



Membrane-Based Ammonia Purge Gas Recovery Units - A Fresh Look at an Established Technology

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Legacy grey hydrogen supply is rapidly being replaced with blue and green hydrogen to support sustainability and decarbonization efforts. The transition to low (or no) carbon hydrogen has not been without consequence, as hydrogen prices have been on the rise. With increasing hydrogen prices impacting the cost to produce ammonia, producers are reexamining hydrogen recovery technology.

Air Products Membrane Solutions has been helping steam methane reformer (SMR) based ammonia plants recover hydrogen since the 1980s with membrane-based purge gas hydrogen recovery units (PGRUs). In total, 10-20 million tons of hydrogen have been recovered through these systems. These PGRUs have consistently provided great value to our customers by recovering valuable hydrogen, saving natural gas, and avoiding millions of tons of CO₂e emissions. Technology has continued to evolve since the introduction of PGRUs, and with the increased value of hydrogen, operators of SMR based ammonia plants would greatly benefit by ensuring their PGRUs are optimized for performance.

This presentation will cover the fundamentals of membrane separation, PGRU options and operation, optimization of legacy PGRUs, and the economic and GHG avoidance benefits for the ammonia industry.

1 DECADES OF MEMBRANE EXPERIENCE

Air Products' PRISM® membranes were successfully developed and implemented for hydrogen separation of process gases in the late 1970s, for which the technology received the 1981 Kirkpatrick Chemical Engineering Achievement Award. Since the first commercialized, large-scale PRISM membrane unit for ammonia purge was built in 1979, hundreds of these systems, delivered by Air Products, have created great value and reduced CO₂ emissions for ammonia plant customers around the world.

2 FUNDAMENTALS OF MEMBRANE SEPARATION

Separation is driven by gas permeability & differential pressure.

PRISM® membrane separators use the principle of selective permeation of gases through semi-permeable membranes. Molecules of a gas will move through or "permeate" a membrane barrier if the partial pressure of the particular gas is lower on the other side (Fig.1).

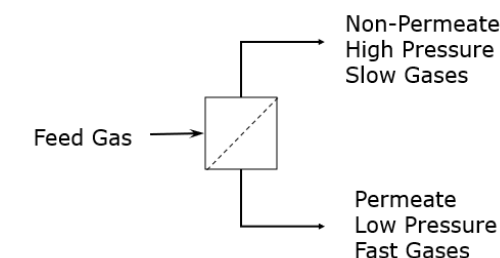


Fig. 1: Membrane separation

Different gases permeate at different rates, even when their partial pressure difference is the same. It is the differences in these permeation rates by which membranes effect a gas separation.

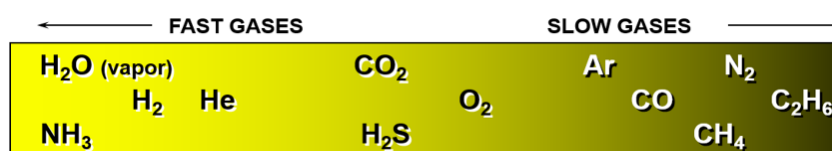


Fig. 2: Relative Permeability of Various Gases

Hydrogen is a fast-permeating gas (Fig.2) and can efficiently be separated from other slow-permeating gases.

3 PURGE GAS RECOVERY BY MEMBRANE IN THE AMMONIA SYNTHESIS LOOP

A PRISM® membrane purge gas recovery unit interacts with an ammonia plant by integrating into the synthesis loop to optimize overall efficiency (Fig.3). Below is a brief summary of this interaction:

1. Purge Gas Extraction:

In the ammonia synthesis loop a portion of the gas is continuously purged to prevent the build-up of inert gases like argon and unreacted methane. This purge gas contains hydrogen, nitrogen, ammonia, methane, and argon.

2. Ammonia Recovery:

The pressurized purge gas is directed first to a water scrubber for removing ammonia from the gas. The aqueous ammonia from the scrubber then goes to a stripper for ammonia recovery.

3. Hydrogen Recovery:

The ammonia-free gas is then heated and enters the membrane modules at high pressure. Hydrogen permeates through the membrane and is directed back to synthesis compressor suction at lower pressure. The remaining gases (methane, nitrogen, and argon) are retained on the non-permeate side and can be used as fuel in the reforming section.

