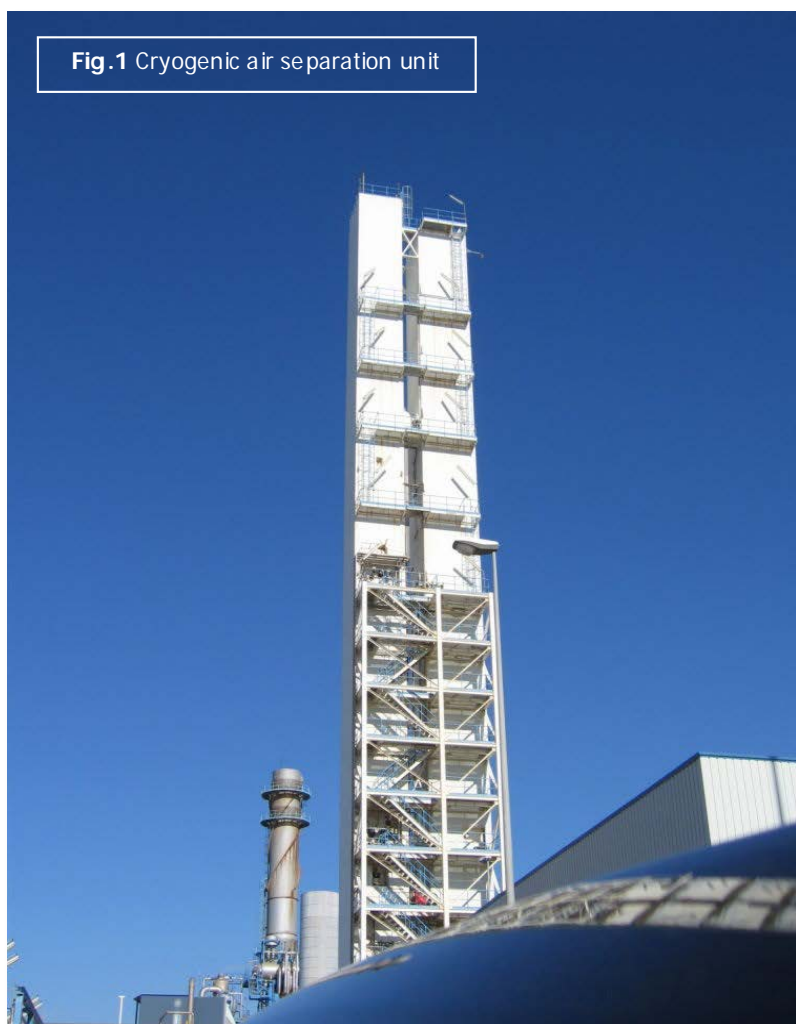


Process oxygen - air separation applications

Application background

Industry consumes vast quantities of oxygen and nitrogen annually, all of which is obtained from the air around us. There are two main techniques used to separate these two primary gases from air. These processes are cryogenic separation and (vacuum) pressure swing adsorption [(V)PSA].

Fig.1 Cryogenic air separation unit



The world's first oxygen air separation plant began operation in 1902, followed in 1904 by the first nitrogen plant. These early plants had a capacity of just 5 kg/hour of purified oxygen or nitrogen. By 2006, capacities for the largest plants had risen to in excess of 1.25 million kg/hour across eight trains.

Regardless of the technique used, the plants producing these pure industrial gases are known as Air Separation Units (ASU's). Such plants may be owned and operated directly by the consumer. In this case the facility is known as an on-site plant, with the plant infrastructure often supplied and sold by one of the major industrial gas (IG) companies as a modular "Packaged Plant" solution. In other situations the ASU is owned and operated directly by the IG company, but is often located directly within, or adjacent to, the end user's site. Occasionally, the plant may be centrally located in an industrial location such as an "Industrial City", and may feed a number of discrete customers. In addition, IG operators run large air separation plants, producing bulk O₂ and N₂ and often argon and other gases, for general distribution, via ad and rail tanker or for supply in cylinders for lower volume use.

Cryogenic separation produces very high purity products (>99.5%). In comparison, (V)PSA are typically smaller than cryogenic plants and are normally located directly at the point of consumption. These are used to produce either O₂ or N₂ at typical purities of up to 94%.

