of a by-product of the oxygen production but is now considered a main product in itself. The growing demand has naturally had its impact on price but as energy costs make up half of the production costs of nitrogen, last year's surge in energy prices only caused an average nitrogen price increase of over 4 percent. Obviously transport costs play an important role here as well. The way nitrogen ends up at the end-user can differ substantially. Smaller user get their nitrogen supplied compressed in cylinders or in bulk tank transport. Larger ones may have nitrogen delivered by pipeline but such an infrastructure is limited to heavier industrialized areas. Others choose to have a nitrogen generation plant on site. So the average price increase does not paint the full picture. All in all smaller and mid-size users, especially in more remote locations, have reported price increases of 15 percent and more since last year.

Headspace gas analysis

One way to increase safety and reduce the use of nitrogen simultaneously is to control inertization as a function of oxygen concentration in the headspace. The idea behind this is the following: depending on the product and the reason for blanketing or inerting, there are tolerances when it comes down to the maximum allowable oxygen concentration. Certain monomers require zero percent oxygen to prevent polymerization. Others require a small amount of oxygen for the same reason. In the case of explosion protection, the oxygen concentration does not necessarily need to be zero. In fact for all solvents a so called limiting oxygen concentration exists. Below this concentration there is no risk of explosion. It is obvious that controlling the nitrogen purge based on the concentration will seriously cut nitrogen costs. Furthermore the measurement of oxygen concentration in the tank headspace provides an important safety parameter.

In more detail the process is as follows (see fig. 1): Goal is to prevent the oxygen concentration from exceeding the so called Limiting Oxygen Concentration (LOC), which is specific for each product that is blanketed and also referred to as MOC or Maximum Oxygen Concentration. These specific values can be found in databases such as CHEMSAFE. For safety reasons two threshold values are established, well below the Limiting Oxygen Concentration; the Lower Intervention Level and the Upper Intervention Level. These two threshold values are the set-points that control the purging of nitrogen. The moment the oxygen concentration reaches the Lower Intervention Limit, the nitrogen flow is intermitted. Purging of the vessel is resumed when the upper intervention limit is exceeded. This means that the inerting system keeps the consumption of nitrogen minimal while safe operation is ensured. Depending on individual process conditions and solvent, the oxygen level is usually maintained somewhere between 2 and 12 vol%. The system consists of an oxygen analyzer system, a PLC, a blanketing regulator, a breathing valve, a safety relief valve etc.

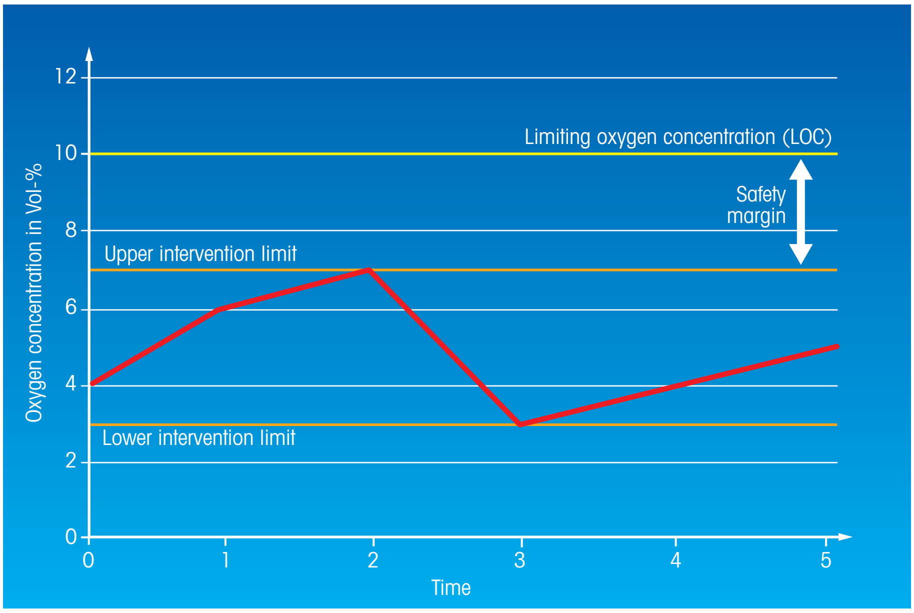


Fig. 1: Typical O_2 controlling in an inertization process with oxygen concentration based regulation.