4. System Configuration:

These systems are typically designed as one-stage units, or two-stage units (as shown in Fig.3) for optimal integration with the synthesis loop, and are complete skid-mounted with valves and instruments for easy installation. PRISM membrane systems are simple to operate and maintain, achieve large turndown range, and enable fast restart after shutdown. The systems can be easily expanded by adding more membranes.

5. Efficiency:

These systems can recover more than 85% of the hydrogen from the purge gas, significantly increasing ammonia production efficiency without increasing natural gas feed to reformer.

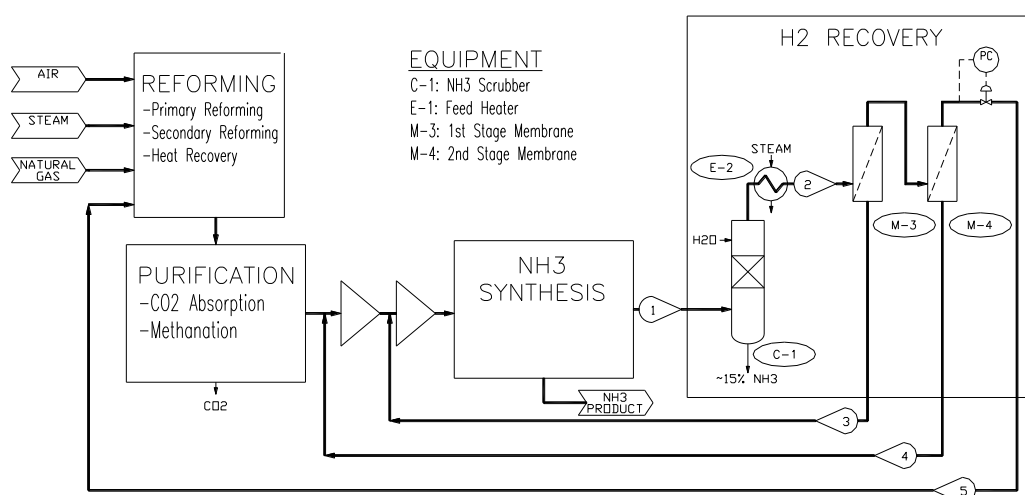


Fig. 3: Conventional NH₃ Process with 2-Stage Membrane PGRU

Since the PGRU enhances the efficiency of ammonia production, it contributes to cost savings and reduces greenhouse gas emissions. As hydrogen increases in value, and as the cost of CO₂ emissions increases, ensuring optimal performance in the ammonia plant has become even more critical.

With over 40 years of expertise in the ammonia PGRU market, Air Products has delivered consistent value and return on investment to customers who take advantage of membrane replacement and optimization services.

4 CASE STUDY – MEMBRANE PERFORMANCE EVALUATION

This case study was done for a customer in Asia, for a PGRU with 20 PRISM® membrane separators in total. The customer observed some decline in performance, and contacted Air Products for a performance evaluation.

System Configuration

This system was a one-stage design with 20 PRISM membranes. All hydrogen recovered from the membrane system is returned to the synthesis compressor suction stage at 32 kg/cm²g. Ten of the PRISM separators (U-01) had been in operation for more than 20 years, and a newer group of 10 PRISM separators (U-02) operated for less than 10 years (Fig.4)

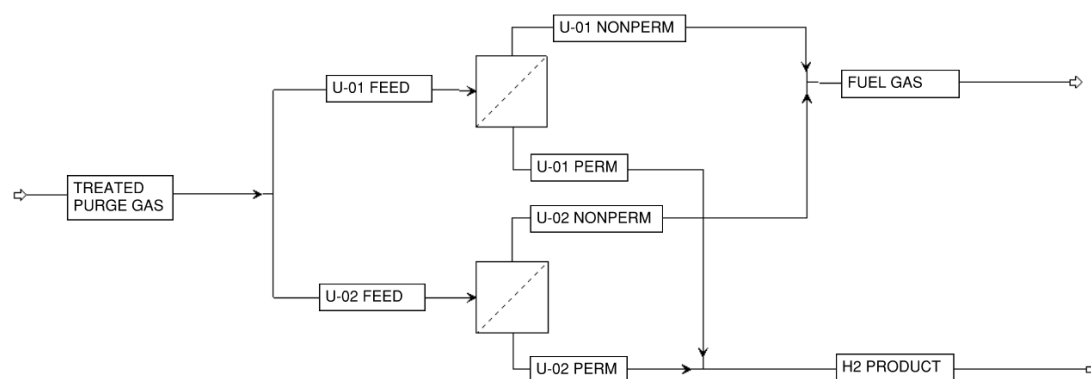


Fig. 4: Case study - Membrane PGRU Process Flow Diagram

Payback Calculations

The payback calculations are based on simulating performance improvement by replacing poor performing membranes, and varying the membrane feed flow to produce the same molar flow of inerts (methane and argon) in the nonpermeate.