Major international IG plant operators include: Linde (inc. BOC), Air Products, Praxair (inc. White Martin, Brazil), Air Liquide, Messer & Taiyo Nippon Sanso.

Smaller, more localized national companies include: NIGC (SABIC Partnership, Al-Jubail, Saudi Arabia) and Airgas Inc. (USA).

Cryogenic air separation

Cryogenic air separation is used when large quantities of N₂ and O₂ are required at the highest purity (>99.5%). In this type of plant, the air is separated by fractional distillation at extremely cold (cryogenic) temperatures. Both a high and low pressure column are used, one placed on top of the other. Large quantities of nitrogen and oxygen are produced by these plants, together with smaller amounts of other gases, principally argon (Ar), but also neon (Ne), helium (He), krypton (Kr) and xenon (Xe). Fig. 2 lists the components commonly extracted from dry air and their percentage of the total composition.

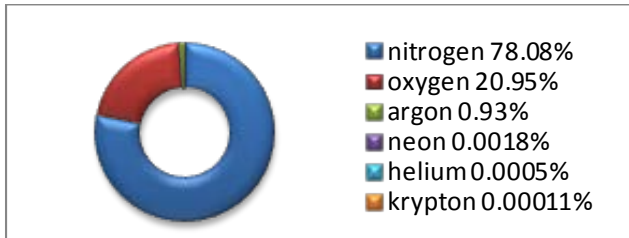


Fig.2 List of gases commonly extracted from Dry Air

The Process

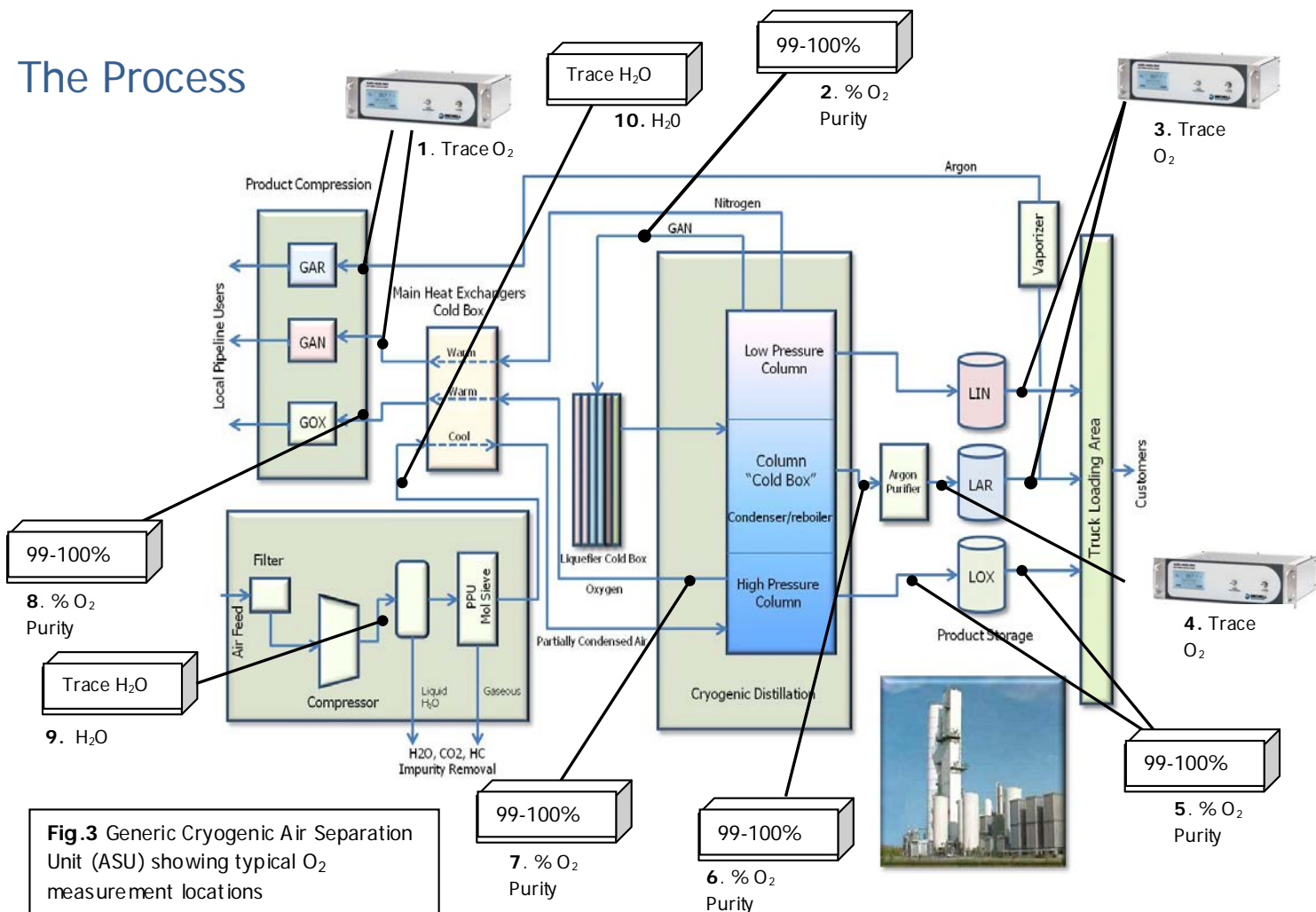


Image source: http://www.uigi.com/new_cryo_plants.html



Atmospheric air is first filtered and compressed before being washed and water cooled. This water wash also removes other components from the air which would affect the final product and possibly damage the plant (these include SO₂, SO₃ and NH₃). Carbon dioxide and water are then removed from the air, using either dual Zeolite (Mol Sieve) absorbers, on alternating duty, or a heat exchanger system, whereby the incoming air is cooled by the outgoing cold nitrogen gas stream, "freezing out" the water and CO₂. The heat exchanger is periodically reversed so that the outgoing N₂ stream is used to flush out the deposited CO₂ and water and to cool the incoming air at the other side of the heat exchanger.

