

# A Review of Conventional and Emerging Process Technologies for the Recovery of Helium from Natural Gas

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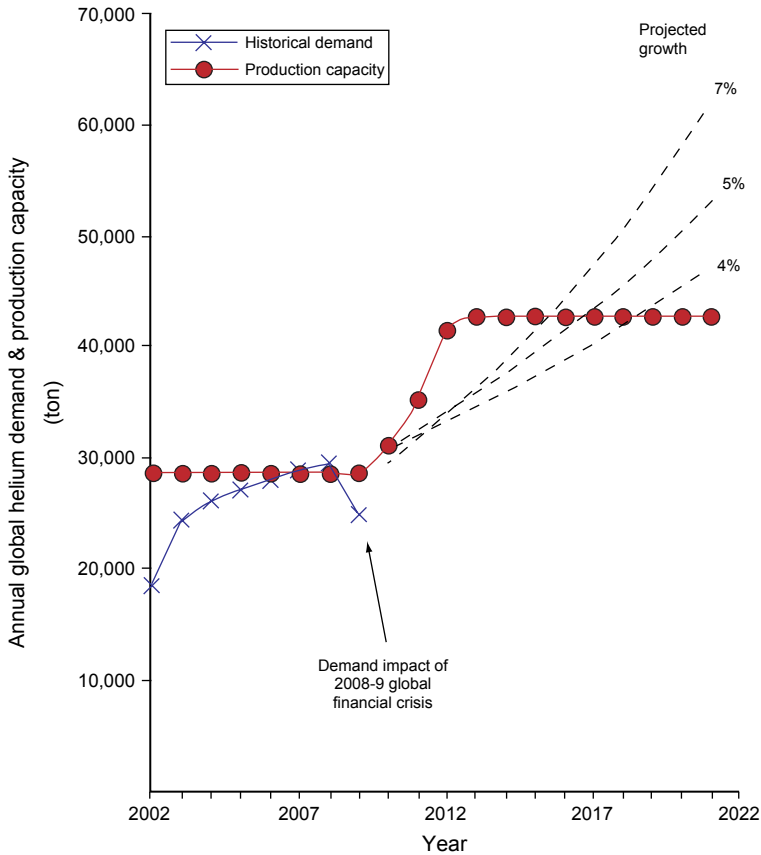
**ABSTRACT:** Helium is a unique gas with a wide range of important medical, scientific and industrial applications based on helium's extremely low boiling temperature, inert and non-flammable nature and small molecular size. The only practical sources of helium are from certain natural gas (NG) fields. As world demand for helium rapidly increases, the value of NG fields that contain it even in very small amounts is likely to rise significantly if the helium can be recovered efficiently. However, recovering the helium from the NG using conventional cryogenic distillation processes is expensive and energy intensive. We review the scope for improving the efficiency of the conventional helium recovery and upgrade processes, and evaluate the potential of emerging technologies based on adsorption or membrane separations for helium upgrade and purification. Helium recovery and purification processes are comparable in many ways with systems designed for hydrogen purification and thus, many of recent technological advances for H<sub>2</sub> separation from CH<sub>4</sub>, N<sub>2</sub> and CO<sub>2</sub> may be applicable to a helium recovery process. Furthermore, some recent patents and pilot plant studies indicate there exist several opportunities for the development of advanced materials, such as helium-selective adsorbents, and optimized process operations for the recovery of helium from NG.

## 1. INTRODUCTION

### 1.1. Helium Market Demand and Sources

Helium is a unique gas with a wide range of important medical, scientific and industrial applications based on its extremely low boiling temperature (4.2 K), inert and non-flammable nature, and small molecular size. The global demand for helium in 2010 was approximately 30,000 t with a value close to USD\$1 billion; (U.S. Geological Survey 2010) and, following a recovery from the economic downturn of 2008–2009, projections show a continued increase in demand for helium of 5–7% per annum (Pacheco and Thomas 2010). Much of this forecast demand growth will be in Asia, especially in the developing economies of China and India. New helium production facilities have recently been commissioned in Algeria, Qatar and Australia: Darwin has the only helium extraction plant in the southern hemisphere (West 2009). However, as the projections in Figure 1 show, the production capacity of these plants and other planned projects currently fail to meet the projected demand for helium.

