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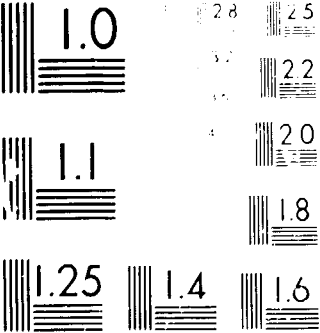
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HYDROGEN RECOVERY FROM AMMONIA PLANT PURGE GAS VIA PRISM® SEPARATORS*

by

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INTRODUCTION

Monsanto's PRISM® separators utilize the principle of selective permeation to effectively and economically separate hydrogen from process or purge gas streams. For ammonia plants, hydrogen recovered from the purge can be returned to the synthesis loop to increase ammonia production or if extra production is not desired, energy savings can be realized by maintaining constant ammonia production and reducing natural gas or naphtha feed to the reformer.

This paper describes the operating performance of a PRISM® separator system recovering hydrogen from a natural gas fed nominal 1000 MTPD ammonia plant. The concept applies equally well to all sizes of ammonia plant purge streams.

PRINCIPLE OF MEMBRANE SEPARATION

Transport of a gas through a membrane is proportional to its intrinsic permeability and driving force for the transport. Intrinsic permeability is characteristic of a specific gas and a membrane and depends on the ability of that gas to dissolve in and diffuse through the given membrane. The driving force is the difference in partial pressure of a gas on the two sides of a membrane. Differences in intrinsic permeability enable membranes to separate gas mixtures even in cases where the differential partial pressure driving forces of the gases are equal. This unique property of selective permeation is the basis for Monsanto's PRISM® separator system.

PRISM® is a trademark of Monsanto.

The selective permeation characteristic of Monsanto's membrane system allows "faster" gases such as hydrogen, helium and carbon dioxide to be separated from "slower" gases such as methane, nitrogen, argon, oxygen, carbon monoxide and hydrocarbons. The relative permeation rates through the Monsanto membrane are shown qualitatively below:

RELATIVE PERMEATION RATES

N_2, CH_4, CO, Ar — O_2 — CO_2 — He, H_2

SLOW — FAST

Monsanto's membrane tolerates significant concentrations of such stream components as ammonia, methanol, aromatics and hydrogen sulfide. The membranes operate efficiently on feeds with aliphatic concentrations of up to 80% of saturation and water concentrations up to 100% of saturation. This tolerance to water allows the use of inexpensive water scrubbing when a contaminant, such as ammonia, may exceed the membrane's resistance level.

Monsanto's oldest commercial installation has been on-stream for five years with no significant changes observed in hydrogen recovery or purity. The oldest ammonia purge system has been on-stream for about 2.5 years. It, likewise, has shown no significant changes in hydrogen recovery or purity.

HOLLOW FIBER GAS SEPARATOR

The Monsanto membranes are formed into hollow fibers to achieve maximum separation surface area in a minimum volume. The hollow fiber bundles are assembled into pressure vessels, resembling a shell and tube heat exchanger. (Figure 1).

A pressurized feed gas stream enters the separator on the shell side or the outside of the hollow fibers. As the gas flows upward along the fiber surface, each component permeates through to the bore side of the fiber in proportion to its permeability and its partial pressure differential across the membrane. The hollow fiber is sealed at the top and open through a tube sheet at the bottom. The hydrogen-rich permeate gas flows down the bore of the fiber, through the tube sheet, and is delivered at the bottom of the separator. The "slow" gases are concentrated on the shell side and exit from the separator at essentially the same pressure as the entering feed gas. To maximize hydrogen recovery, the exiting non-permeate gas is then used as the feed stream to a succeeding separator. For a given feed gas composition and pressure, the system product composition is controlled by the "space velocity", the ratio of volume flow to membrane surface area. Highest hydrogen purity is obtained by high flow rate over a small membrane surface area. Conversely, highest hydrogen recovery is achieved by low flow rate over a large membrane surface area. Each system is custom designed to meet the specific customer application requirement for hydrogen recovery and hydrogen purity.