After the air has been purified, it enters the distillation column. Here it is fractionally separated into pure N₂ at the top and pure liquid O₂ at the bottom of the column. Some of the liquid N₂ produced is used as reflux for the column while the remaining is super cooled and sent to the top of the low pressure column. Liquid N₂ can then be removed and sent to liquid nitrogen (LIN) storage while the liquid oxygen (LOX) is removed from the bottom (bath) of the condenser and sent to the LOX storage tanks. The liquid oxygen and nitrogen can also be passed through the main heat exchanger to vaporize them to gaseous O₂ and N₂ to meet customer requirements. Additionally, liquid argon can also be extracted from the column and sent via an argon purifying stage to liquid storage or again vaporized for shipment in gaseous form. Other trace gases such as Ne, He, Kr and Xe are extracted, as required, in a similar way.

The measurements

Loc	Typical IG gas measurements (Cryogenic)	Reason for measurement
1.	Trace O ₂ in gaseous N ₂ /Ar product (0.5 to 10ppm typ.)	Product quality control
2.	% O ₂ in gaseous Ar feed to heat exchanger	Process control/Product quality control
3.	Trace O ₂ in liquid N ₂ and Ar product (0.5 to 10ppm typ.)	Product quality control
4.	Trace O ₂ in crude argon (2% Typ)	Purifier operation & QA
5.	O ₂ purity in inlet & outlet of LOX storage tank	Product quality control
6.	% O ₂ inlet to Ar purifier	Purifier operation/process control
7.	% O ₂ Purity from high pressure column	Process control
8.	O ₂ purity in gaseous O ₂ storage tanks (>99.5%)	Product quality control
9.	Trace H ₂ O – Outlet from compressor	Air feed quality
10.	Trace H ₂ O – Outlet from mol. sieve scrubber	Scrubber efficiency

Pressure Swing Adsorbers (PSA)

Pressure swing adsorbers can vary from small skid size packages to quite large installations. They are typically installed to satisfy local plant requirements. They tend to offer less efficiency than cryogenic plants, typically providing gas purities of >90% or higher, depending on design and operation, but are far easier to operate and maintain. However, more recent design improvements have led to efficiencies of 99% with some vendors offering purities apparently as high as 99.999%!

Typically, the purity of the product is dependent on the required gas flow rate, i.e., higher purity can be achieved with lower flow rates, with a reduced purity specification achieved at higher flow rates.