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**Figure 1.** Historic (x) and projected (dashed lines) demand for helium with a predicted short fall in helium production capacity assuming the current projects proceed (circles). Statistical data from Pacheco and Thomas (2010).

The single largest use of helium is as a liquid coolant in superconductors for magnetic resonance imaging equipment in hospitals. Other helium uses are as a coolant in particle accelerators and high-energy physics research; a carrier gas in analytical equipment such as gas chromatographs; a blanket gas for welding; and helium/oxygen breathing gas mixtures to avoid nitrogen narcosis in deep-sea divers and operating-room patients (Daly 2005). In addition, the next generation of gas-cooled nuclear power reactors are expected to consume large volumes of helium: gas-cooled reactors are more efficient and safer than the older water-cooled reactors. Twenty-one nuclear power plants are under construction with plans to build 150 more reactors (most are in Asia), and therefore, further pressure on helium supplies is likely.

Although air contains a large volume of helium, the concentration of 5 ppm (Kidnay and Parrish 2006) is too low for viable extraction of helium from the atmosphere. Instead the only practical helium source is from certain natural gas (NG) fields. The best of these still contain only very small concentrations of He, with helium-rich gas fields typically described as those with concentrations greater than 0.3% (Kidnay and Parrish 2006). As the demand for helium increases in the future, the value of NG fields that contain helium even in very small amounts is likely to rise significantly if the helium can be recovered efficiently. Recovering the helium from the NG by conventional cryogenic

distillation methods is expensive and energy intensive. However, gas field developments based on liquefied NG (LNG) plants have a natural advantage in terms of helium recovery because the marginal extraction cost can be small relative to the potential additional revenue. New technologies that more efficiently extract and purify the helium could make that natural advantage even more lucrative and/or lower the concentration of helium needed in the gas to make extraction worthwhile economically. The global LNG industry is undergoing a rapid expansion in capacity to meet the growing demand for NG; the International Energy Agency predicts that by 2020 the total annual liquefaction capacity will increase from an estimated 370 billion cubic meters in mid-2011 to nearly 870 billion cubic meters by 2020 (International Energy Agency 2011). Several of the proposed LNG projects may present opportunities to recover helium as a saleable product in the liquefaction process.

Helium extraction facilities currently in operation are listed in Table 1. There were 22 helium plants operating in the continental USA in 2009, of which all but two used a cryogenic separation technology (Pacheco and Thomas 2010). The helium plants in the USA accounted for 71% of global helium production in 2009 with the remainder produced in Algeria, Qatar, Poland and Russia. The first helium production plant in the southern hemisphere was commissioned in Darwin in March 2010 (liquid He product 860 l/hour = 2.6 t/d; Lindemann *et al.* 2010).

Besides the Darwin LNG plant, other recently constructed helium production plants are those designed by Air Liquide in Ras Laffan Qatar (2005, 660 MMscf/year = 8.65 t/d; Daly 2005), and another by Linde Engineering in Skikda Algeria (start-up 2006, 10 t/d; Linde-Engineering 2010). Air Liquide and RasGas announced in May 2010 plans to build a second helium extraction unit at Ras Laffan (Air Liquide 2010). Other significant He extraction plants under development include an expansion of the Skikda plant in 2012 (Chemical Week 2007) and the construction of a new 1 MMscfd (4.78 t/d) He plant in Wyoming, USA (Air Products & Chemicals 2010). Conventional cryogenic distillation processes are used for He recovery in each of these new projects.

The largest scale He recovery plants recently constructed or in development all use cryogenic distillation to perform the bulk of gas separations. Adsorption processes are used in the He purification stages to adsorb trace amounts of N<sub>2</sub> (and Ar) from the upgraded He (>90% He), but at present there is no alternative commercially available process technology that is competitive with cryogenic distillation for the He recovery from low concentration He streams at the gas flow rates characteristic of large LNG developments. In other industrial applications, such as the production of hydrogen in the chemical and petrochemical industries (Ritter and Ebner 2007), the potential has been demonstrated for adsorption and membrane separation processes to achieve large capital and energy-cost savings compared with cryogenic distillation processes. One pilot-plant scale pressure-swing adsorption (PSA) process for He recovery from a 0.04-MMscfd NG feed containing 6% He is reported by Das *et al.* (2008). Several adsorption-based processes for He recovery disclosed in patents are described later in this review. Helium extraction plants using membrane separation have reportedly been used since 1985 (Häussinger *et al.* 2005) and we provide here a summary of the available literature on membrane units for He recovery.