MONSANTO PRISM® SEPARATOR SYSTEM

A typical PRISM separator system for ammonia purge applications consists of pretreatment, PRISM separators, and ammonia recovery. A flow diagram for this system is shown in Figure 2.

PRETREATMENT

Because extended exposure of the fibers to high concentrations of ammonia will diminish the performance of the separators, the purge gas stream is water scrubbed to reduce the ammonia concentration to less than 200 ppm prior to membrane contact.

The purge gas is typically received at about 135 Kg/cm^2 and -25°C. This gas is heated to 4°C. The heated purge gas, which normally contains 1.5-2.5% ammonia, enters the scrubber at the bottom and flows counter-current to the water. The scrubbed purge gas, containing less than 200 ppm ammonia, leaves the top of the absorber column. The aqueous ammonia stream leaving the bottom of the absorber is sent to ammonia recovery.

The scrubbed purge gas is heated to 35°C and sent directly to the PRISM® separators. Trace concentrations of ammonia and water vapor in the gas stream pose no problem to the membrane; therefore, an energy consuming dryer/adsorber system is not required.

PRISM® SEPARATORS

The scrubbed purge gas, containing about 61% hydrogen, is fed to the first bank of separators at 135 Kg/cm^2. To meet the requirements of a nominal 1000 MTPD ammonia plant, eight separators of 20 centimeters in diameter and 3.1 meters in length are used. These separators are arranged in two banks and operated in series.

From the first bank of separators, about 40% of the recovered hydrogen, at 92% purity, is returned to the second stage of the syngas compressor at 70 Kg/cm^2.

Since hydrogen permeation is driven by the hydrogen partial pressure differential, the rate of permeation decreases when the hydrogen partial pressure on the shell side approaches the hydrogen partial pressure of the bore side. Therefore, additional hydrogen is recovered from the first bank non-permeate stream by lowering the hydrogen partial pressure at the bore side of the second bank of separators. Because the non-permeate gases exit the top of the separators at essentially the same pressure as the entering gas, the feed pressure to the second bank of separators is 134 Kg/cm^2. The second bank permeate hydrogen, at 86% purity, is recovered at 28 Kg/cm^2 for return to the first stage suction of the syngas compressor. The second bank, in this example, thus utilizes an absolute pressure differential of 106 Kg/cm^2. The hydrogen content of the second bank non-permeate stream is reduced to about 7% and, after pressure reduction, is sent to the primary reformer as fuel.

The material balance for the example system is shown in Table 1. An overall hydrogen recovery of about 96% is obtained from this system, with an associated overall hydrogen purity of about 88%.

AMMONIA RECOVERY

The aqueous ammonia stream from the purge gas scrubber is sent to the stripper feed heat exchanger at approximately 21 Kg/cm^2. This shell and tube exchanger uses the bottoms from the stripper as a heat exchange fluid to raise the temperature of the ammonia-bearing water to 127°C for distillation in the stripper. The heated ammonia-bearing water and steam are fed to the stripper, which produces an ammonia vapor from the tower top and very high purity water from the bottom. The ammonia vapor is sent to a reflux condenser. Part of the condensed ammonia is returned to the top of the stripper as reflux while the remainder is sent to storage as product ammonia (>99 mole%).

CONSTRUCTION AND STARTUP

Monsanto's hydrogen recovery system is delivered to the plant as a shop-constructed, pre-tested, skid-mounted unit. The use of a skid-mounted system minimizes field installation time and expense, and reduces potential construction errors. The skid design achieves excellent space utilization while allowing sufficient access for operation and maintenance. Because of the system's compact size, 3.5m x 3.7m skid for the pretreatment and PRISM® separators and 2.5m x 3.7m skid for ammonia recovery, it is easily retrofitted into the plant.

Installation is easy. It involves construction of a concrete support pad plus providing the necessary tie-ins for feed, product returns, utilities, and control-room instrumentation. The cost of installation, which includes labor, materials, piping, control room instruments, and customer engineering is estimated at about $200,000.