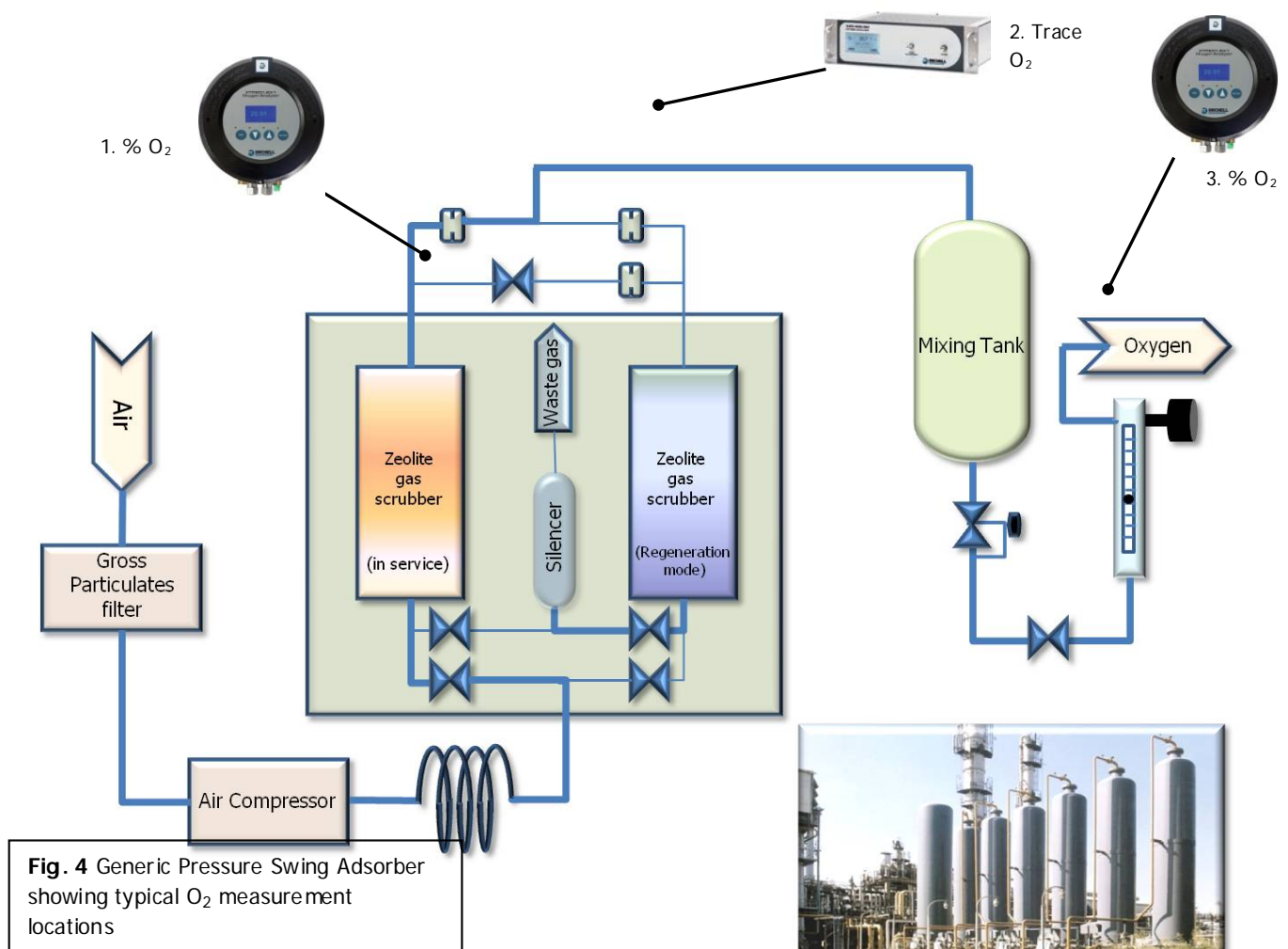


Image sources: http://www.uigi.com/new_cryo_plants.html
<https://wastewaterstudy.wordpress.com/plant-equipment/secondary-treatment/>

The process

PSA's can be used for either oxygen or nitrogen production. For oxygen production, air is first drawn through a filter and then compressed, before being sent to a Zeolite adsorption column. Here, at elevated pressure, the Zeolite absorbs N_2 , CO_2 and water while the oxygen passes through. When the column is fully saturated the pressure is reduced to vent the N_2 and regenerate the Adsorption bed. As this regeneration is taking place, the process switches to the second adsorption column, allowing for continuous operation, each column being switched as it becomes exhausted. Where nitrogen is the required end product, a carbon mol sieve gas scrubber is used instead of Zeolite (to absorb the oxygen). Otherwise the process is very similar in operation.