This paper reviews the conventional cryogenic processes for helium recovery, including the recently constructed helium plants in Qatar and Australia, and then examines the potential of emerging technologies for more efficient helium production processes. Conventional helium plants generally use cryogenic distillation to produce crude helium and then use PSA to purify it to the level required for liquefaction and sales. The conventional PSA processes used in helium purification adsorb the non-helium components present in the feed gas. Scope exists to optimize these standard PSA processes by operating at lower temperatures, using improved adsorbents, and with rapid PSA cycles. Emerging technologies for helium upgrade and purification are either based on adsorption or membrane separations.

**TABLE 1.** List of Helium Extraction Plants around the World (Pacheco and Thomas 2003; West 2009)

Owner or operator	Location	Year commissioned	Type of He product	Capacity t/d
<i>Plants located outside the USA</i>				
Linde	Darwin, Australia	2010	Pure He	2.6
Helison	Skikda, Algeria	2006 (2012)	Pure He	10
RasGas	Qatar	2005 (2013)	Pure He	8.65 (17.7)
Orenburg Gazprom	Orenburg, Russia	Before 1993	Pure He	3.0
Polish Oil & Gas Co.	Odolanów, Poland	1977	Pure He	1.6
HELIOS	Arzew, Algeria	1995	Pure He	7.4
ONGC ( <i>PSA pilot plant</i> )	Kuthalam, India	2008	Pure He	0.00023
<i>Plants located in the USA</i>				
Total U.S. capacity including plants on standby = 86.6 t/d (Pacheco and Thomas 2010)				
Cimarex	Big Piney, WY	(Q4, 2011)	Pure He	(4.78)
Air Products Helium, Inc.	Hansford County, TX	–	Pure He	–
Air Products Helium, Inc.	Liberal, KS	1966, 1991	Pure	13
BP America, Inc.	Sunray, TX	1995	Crude He	–
BP America, Inc.	Ulysses, KS	1998	Crude He	–
DCP Midstream, LLC	Cheyenne Wells, CO	–	Crude and pure He	–
DCP Midstream, LLC	Hansford County, TX	–	Crude He	–
DCP Midstream, LLC	Liberal, KS	–	Crude He	–
DCP Midstream, LLC	Borger, TX	–	Crude He	–
EnCana Oil & Gas (USA) Inc.	Moab, UT	–	Crude and pure He	–
ExxonMobil Gas & Power Marketing Co.	Shute Creek, WY	1986	Crude and pure He	–
IACX Energy2	Otis, KS	–	Crude He	–
K-L Energy Partners, LLC3	Lakin, KS	1995	Crude He	–
Linde Global Helium Inc.	Otis, KS	–	Pure He	–
Midstream Energy Services, LLC	Keyes, OK	1996	Crude and Pure He	–
Nacogdoches Oil & Gas, L.L.C.4	Shiprock, NM	–	Pure He	–
ONEOK Field Services Co.3	Bushton, KS	–	Crude He	–
ONEOK Field Services Co.3	Scott City, KS	–	Crude He	–
Pioneer Natural Resources Co.	Fain, TX	–	Crude He	–
Pioneer Natural Resources Co.	Satanta, KS	–	Crude He	–
Praxair, Inc.	Bushton, KS	–	Crude and Pure He	–
Praxair, Inc.	Ulysses, KS	1962, 1998	Crude and Pure He	–
SemGas, LP6	Dodge City, KS	–	Crude	–

In most cases, the reliance on cryogenic distillation methods means that the recovery of He from a gas reserve is not just dependent on the He content of the reserve but also strongly dependent on development of LNG production facilities. Although when the marginal cost of He