Because plant tie-ins can be completed during a previously scheduled plant shutdown and the concrete pad prepared before system arrival, the system can be fully operational four weeks after delivery. Hydrogen recovery begins immediately after the purge gas is introduced, as no cool-down or pre-conditioning is required.

SYSTEM PERFORMANCE

A. Incremental Production: When operating in the maximum production mode, approximately 55 metric tons/day of incremental production are obtained using the example system. This includes the 5 metric tons/day which are recovered under all modes via the ammonia scrubber/stripper system. For maximum incremental production about 1350 Nm^3/hr of natural gas must be added to the example ammonia plant. If overall natural gas usage is held constant, about 25 metric tons/day of added production are obtained.

B. Energy Savings: When operating in the energy savings mode, reductions in energy usage of about 0.25MM Kilocalories/metric ton are achieved.

C. Reliability: Experience has shown that because PRISM® separators contain no moving parts and operate efficiently under varying process conditions, system on stream time in excess of 99% can be expected.

If the ammonia plant trips out, the PRISM separator system shuts down and is maintained under pressure to minimize startup time. For long shutdowns, process steam is turned off. No attention is required until the plant problem is solved. The system can be restarted in about 15 minutes.

D. Recovery: Overall hydrogen recovery will be about 96%.

E. Purity: The average composite of both recovered hydrogen streams yields an 88% hydrogen product.

F. Operator Attention: Minimal operator attention is required to operate the system (i.e., well below 1 hr/day). The separators function without complicated operating procedures. One operator summed it up by saying, "It's like operating a piece of pipe."

G. Utility Requirements: The system requires a minimum of utilities as summarized below:

3.5 Kg/cm^2 steam - 210 Kg/hr

18.2 Kg/cm^2 steam - 400 Kg/hr

Electricity - 20 KWH/hr

Instrument Air - 40 Nm^3/hr

Cooling Water - 20 m^3/hr

Nitrogen - Intermittent purge (used only during initial startup and prolonged shutdowns.)

H. Operational Flexibility: Beside the standard mode of operation of recycling the recovered hydrogen to the ammonia synthesis loop, PRISM® separator systems have been utilized to meet other plant needs for high purity hydrogen by exporting portions of the permeate to the new users while continuing to return the remaining hydrogen product back to the synthesis loop. The highest purity hydrogen is available from the first separator bore. Hydrogen purity then gradually declines as the concentration of hydrogen is depleted in the feed to each succeeding separator.

Capacity increases can be handled by incremental separator additions. Therefore, if equipment is installed which raises the operating capacity of a plant and this increases the purge volume, the system can be upgraded to its original design recovery value by the simple addition of separators.

CONCLUSION

In the nineteen commercial installations in which they are being used, PRISM® separator systems have demonstrated high recovery, good selectivity, and excellent tolerance to commercial environments.

The ten PRISM® separator ammonia purge systems, operating on ammonia plants ranging from 550 MTPD to 1350 MTPD capacity, have proven to be economical, reliable, flexible and maintenance-free hydrogen recovery units.