Fig.5 Skid mounted Pressure Swing Adsorber (PSA)

A variant of the PSA is the Vacuum-Pressure Swing Adsorber, often abbreviated to VPSA, VSA or PVSA. The process is similar to a PSA, except that a VPSA utilizes vacuum blowers to reduce the desorption pressure, creating a vacuum in the scrubbing columns. This lower pressure also reduces the required inlet pressure to the scrubbers. The advantage of this technique is that the efficiency of the desorption process is significantly improved as the Zeolite is more fully regenerated, resulting in a higher percentage of oxygen extraction from the air during each scrubbing cycle. However, due to the lower discharge pressure, air compressors are usually required to increase the delivery pressure. This, together with the increased manufacturing costs, does offset, to some extent, the efficiencies gained. Therefore, VPSA's typically become a cost effective solution when the required delivery rate is greater than 20 tons per day.

The measurements

Loc	Typical IG gas measurements (PSA)	Reason for measurement
1.	O_2 concentration from scrubber exit	Product quality control/scrubber efficiency
2.	*Trace oxygen in N_2 product (0.5 to 10ppm typ.)	Product quality control/scrubber efficiency
3.	O_2 concentration at delivery	Product quality control

* If PSA is producing N_2 product

Image source: <http://www.carbotrade.com>

Why is oxygen measurement important?

Cryogenic air separation units require critical and reliable gas analysis for plant control and product quality. These measurements are fundamental to the safe and efficient operation of the plant and to provide final product quality assurance. If process control is compromised, then product quality and/or plant safety will be jeopardized, with huge financial implications to the operator. PSA's also require similar measurements, although the purity specification may be less onerous and the plant is usually producing only O₂ or N₂. The quality of the final product is again critical as potentially, "off spec" O₂ or N₂ may have undesirable consequences to plant operations and product quality. In addition, if the output from a N₂ ASU is being used to provide N₂ blanketing or N₂ purging of equipment, entrained O₂ could be extremely hazardous or, at least, affect instrument performance. The two process diagrams (fig. 3 & 4) provide indication of the key measurements and their locations within the process.

Measurement technique

Usually, paramagnetic oxygen analyzers are utilized for gaseous % and purity O₂ measurements, while for the trace oxygen measurements, either zirconium oxide or electrochemical sensors are used. The advantage of zirconium oxide technology is that it is non-depleting, whereas electrochemical cells need to be replaced on a regular basis. When they do fail, electrochemical cells can provide a false low oxygen reading, possibly leading to the operator assuming that the process is in control, when this may not be the case. In addition, the typical response time of electrochemical cells can be considerably slower than zirconia based devices, especially following exposure to high O₂ levels during plant upsets. For these reasons, zirconium oxide sensors have generally become the preferred technology for most IG producers, as they provide many years of trouble-free service, although some older plants still use electrochemical analyzers. Sometimes a combination of both technologies is utilized to provide for fall back security or cross checking of analyzer performance.