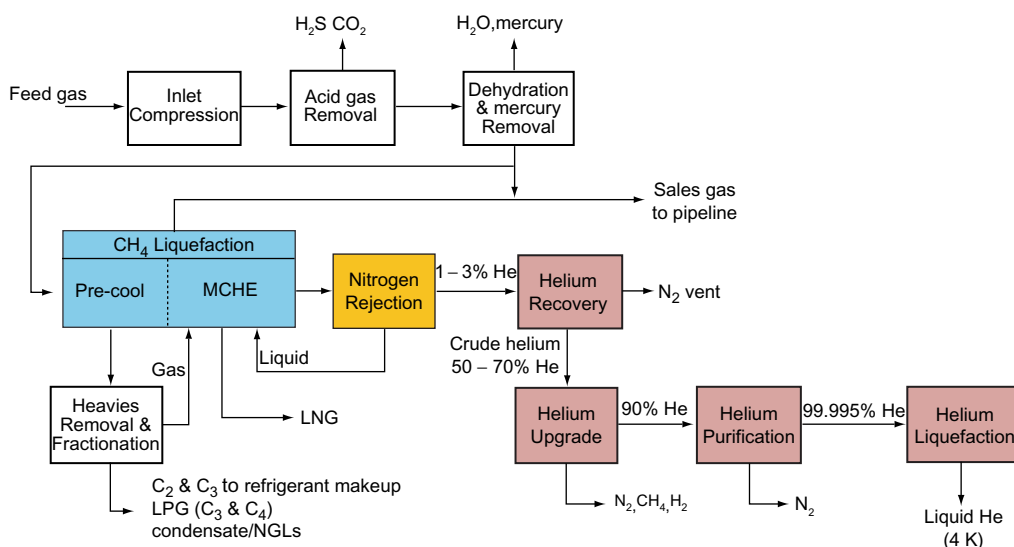
extraction may be relatively small compared with the total LNG plant costs, the additional capital cost of cryogenic He extraction and purification plants means that a significant investment decision to install them is still required. New technologies that more efficiently extract and purify helium could lower the concentration of helium needed in the gas to make extraction worthwhile economically. Furthermore, the opportunities for alternative non-cryogenic He extraction processes may be increased in specific cases such as the development of remote, stranded or unconventional gas reserves including depleted gas fields like Hugoton, USA which may contain predominantly nitrogen (Kammerzell 2011; Clarke *et al.* 2013). Similarly, novel or unusual field development scenarios, such as floating LNG production or reserves for which non-cryogenic technologies, such as PSA, need to be considered for N<sub>2</sub> rejection (Mitariten 2009) also present multiple opportunities for the application of emerging helium recovery technologies.

## 2. CONVENTIONAL HELIUM RECOVERY AND UPGRADE TECHNOLOGY

### 2.1. Overview of Helium Extraction from NG

The three process steps required before liquefaction of the helium are (1) *helium recovery* (or extraction) from NG, (2) *helium upgrading* to a 90% He product, and (3) *helium purification* to remove any remaining impurities such as hydrogen and neon to produce a He product of 99% or higher purity. As bulk helium is commonly shipped as a liquid in vacuum- and super-insulated liquid nitrogen–shielded containers (Shed 2009), the final stage of the He production process is liquefaction.

A schematic overview of the route of He through an LNG plant is shown in Figure 2. Before the cryogenic sections of the LNG plant, the feed gas must be treated to remove acid gases (e.g. CO<sub>2</sub> and H<sub>2</sub>S), water, mercury and heavy hydrocarbons. Helium has an extremely low boiling point and so any He in the NG feed to an LNG plant is concentrated in the overheads product of an N<sub>2</sub> rejection unit (NRU), which is conventionally a cryogenic distillation process. Thus, helium



**Figure 2.** Overview of LNG process and location of helium concentration operations after the nitrogen rejection unit.

recovery units are generally integrated with the NRU. If the LNG plant does not have a helium recovery unit any He in the feed gas will be vented to atmosphere with the N<sub>2</sub> vent stream. Table 2 provides a summary of the key physical properties of He and other gas components that may be in the NRU overheads product or generated during He purification.

