MEMBRANES IN SEPARATIONS

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1 GASEOUS DIFFUSION – POLYMERIC MEMBRANES

For many years now, promising large-scale applications of gaseous diffusion as a separation process have been just around the corner.

In 1968 the status of large-scale use of the gaseous-diffusion process was summarized [6]. The essential conclusion was that, except for the Atomic Energy Commission’s gaseous-diffusion plants and Union Carbide’s hydrogen purification with palladium alloy foils, no other industrial applications had materialized.

At that time the technology of preparing hollow fibers was not sufficiently advanced to make them readily available. Today, however, the experience gained with hollow fibers in large-scale reverse-osmosis installations can be utilized to design and construct gaseous-diffusion cells with an effective area-to-volume ratio, and capable of operation at substantial pressure differentials across the fiber wall.

Du Pont Gaseous-Diffusion Plants

The Du Pont Company has extended its Permasep design to gaseous-diffusion applications. In 1958 Jolley [7] filed a U.S. Patent application covering films of polyacrylonitrile and polyethylene terephthalate for separating hydrogen or helium from gas mixtures. A later patent, issued in 1965 to Lewis et al. [8], describes in considerable detail the design and construction of a permeation apparatus for the separation of fluids, gas or liquid, by using hollow filaments. Thus, it covers gaseous-diffusion as well as reverse-osmosis applications. Figure 15.1 shows a diagrammatic picture of the Permasep construction. The permeator is said to contain 50 Million hollow polyester fibers, 50 μ o.d. with a surface area of 5 acres. A listing of pertinent patents dealing with the various aspects of equipment development is given in the reference section of Chapter XIV. In the design illustrated, the high-pressure gas is fed to the inside of the fibers.

The first commercial installation for the recovery of hydrogen from refinery gases has been in operation since about 1969, operating at a temperature of 100°F and a high side pressure of 550 psig. A diagrammatic flow sheet of a hydrogen recovery unit that was put on stream in October 1972 is demonstrated in Fig. 15.2 [9].

The hollow fibers used in the permeators are of Dacron polyester type, 18 μ i.d. and 32 to 38 μ o.d. They are encased in a steel shell rated at 650 or 1500 psi, depending on which operating pressure is needed. The overall length of each permeator is 18 ft, with a 12-in. i.d. for the 650-psi unit. The permeabilities of the particular polymer for various components are listed in Table 15.1. Magnitudewise, the permeabilities are very low, but the mechanical ruggedness
Fig. 15.1 Du Pont Permasep module construction for gas separation. (Courtesy Du Pont Company.)

![Diagram of Du Pont Permasep module construction for gas separation.](image)

Table 15.1

<table>
<thead>
<tr>
<th>Case 1 (95% hydrogen recovery) 6 permeators</th>
<th>Feed gas</th>
<th>Product H₂</th>
<th>Fuel gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>1,000,000 SCFD</td>
<td>950,000 SCFD</td>
<td>50,000 SCFD</td>
</tr>
<tr>
<td>CH₄</td>
<td>540,000 SCFD</td>
<td>50,000 SCFD</td>
<td>490,000 SCFD</td>
</tr>
<tr>
<td>Total</td>
<td>1,540,000 SCFD</td>
<td>1,000,000 SCFD</td>
<td>540,000 SCFD</td>
</tr>
<tr>
<td>%H₂</td>
<td>(65)</td>
<td>(95)</td>
<td>(9)</td>
</tr>
<tr>
<td>%RH₂</td>
<td>(95)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 15.2

<table>
<thead>
<tr>
<th>Case 2 (75% hydrogen recovery) 5 permeators</th>
<th>Feed gas</th>
<th>Product H₂</th>
<th>Fuel gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>1,300,000 SCFD</td>
<td>970,000 SCFD</td>
<td>330,000 SCFD</td>
</tr>
<tr>
<td>CH₄</td>
<td>700,000 SCFD</td>
<td>30,000 SCFD</td>
<td>670,000 SCFD</td>
</tr>
<tr>
<td>Total</td>
<td>2,000,000 SCFD</td>
<td>1,000,000 SCFD</td>
<td>1,000,000 SCFD</td>
</tr>
<tr>
<td>%H₂</td>
<td>(65)</td>
<td>(97)</td>
<td>(33)</td>
</tr>
<tr>
<td>%RH₂</td>
<td>(75)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 15.2 Flow diagram for off-gas hydrogen recovery [9]. Minimum requirements: 1,000,000 SCFD, 95% H₂.
of the hollow fibers allows the use of rather higher pressures that make it possible to obtain economical flow rates.