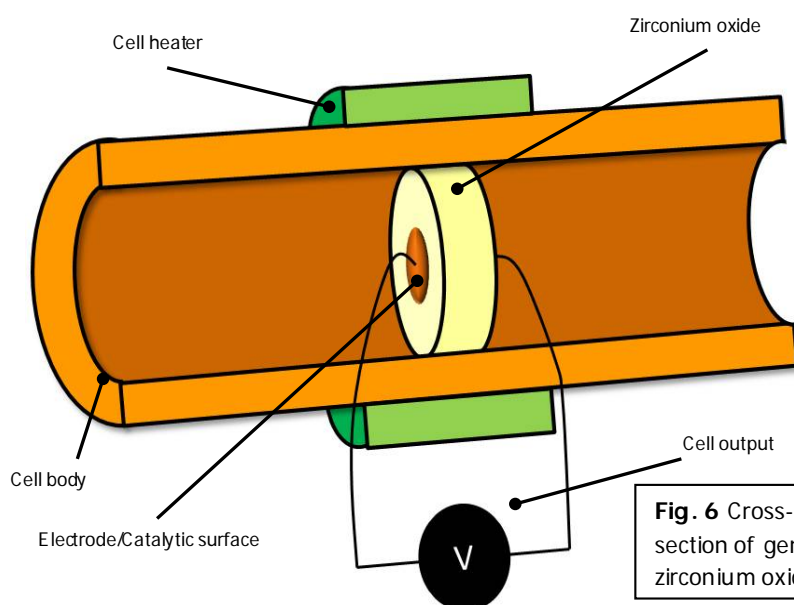


Fig. 6 Cross-section of generic zirconium oxide cell

With reference to Fig. 6, 9, 10 & 11, it is easiest to consider a zirconium oxide measuring cell as an oxygen balance. The zirconium oxide is a ceramic material and, as such, is a good electrical insulator. For the cell to work, the inherent resistance to electrical current flow must first be reduced. This is achieved by heating the zirconia to a high temperature. To achieve this, the cell is fitted with an electrical heater, typically operating at a temperature of between 500 and 750°C (932 and 1382°F), dependent on the application and type of electrode/catalyst used. Fig. 8 below shows how the electrical resistance of the material decreases with increasing temperature.

To create the electrical circuit, two electrodes are bonded to the zirconium surface, one on each side, to allow connection of the cell output wires. In addition, the surface of the zirconium is coated with a suitable catalytic material to enable the "tunneling" of the oxygen ions through the zirconium. The catalyst is often combined with the electrode in a single coating material. This coating is critical as it must provide a reliable electrical connection and permanent bond to the zirconium, while remaining porous to the oxygen ions.

The zirconia has “gaps” in its crystalline structure (Fig. 7) created by the addition of small amounts of yttrium (a transition metal) to the material, this is known as stabilized zirconia. These gaps, or oxygen vacancies, allow for the passage of oxygen ions through the crystal lattice.

