

*In focus...*

© APCI | Nitrogen generator

# Nitrogen generators for green hydrogen, ammonia, and fertilisers

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Nitrogen generators use a cryogenic process that is a simplified version of a full air separation unit (ASU). Alternatively, they can be based on pressure swing adsorption (PSA) technology. If all three main component gases of air are needed, air separation is the answer, but if only nitrogen is required then a nitrogen generator is likely to be more cost-effective.

Nitrogen generators are not designed to produce oxygen and argon as co-products. The focus on nitrogen reduces the specific power requirement, simplifies operation, and reduces the plant capital cost compared to an equivalent nitrogen flow derived from a full ASU.

The inputs required to operate a nitrogen generator are electrical power, cooling water and ambient air. Using renewable electricity from wind, solar or hydro power generation, the operation of these plants can be fully

sustainable, and they can produce green air gases for green hydrogen and hydrogen derivatives such as ammonia and fertilisers.

## Nitrogen for electrolyser safety

Electrolysis splits water to create oxygen and hydrogen gases. In the PEM and AEM electrolyser types, the two gases are separated by a membrane. In pressurised and atmospheric pressure alkaline electrolyzers, both gases are present together, dissolved in the lye electrolyte that circulates around the electrolyser. This means that when the electrolyser ramps down, the oxygen concentration in the hydrogen gas increases.

The lower flammable limit (LFL) of hydrogen in pure oxygen at atmospheric pressure and 20°C is 4%. However, electrolyzers generally operate at elevated temperatures around 80°C and at this temperature the LFL is slightly reduced to

3.8%. Pressurised alkaline and PEM electrolyzers operate at between 15 and 30 bar. At 20 bar and 20°C, the LFL is slightly increased to 5%. We can see that both the operating pressure and temperature have slight influence on the flammability limit of hydrogen in pure oxygen<sup>1</sup>.

Safety systems are incorporated into the electrolyser to prevent the hydrogen concentration in the oxygen gas rising to a dangerous level. When activated, these flood the electrolyser with inert nitrogen gas. The pipework transporting the oxygen and hydrogen from the electrolyser are also purged with nitrogen in the event of a system shutdown.

For a GW-scale green hydrogen alkaline electrolyser system working with variable or intermittent renewable power source, there would be several occasions per year where the system may need to ramp down and initiate a nitrogen purge. At GW-scale operation the amount of nitrogen required may justify an onsite nitrogen generator. Furthermore, the optimum locations for GW-scale green hydrogen electrolyser schemes are remote and on-site generation may be more cost effective than nitrogen deliveries by road tanker or pipeline.

A large green hydrogen scheme can be configured to purify the oxygen co-product that is generated on the anode of the electrolyser. The incremental additional cost of doing this is small. The implication is that there would be very few cases where the nitrogen demand for the electrolyser safety purge systems should be generated on an air separation unit (ASU). The air separation unit would simultaneously produce oxygen in addition to nitrogen, but if cheap oxygen is produced on the electrolyser, the additional investment in the ASU (compared to the simpler nitrogen generator) would not be justified unless there is a strong local merchant market for the oxygen.

## Nitrogen generators for green ammonia

Ammonia is derived from nitrogen and hydrogen. Many of the largest green hydrogen schemes that have been proposed worldwide will convert the green hydrogen to green ammonia for cost-effective shipping to international markets.

In recent years small to medium ammonia plants have

tended to use a pure nitrogen feed. A PSA or cryogenic nitrogen generator is ideal to supply the required gas to react with green hydrogen to produce the green ammonia.

Only the largest ammonia plants continue to use air to introduce the required nitrogen. The advantage of using pure nitrogen on the smaller and mid-scale facilities is that there is no oxygen circulating in the ammonia synthesis loop. This minimises energy losses and reduces the required plant size, resulting in OPEX and CAPEX cost reductions.

## Selection of an ASU enables process integration for ammonium nitrate production

In southern Africa, between Zambia and Zimbabwe lies the Kariba dam. Hydropower from that facility was fed to 100 MW of pressurised alkaline electrolyzers installed by Lurgi at Sable Chemicals. The electrolysis plant started up in 1973 and was made from 28 modules, each rated at 3.5 MW. It could produce up to 21,000 Nm<sup>3</sup>/hr of green hydrogen at 30 bar pressure. The hydrogen was converted to ammonia and then reacted with nitric acid to make ammonium nitrate, which has applications as a fertiliser and to make explosives for mining.