Table 15.1 Permeability—Du Pont Fiber

<table>
<thead>
<tr>
<th>Gas</th>
<th>Permeability (\times 10^{12}) (cc)(cm) ((\sec)(cm^2)(cm\ Hg))</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>165.0</td>
<td>61.1</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>31.0</td>
<td>11.5</td>
</tr>
<tr>
<td>A</td>
<td>7.5</td>
<td>2.8</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>3.5</td>
<td>1.3</td>
</tr>
<tr>
<td>N(_2)</td>
<td>3.1</td>
<td>1.2</td>
</tr>
<tr>
<td>CO</td>
<td>2.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Union Carbide—Helium Recovery

Union Carbide has conducted a large-scale test on helium recovery from natural gas. Considerable details on technology and operating data were reported by Litz and Smith [10]. The test was carried out at the Navajo Helium Facility in Shiprock, New Mexico, where a natural-gas supply was available with about 5% helium.

Figure 15.3 is a schematic of the flow sheet for the two-stage operation. The first stage bank of permeators was operated at 850 psig pressure, and the second stage at 950 psig. The downstream pressures in each of the stages were near atmospheric, so that appreciable interstage compression was necessary. It should be noted that the process arrangement is somewhat unusual, in that the feed streams to the modules in the stages are in series, whereas the product take-off streams are in parallel.

The membranes used for the separation were Eastman Chemical Company's KP-98 cellulose acetate films previously used in reverse-osmosis desalination.* These asymmetric-type membranes contain a very thin layer of dense film, about 0.00001 in. thickness, with a rather porous sublayer about 0.003 in. thick. The permeator design was that developed by Stern and his co-workers [11]. It is a flat-sheet arrangement with spacers between successive layers of the membrane as illustrated in Fig. 15.4. A sandwich type of structure is enclosed in a cylindrical steel shell, so that about 200 ft\(^2\) of active permeation area are available in a module approximately 10 in. in diameter and 5 ft long.

*Eastman Kodak no longer markets such membranes.
Fig. 15.3 Flow diagram for two-stage helium recovery from natural gas [10].

The magnitude of the operation is expressed by the following quantities of gas flow (average values):
Fig. 15.4 Structure of Union Carbide gaseous-diffusion membrane [10].

To 1st Stage
Fresh gas to 1st stage: 16,300 std ft³/hr
Helium content: 5.7%
Additional recycle of tail gas from 2nd stage
Helium content: 11.5%
(amount depends on operational splits).

From 1st Stage:
Tail gas: 14,200 std ft³/hr
Helium content: 2.3%
To 2nd Stage:
All of product gas from 1st stage
Some tail gas from 2nd stage as recycle
(amounts depend on operational splits)

From 2nd Stage:
Product gas: 645 std ft$^3$/hr
Helium content: 82.5%
Total gas: 2880 std ft$^3$/hr
Helium content: 11.5%
Recovery: 62% of helium in fresh feed
Temperatures: 116°F in 1st stage
78°F in 2nd stage

Pending Developments
An indication of further growing interest in the gaseous-diffusion process is a news item from C&EN [12], as follows:

“A cost-cutting helium recovery process has been developed by Teijin, Ltd. The Japanese method, based on selective permeability of a synthetic hollow-fiber material, operates at room temperature and about 425 psig. Compared to conventional helium recovery/purification methods—removal of other gases by liquefaction or by adsorption—the Teijin process features a 30% saving in operating cost at about the same initial investment. It’s also usable to purify hydrogen streams in refineries.”

No further details are available at present. However, one would infer that the process parallels the Permasep design of the Du Pont Company.

2 METALLIC MEMBRANES

The only known large-scale process is the separation or purification of hydrogen by means of palladium alloy membranes. The status of this process was reviewed in 1968 [6], where the pertinent literature was surveyed. For the sake of convenience a few essential items should be repeated here.

Union Carbide Hydrogen Purification
The most informative description of the process still is that of McBride and McKinley [13] reported in 1965. Operating conditions require feed pressures of 500 psi and temperatures of 300 to 400°C or higher. The potentially deleterious effect of gas impurities, such as CH$_4$, C$_2$H$_4$, CO, and H$_2$S, especially at higher temperatures, imposes a practical upper temperature limit. Economic evaluations are presented and show that profitable operation is attainable with plants that produce about 4 million ft$^3$ of high-purity hydrogen
are already being thought of in terms of multimillion gallons per day. This situation holds in a very general way for all liquid-phase processes.

One prediction can be made with a reasonable degree of safety. It is that polymeric nonporous membranes are likely to experience a high degree of use in gas and vapor separation. Microporous media will find application only to limited extent in special situations or in separation of gas mixtures having very large separation factors.

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