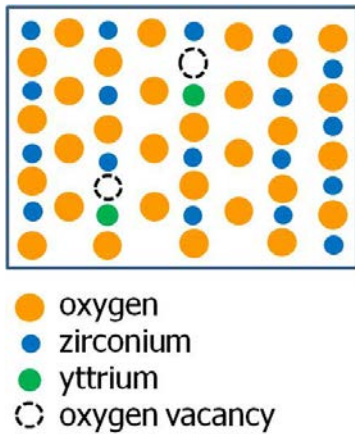


Fig.7 2D zirconium oxide crystal structure

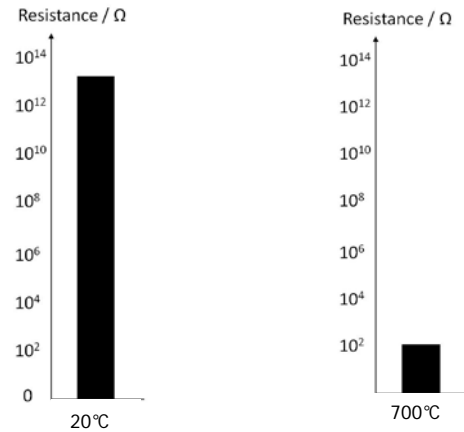


Fig.8 Electrical resistance of stabilized zirconium at 20°C and 700°C

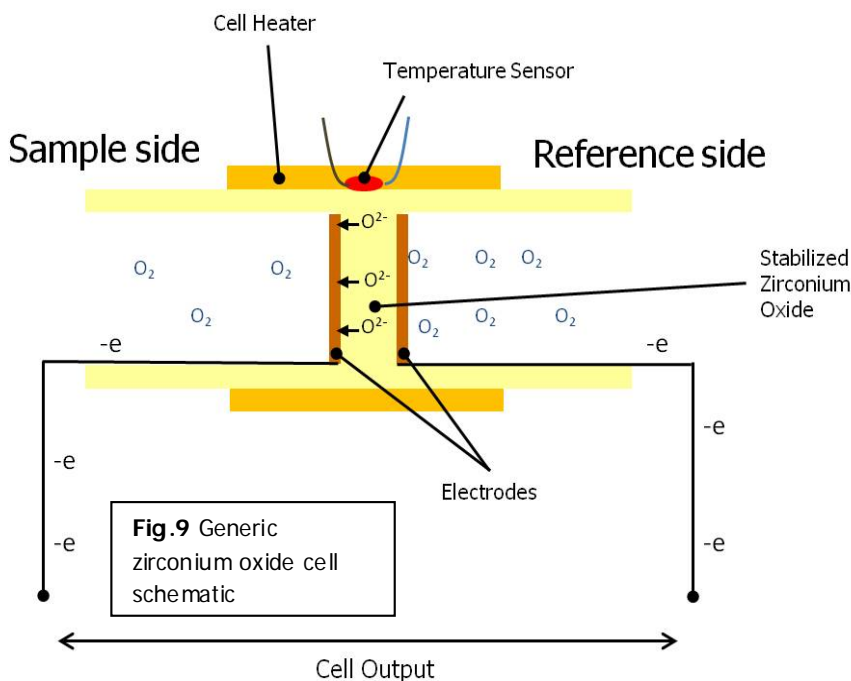


Fig.9 Generic zirconium oxide cell schematic

If the cell is arranged to have a higher concentration of oxygen on one side than on the other, then oxygen ions will migrate through the zirconia to the side of lower oxygen concentration, in an attempt to reach equilibrium. As this occurs, a flow of electrons will be established if the cell is connected into an electrical circuit.

If, for example, we seal off the reference side of the cell with air trapped inside and expose the sample side to low levels of oxygen, then the oxygen in the sealed reference side would migrate to the sample side, until both sides had the same oxygen concentration. Once this was achieved, the cell output would fall to zero. This is an important point, as the maximum output from the cell will always be

achieved when the cell is imbalanced, i.e. high O₂ concentration on one side and low O₂ concentration on the other side. This explains why zirconia cells are so well suited to low level oxygen measurement.

In most cell designs the reference side is exposed to a continuous feed of air, normally from the air surrounding the analyzer.

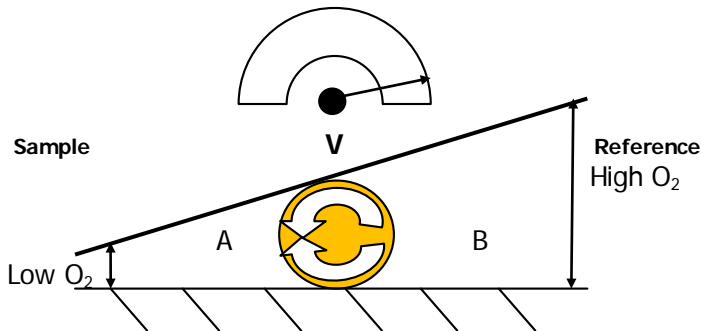


Fig. 10 "Seesaw" unbalanced – large output signal - $A \neq B$

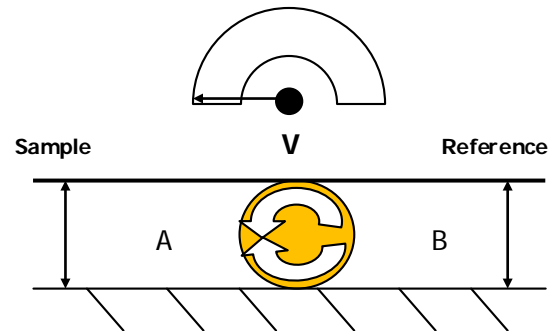


Fig. 11 "Seesaw" balanced – no output signal - $A = B$

TIP. Think of the zirconia cell just like a child's seesaw. If unbalanced (i.e. very little O_2 in the sample), then the output voltage will be high (see Fig.10). If the cell is balanced (i.e. the same O_2 concentration on each side), then the output voltage will be zero (see Fig. 11).

Advantages of the Michell zirconia cell

The Michell XZR400 utilizes a metallic sealed reference (MSRS) technology (see Fig.12); with a special metal compound that generates controlled quantities of oxygen within the reference side of the cell. This has the advantage that the reference side is not exposed to any possible contamination from reference air, as is the case with other designs. This offers a very compact, reliable and high performance measurement solution.

Our MSRS is the measurement technology of choice for many industrial gas plants worldwide.