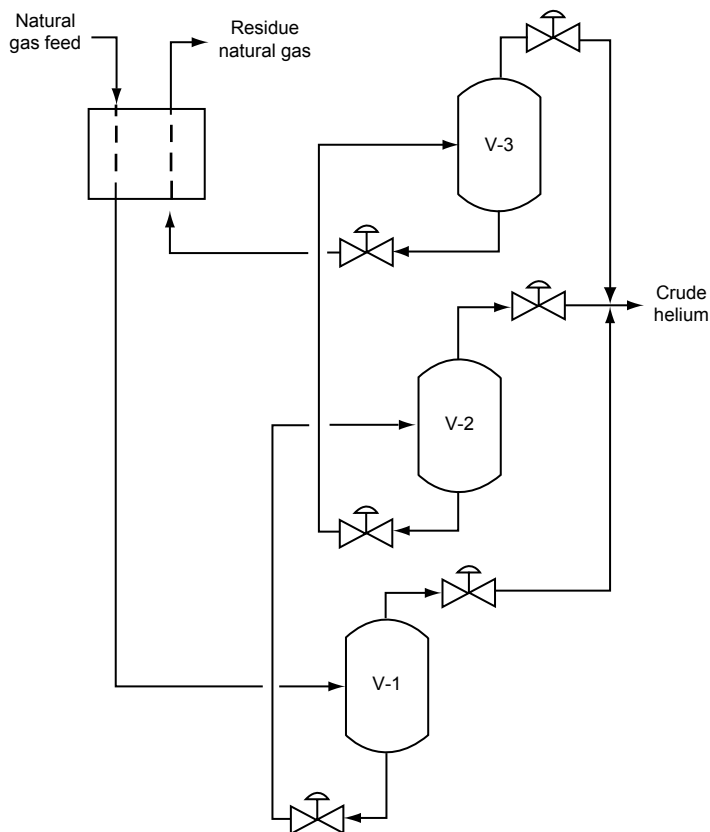
**TABLE 2.** Physical Properties of Helium and Other Gas Components Encountered in the Helium Recovery and Purification Process

	He	Ne	H <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> O
Kinetic diameter, Å (Tagliabue <i>et al.</i> 2009)	2.60	2.59	2.89	3.64	3.80	3.30	2.65
Normal boiling point, K (Lemmon <i>et al.</i> 2010)	4.23	27.1	20.4	77.4	111.7	–	373.1
Critical temperature, K (Lemmon <i>et al.</i> 2010)	5.20	44.5	33.1	126.2	190.56	304.1	647.1
Polarizability, Å <sup>3</sup> (Tagliabue <i>et al.</i> 2009)	0.208	0.401	0.787	1.710	2.448	2.507	1.501
Quadrupole moment, DÅ (Tagliabue <i>et al.</i> 2009)	0	0	0.43	1.54	0.02	4.3	2.3
ΔH <sub>vap</sub> at boiling temperature, J/g (Agrawal <i>et al.</i> 2003)	20.82	84.7	444.74	198.77	509.34	571.08	2257

## 2.2. Helium Recovery by Cryogenic Fractionation

As processes to recover helium from NG are closely integrated with the cryogenic distillation processes to remove N<sub>2</sub> from the NG (Häussinger *et al.* 2005), this section of the review describes the main design features of NRUs. The four basic cryogenic distillation processes used for N<sub>2</sub> rejection from NG are multi-stage flash separators, the single-column heat-pumped process, the double-column process, and the dual-column cycle (Agrawal *et al.* 2003). The choice of process to achieve the N<sub>2</sub> rejection task depends largely on the volume flow and composition of the feed (West 2009), including whether there is sufficient concentration of He to make helium recovery economically viable. Multi-stage flash separator processes have lower capital costs than cryogenic distillation column processes, but have higher energy requirements and typically only produce overhead vapour streams with low concentrations of He. In a single-column NRU, or in a process with a single-stage flash separator, the N<sub>2</sub>-rich overhead stream may contain 1–3% He depending on feed gas composition. More complex, double-column NRU processes can operate in a partial condensation mode to produce a *crude helium* vapour stream containing 50–70% He, together with N<sub>2</sub> and small amounts of CH<sub>4</sub>, H<sub>2</sub>, Ne, Ar and CO<sub>2</sub> (Agrawal *et al.* 2003; West 2009).