Nitric acid is made using the Ostwald process in which ammonia is oxidised over a 95% platinum and 5% rhodium catalyst at over 900°C and at 6.5 bar pressure to form nitric oxide and superheated steam. The gases are cooled and passed into a sequence of absorption columns where air or oxygen is added to further oxidise the nitric oxide to nitrogen dioxide. As the nitrogen dioxide gas passes up each column, it is absorbed into the water or dilute nitric acid water flowing down. In the final column, the concentration can reach more than 50% nitric acid.

In the above nitric acid production process, air or oxygen can be added in either or both oxidation reactions. When an air separation unit is used to generate nitrogen for ammonia production, the oxygen co-product can be used in the oxidation reactions. The use of oxygen in place of air reduces the reactor volume since there is no inert nitrogen introduced as a ballast gas. This form of process integration utilises the full



► range of products from the ASU and increases the overall economic viability of nitrogen-fed ammonia production.

The final stage of ammonium nitrate production is to react the ammonia with nitric acid and finally evaporation of the water to yield solid ammonium nitrate granules.

#### A green hydrogen phoenix

The Sable Chemicals ammonia plant had a capacity of more than 200,000 tonnes per year (tpy). However, rising electricity demand in the region and escalating power prices, combined with the advent of cheap coal to ammonia production in neighbouring South Africa eroded the economic viability of the Kwekwe electrolysis-based process for green ammonia production. In 2015, Sable Chemicals switched to importing grey ammonia from South Africa by rail.

Whilst green ammonia production was taking place at Kwekwe, an ASU produced pipeline gaseous nitrogen for the ammonia plant and some additional liquid nitrogen as back-up supply for the nitrogen pipeline to the ammonia plant and for local merchant markets. 2,000 tonnes per day (tpd) of liquid oxygen was also produced for the local market. Gaseous oxygen Nitrogen from the ASU was compressed to 30 bar prior to transfer to the ammonia plant.

It is possible that the Sable Chemicals electrolyzers will run again to produce either green hydrogen or green ammonia. Several years ago, Tatanga Energy declared plans to build a 400 MW solar park to supply Kwekwe. During peak sunlight hours, a portion of this solar power could be fed to the decommissioned 100 MW of pressurised alkaline electrolyzers. During the overnight period, when the solar park would not be producing electricity, battery energy storage, wind power or grid back-up power could be used to ensure that the alkaline electrolyzers have sufficient protective current to avoid electrode degradation during shutdown.

#### Urea fertiliser production relies on CCU

As an alternative to ammonium nitrate, urea can be used as a nitrogen-rich fertiliser. Urea is produced by reacting ammonia with carbon dioxide (CO<sub>2</sub>).

Most urea plants generate grey hydrogen from natural gas on a steam methane reformer (SMR). During the hydrogen production process, CO<sub>2</sub> is generated and captured using an amine solvent. Hydrogen from the SMR is converted to ammonia and the CO<sub>2</sub> that was captured from the SMR is utilised (CCU) to react with the ammonia and yield urea.

The ammonia production process in the grey urea value chain could potentially use nitrogen from a nitrogen generator. However, urea requires CO<sub>2</sub> so, when urea is the

“The ammonia production process in the grey urea value chain could potentially use nitrogen from a nitrogen generator...”

target molecule the SMR process has some process integration advantages over the electrolysis and green hydrogen pathway.

When urea is required in a defossilised future, the required CO<sub>2</sub> can be captured from a nearby point emission source, such as a biomass fired thermal power plant or a direct air CO<sub>2</sub> capture facility and reacted with green ammonia. [GW](#)



© miraflores | Yara Nauma on the Kiel Ship Canal, in Germany.



A typical ammonium nitrate plant.

#### REFERENCES

1. Explosion Characteristics of Hydrogen-Air and Hydrogen-Oxygen Mixtures at Elevated Pressures, Schroeder, V and Holtappels, K, BAM, Berlin, Germany