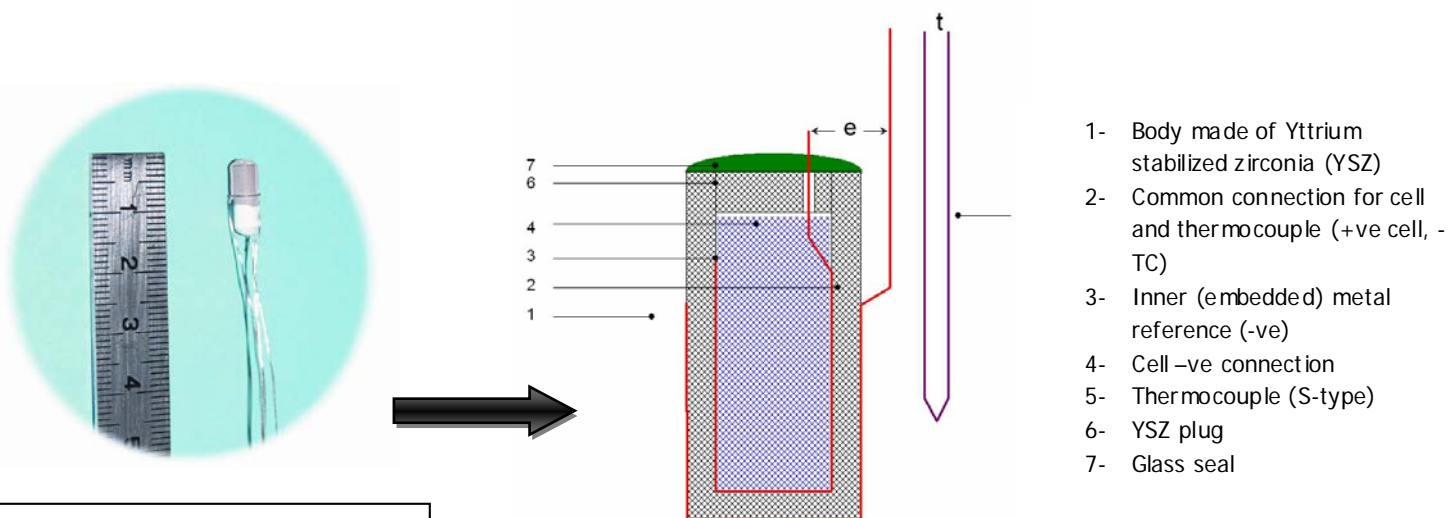


Fig. 12 SMRS Zirconia oxygen cell



An important practical consideration before installing a zirconia-based oxygen analyzer in an air separation application is to ensure that the sample contains no oil mists. In a well run modern plant this is very unlikely to occur and of course is highly undesirable. However, contamination of the sample can occur if the compressor seals become damaged or worn, allowing lubricating oil mists to enter the gas stream. This can be a problem particularly at some older cryogenic air separation plants. Since zirconium oxide cell technology utilizes a catalytic surface, hydrocarbons in the form of oil mists will inhibit the catalyst surface, causing loss of response and potentially permanent damage to the cell. To prevent this occurring, and to protect the cell, it is always advisable to install an in-line oil mist filter upstream of the analyzer, at the sample inlet. It is highly unlikely that a customer will ever mention or admit that oil mist can get into the gas stream, but the addition of this simple filter will ensure a long life for the zirconia cell and a reliable measurement for the customer, should such a situation occur.

Products



The XZR400-RM zirconium oxide based oxygen analyzer is ideally suited for the measurement of trace oxygen in nitrogen in air separation plants. It offers the customer simple and reliable operation. Its 19" rack configuration provides the analyzer format currently preferred by most IG customers.



Where a wall or panel mounted installation is preferred, the XZR400-WM fully meets this requirement. Offering the same benefits as the rack mounted version, but with greater flexibility with regard to mounting options. It is particularly suited to tanker loading bay applications.



The XTP601 is suitable for use on PSA or VPSA plants, which typically produce lower purity gases. The unit offers a compact, wall or panel mount configuration, ideal for oxygen measurement on these types of O₂ and N₂ generators.



Key IG companies:

Linde	BOC
Air Products	Messer
Praxair	Airgas
Air Liquide	NIGC
Taiyo Nippon Sanso	Plus many smaller local suppliers & operators

Most of the large IG companies periodically sign supply agreements for analysis equipment and operate preferred vendor lists. However, they are also keen to ensure that they do not single source equipment, so there are real opportunities to secure business. It is typical that the large companies will require test units for strenuous validation testing before accepting a new supplier. However, as previously stated, the SMRS cell design and technology is well established in this market. In addition, opportunities exist for sales to local IG companies and operators of cryogenic and (V)PSA air separation plants.



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