This method is suitable for most inerting operations and processes that require an exact oxygen level. For tank blanketing things are however slightly more complicated as the main objective still is to allow breathing of the tank which, after all, still depends solely on headspace volume changes. It is obviously not possible to stop the nitrogen flow just because the oxygen level has reached the set-point whilst product continues to be pumped from the tank. As discussed the created vacuum could seriously damage the tank. This problem can be overcome by replacing some of the nitrogen by air. Once again, the aim is not zero oxygen. So instead of purging with pure nitrogen a mix of nitrogen and air can be used. Technological developments in on-site nitrogen generation make this even easier. With membrane filters or molecular sieve type technologies it is possible to produce any purity of nitrogen up to 99.9 percent on demand. The oxygen analyzer makes a reliable and cost efficient nitrogen supply and safe blanketing process possible.

Oxygen analyzer solutions

Often however the use of oxygen analyzers encounters resistance. The reason being typically the oxygen analyzer system with its complicated installation and the high capital and operation costs. A conventional system usually consists of an extractive type oxygen analyzer, typically based on paramagnetic- or, less frequently, zirconium oxide technology. Both types of analyzer require extensive sample conditioning, a pump to drag the sample, tubing, valves, filters, coolers, heaters, dryers and so on. In short it means a huge amount of maintenance and potential for failure due to the complexity of the system and the fragility of the analyzers. Apart from all the peripherals that substantially contribute to the investment, the analyzer itself is very costly. The reluctance to install such an system to control a blanketing operation is understandable.

Advantages of direct in-line measurement

The solution can however be much simpler and definitely more reliable. With amperometric oxygen measurement, METTLER TOLEDO offers a cost efficient and safe solution in a 12 mm probe that totally eliminates the need for a sample conditioning system. The amperometric or polarographic oxygen electrode can be mounted directly into the vessel or nitrogen discharge piping and is not sensitive to dust, moisture or solvents. A retractable sensor mounting assembly allows retrieval of the sensor without interrupting the process, e.g. for easy calibration. No special calibration gases are needed as a one point calibration with air is all it takes to keep the probe's accuracy. In very critical applications, the system can be equipped with redundant oxygen probes for additional safety and self check purposes. Compared to traditional extractive analyzer technology the METTLER TOLEDO solution is available at only a fraction of the costs. First of all the analyzer itself is certainly lower priced, secondly, the absence of the sampling and sample conditioning system contributes to even lower costs. The most valued perceived benefit however is the enormous savings on maintenance. The only maintenance needed is the occasional refilling of electrolyte which is merely a 2 minute operation.

Theory

Amperometric oxygen measurement is a well established method for both dissolved and gas phase oxygen measurement. The basic principle is the chemical reduction of an oxygen molecule and the measurement of the resulting current between a cathode and an anode.

Cathode reaction

$O_2 + 2\,H_2O + 4\,e- = 4\,OH-$

Anode reaction

$4\,Ag + 4\,Cl- = 4\,AgCl + 4\,e-$

Between the Anode and the cathode a constant voltage of around –600mV is applied to induce the oxygen reduction.
This reaction is linked to a current flow which is proportional to the partial pressure of oxygen.

Different system options are available depending on the process conditions and application requirements.

The advantages of amperometric measurement are on the one hand in the robustness of the sensor that allows installation directly into the process without the need for complex and maintenance intensive sample conditioning systems. The absence of such a sample handling installation greatly reduces failure potential.