In the multi-stage flash process, the pressure of the LNG feed, which contains the dissolved helium and some dissolved N<sub>2</sub>, is reduced in a series of *flash* vessels (West 2009) as shown in Figure 3. In each flash stage, the helium will be vaporized along with the N<sub>2</sub>. The liquid NG product is used to pre-heat the feed. Although this example of a multi-stage flash process described by West (2009) has an LNG feed containing He, a similar multi-stage flash process could be applied to the overheads product of the NRU, in which case the overheads product would need to be cooled to be at least partially condensed. The He content of the crude helium product

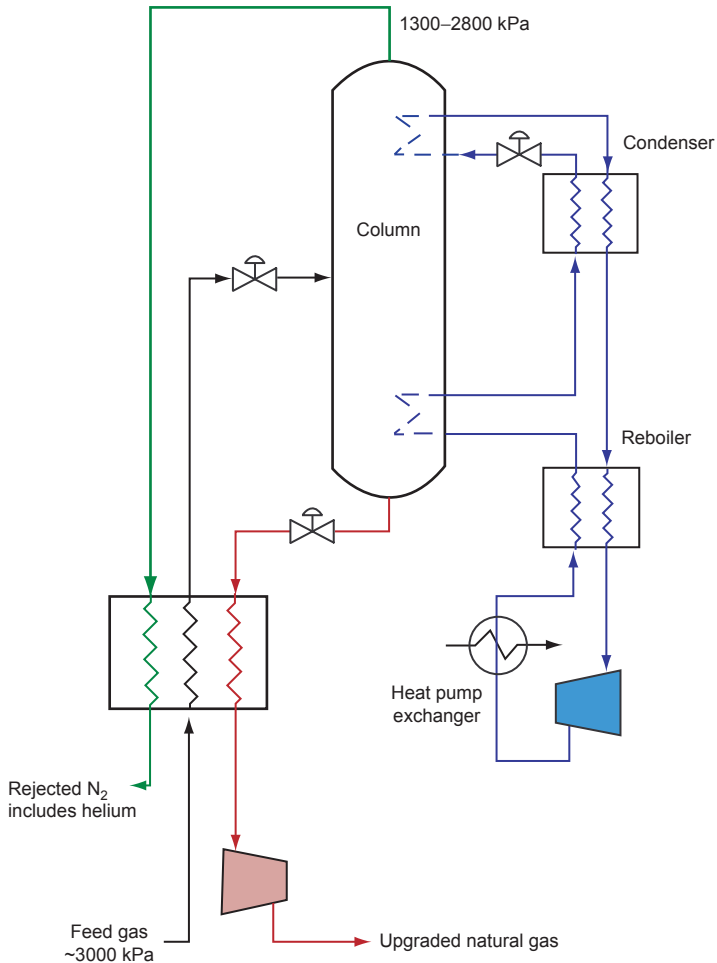


**Figure 3.** Schematic of a multi-stage flash process for the recovery of helium from natural gas.

will depend on the feed's He concentration, as well as the available pressure drop and resulting temperature change.

In the single-column heat-pumped process (Figure 4), a purified NG feed is pre-cooled in the main cryogenic heat exchanger (MCHE; against the rejected  $N_2$ ) and then fed to a high-pressure column (1.3–2.8 MPa). The vapour rejected from the top of the column contains  $N_2$  and He. Methane is condensed and drawn from the bottom of the column. A closed-loop heat pump (that uses methane as the working fluid) supplies both the reboiler heating and the condenser cooling duties to the column. The methane bottoms stream is flashed across a control valve to a low pressure and warmed with the feed gas and the rejected  $N_2$  in the MCHE. The single-column process produces only one  $N_2$ -rich vapour stream with a He concentration of typically 1–3% depending on the He content of the feed gas.