To help quantify the economic benefits of the replacement membranes, Air Products analyzed changes in compression power and changes in natural gas consumption for syngas and heating, balancing the extra costs with increased ammonia product revenue. These calculations allowed estimation of the payback period for replacing the membranes, showing how quickly the customer could expect to recover their costs. This information helped the customer assess how the overall ammonia production process utilizes the membranes, and how important membrane performance is to their bottom line.

Membrane performance decline results in additional methane and argon entering the permeate with hydrogen thus causing an increase in the feed purge flow to maintain inert rejection. The new membranes allow more hydrogen to be recovered in the permeate and decrease the amount of inerts returned to the synthesis loop (purity of H₂ product stream is higher). The recovered hydrogen is converted into ammonia, increasing ammonia production.

Table 1 Case Study – Input from customer.		
Parameter	Value	Units
Cost of natural gas	403	\$/1000 SM3
Cost of power	130	\$/MWh
Price of ammonia	387	\$ per 1000 kg
Annual plant onstream	8760	hours
SYN compressor discharge pressure (Syn loop pressure)	190	Kg/cm2g
<i>PGRU performance data, including instrument measurement and lab analysis of feed, permeate and nonpermeate streams, was also provided by customer for Air Products analysis and mass balance validation.</i>		

The analysis also considered:

- Additional NH₃ produced by reducing H₂ lost to fuel (Saved H₂)
- Cost to compress the additional H₂ recovered
- Cost to compress air and N₂ required to produce additional NH₃
- Cost to use natural gas to make up for the H₂ saved from fuel gas

The total cost of achieving the net increased revenue stream also considers the cost of the replacement PRISM membrane elements plus the cost of installing them.

Results

The calculation results are shown in Table 2.

Table 2 Case Study - Payback calculation summary					
Case	Membrane separators replaced	Total # Separators replaced w/New	Total # Operating Separators	H2 Recovery mol%	Estimated Payback time weeks
1	Base model	0	20	89.4	-
2	Replace 5 LAST 'U-01'	5	20	92.8	45.4
3	Replace all 10 'U-01'	10	20	93.9	72.5
4	Replace 5 LAST 'U-01' and 5 LAST 'U-02'	10	20	95.1	98.2

Based on these results, the customer opted for case 3, replacing the 10 membranes which had been in operation for 20 years, with a payback time of less than one year and five months.

5 VALUE OF MEMBRANE PERFORMANCE EVALUATION IN FUTURE

For the case study, the overall hydrogen recovery increased from 89.4% to 93.9% by replacing membranes. In mass, this equals approximately 700 tons/year added hydrogen recovered for an increase of approximately 3,900 tons/year of ammonia production, assuming the PGRU continues to operate at design capacity and the conversion rate in the synthesis loop is 30%. With an average price for gray ammonia of \$490 USD/mt per the S&P Global Platts Ammonia Price Chart, the plant was able to recognize approximately \$1.9MM USD in additional ammonia revenue.

In addition to increased revenues, optimization of the PGRU allowed for sustainability benefits. The European Commission estimates that the production of 1kg hydrogen by SMR emits 8.85 kg CO₂. The additional 700 tons/year of recovered hydrogen represents about 6,200 CO₂e greenhouse gas avoidance. While the actual number is lower when discounting for make-up natural gas for furnace, added compression, and other factors, there is a tangible CO₂ reduction benefit to PGRU optimization. Between the economic and sustainability benefits of PGRU optimization, operators of SMR based ammonia plants would greatly benefit from ensuring their PGRUs are optimized for performance.

Extrapolating performance over 85 ammonia purge gas recovery reference installations running world-wide that have been in operation for 15+ years, Air Products could help customers save up to 525,000 tons/year CO₂e and recognize additional revenue of \$164MM USD by exploring optimization efforts.