FIGURE 1
PRISM® SEPARATOR

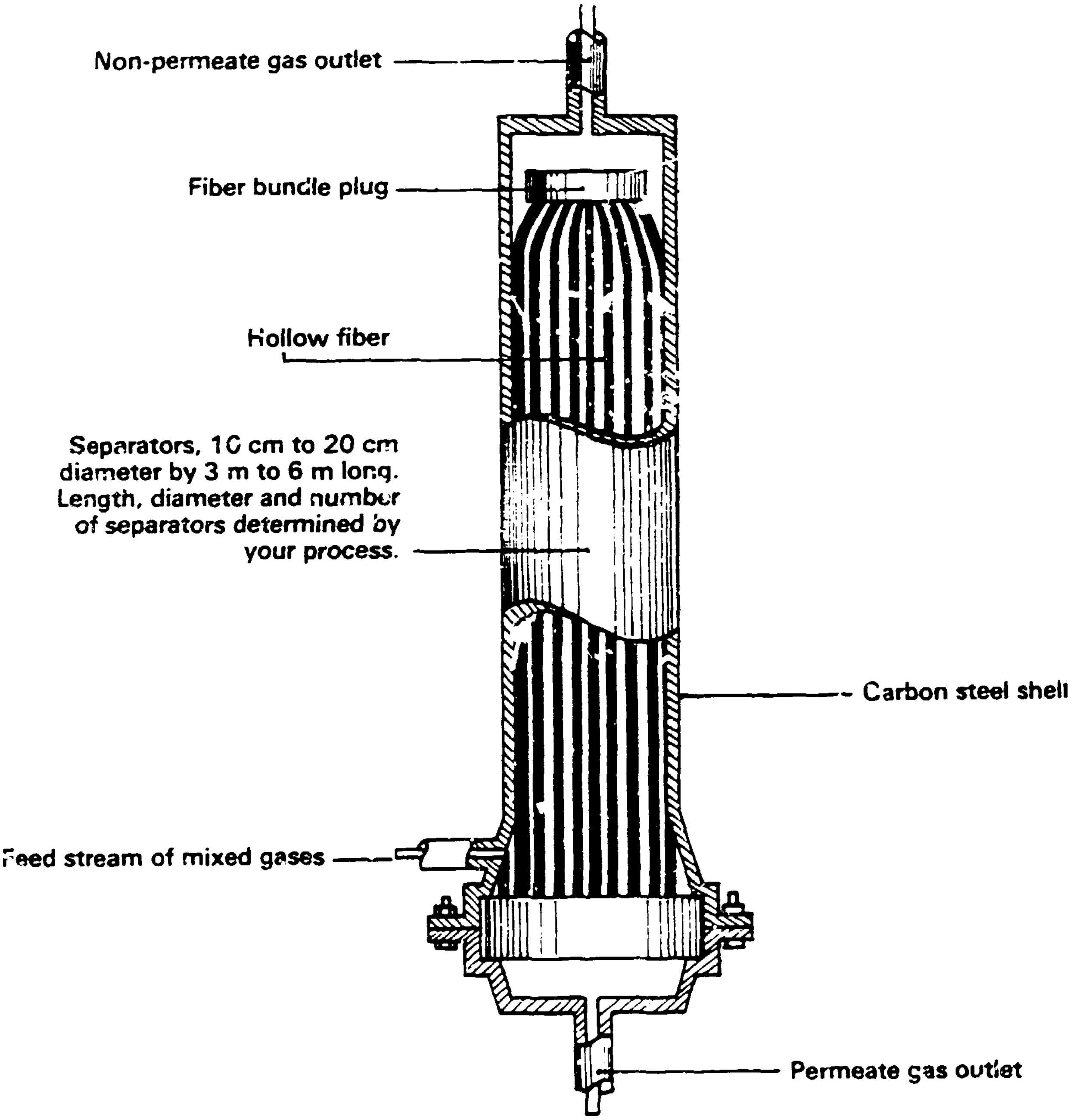

FIGURE 2

PRISM® SEPARATOR

AMMONIA PURGE GAS HYDROGEN RECOVERY SYSTEM

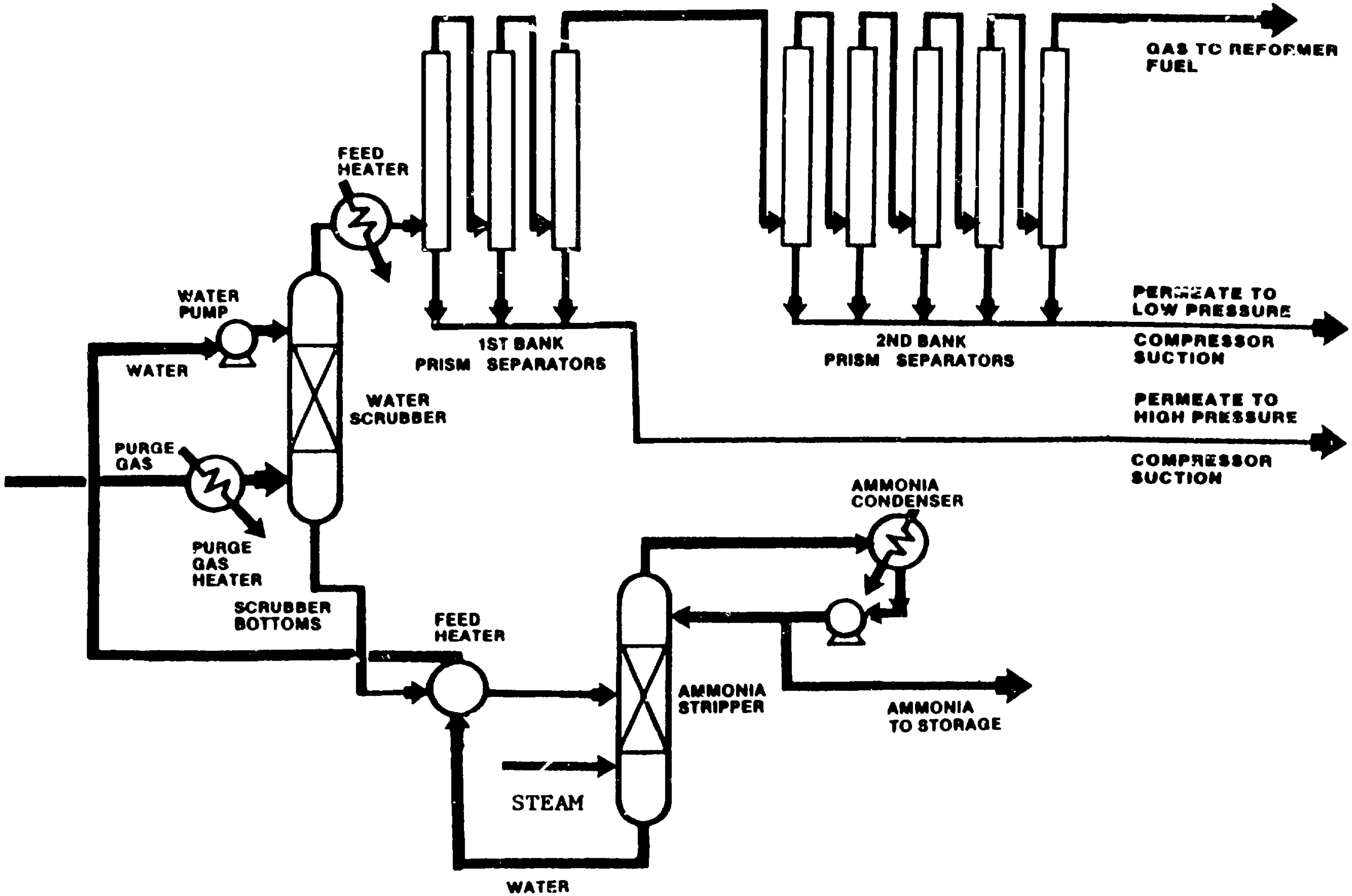

TABLE 1

MATERIAL BALANCE FOR PRISM® SEPARATOR SYSTEM

COMPONENT	FEED TO WATER SCRUBBER	FEED TO SEPARATORS	HIGH PRESSURE HYDROGEN PRODUCT	LOW PRESSURE HYDROGEN PRODUCT	FUEL GAS	AMMONIA STRIPPER PRODUCT
Hydrogen, Mole%	60	61	92	86	7	-
Nitrogen, Mole%	22	23	4	7	54	-
Methane, Mole%	10	10	2	4	25	-
Argon, Mole%	6	6	2	3	14	-
Ammonia, Mole%	2	(200ppm)	(330ppm)	(270ppm)	-	99
Water, mole%	-	0.03	0.05	0.04	-	1
Pressure, Kg/cm^2	135	135	70	28	132	17
Temperature, °C	4	35	35	35	35	46
Flowrate, Nm^3/hr	10200	9950	2470	4150	3330	250