On the other hand the simplicity of the analyzer also reduces the cost of ownership to a fraction of that of extractive analyzer systems. Maintenance does not require specialist know-how and can be carried out in just two minutes.
In a nutshell, amperometric oxygen measurement provides an attractive alternative to oxygen analyzers based on extractive technology.

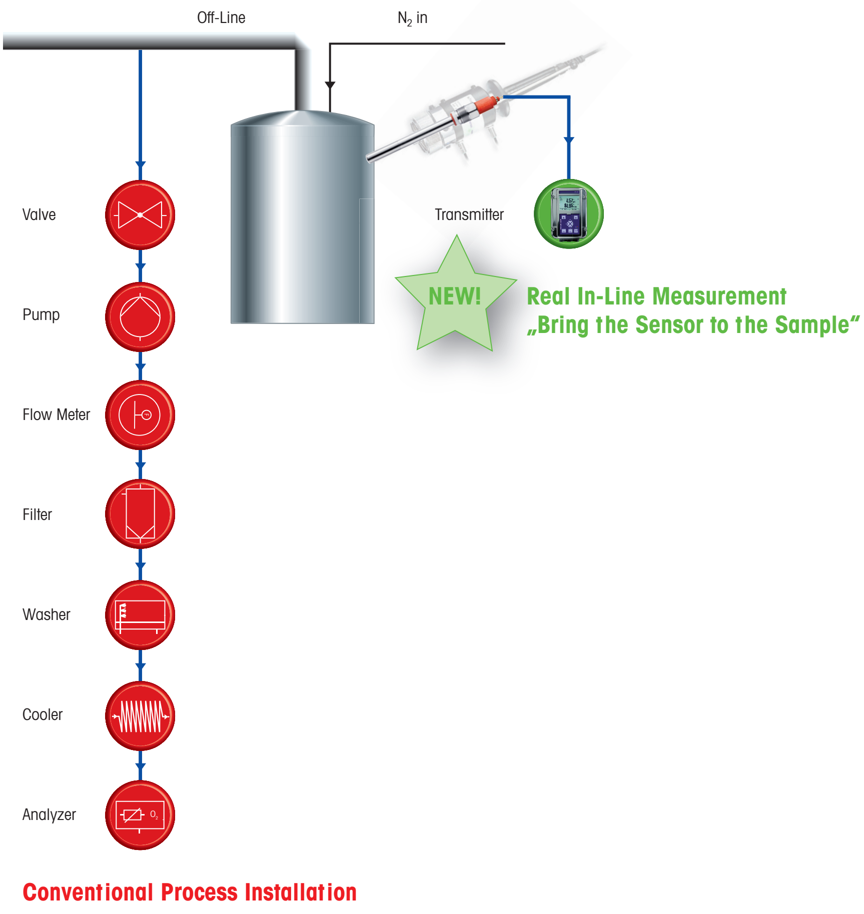
Conclusion

Inertization and nitrogen blanketing of vessels and process equipment is gaining ground globally thanks to safety- and product quality awareness. Price increases on the world nitrogen market however, cause users to look for more economical technologies with lower nitrogen consumption. One of the most efficient ways of minimizing the use of nitrogen and increase safety at the same time is controlling the inerting or blanketing based on oxygen concentration. Drawbacks however are the high maintenance demands and the high installation costs. Advances in sensor technology and intelligent automation of the measurement point, enable reliable oxygen measurement in an extremely simplified way, eliminating the need for extensive sample conditioning. Nitrogen savings and the lowest possible maintenance needs allow for a fast pay-back of the oxygen analyzer.

Intelligent Sensor Management

Though the principle of polarographic oxygen measurement is more than fifty years old, the technology has not ceased to develop. Significant improvements have been made to the cell itself and high performance membranes now allow for fast and accurate measurement in a wide range of applications. One of the most recent added features is the integration of the ISM (intelligent Sensor Management) platform. Using the power of intelligent sensor technology greatly improves reliability and reduces maintenance efforts at the same time. Continuous self-diagnosis provides real-time status information and predicts maintenance requirement in detail.

Simplified system setup with real in-line measurement



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