A simplified process flow scheme of a modern, double-column process for  $N_2$  rejection and He recovery from NG is shown in Figure 5 (this process is described by Häussinger *et al.* 2005). The feed gas is cooled against cold product streams in a cryogenic heat exchanger (Main Feed/product HX) and is fed to the bottom of the high-pressure column. In this high-pressure column, the helium is recovered from the feed at typical operating pressures within the range of 1–2.5 MPa (Agrawal *et al.* 2003). The high-pressure column's partial condenser provides reflux

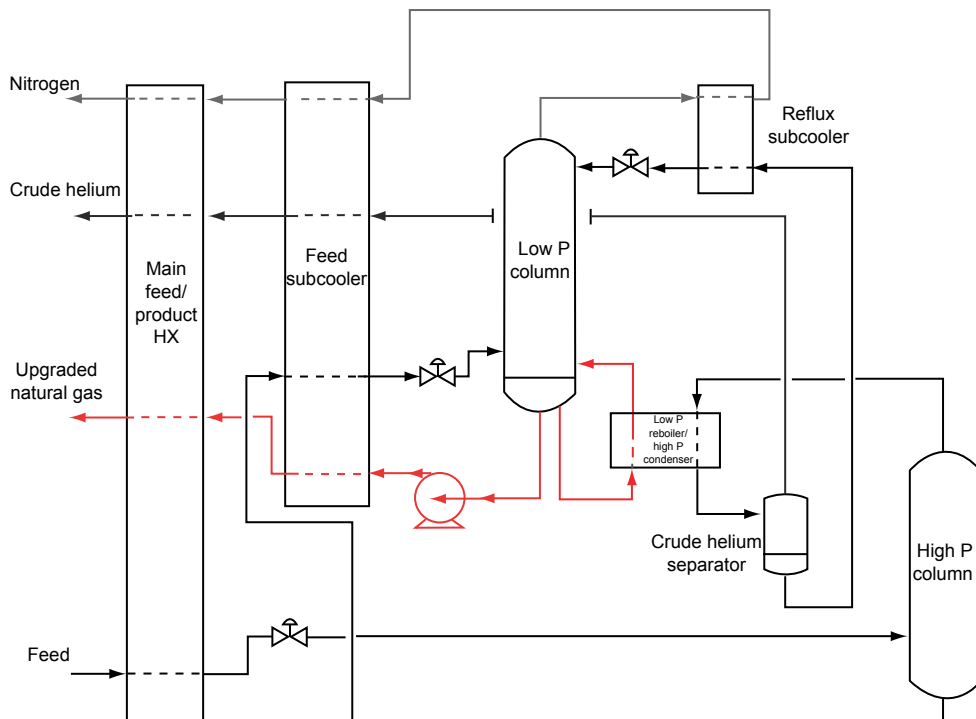


**Figure 4.** In the single-column heat-pumped process for N<sub>2</sub> rejection, any helium in the natural gas feed will be concentrated with the rejected N<sub>2</sub> overheads (Agrawal *et al.* 2003).

for both the low-pressure column and the high-pressure column (reflux not shown on this schematic). The non-condensed part of the high-pressure column overheads contains most of the He, and this vapour is fed to the crude helium separator. The crude helium product from this separator typically contains 50–70% He, associated H<sub>2</sub> and Ne, 1–3% CH<sub>4</sub> with the balance being N<sub>2</sub> (Agrawal *et al.* 2003). This crude helium stream can be fed directly to He purification and liquefaction units.

The final separation of N<sub>2</sub> from CH<sub>4</sub> in the bottoms from the high-pressure column is performed in the low-pressure column. The N<sub>2</sub>-rich overhead product of the low-pressure column is warmed in a heat exchanger against the bottoms of the high-pressure column. To achieve a low concentration of N<sub>2</sub> in the CH<sub>4</sub>-rich residual product, a reboiler is required at the bottom of the low-pressure column. The reboiler duty is provided by condensing N<sub>2</sub> at the top of the high-pressure column in condenser. This heat transfer is possible because the column pressures are such that the condensation temperature of N<sub>2</sub> in the overhead of high-pressure column is higher than





**Figure 5.** Nitrogen rejection and crude helium recovery from natural gas with a double-column process (adapted from Häussinger *et al.* 2005).

the boiling temperature of the  $\text{CH}_4$ -rich liquid in the low-pressure column. The bottom of the low-pressure column provides a  $\text{CH}_4$ -rich residual liquid product, which is pumped to an elevated pressure, vaporized and rewarmed against the NG feed.

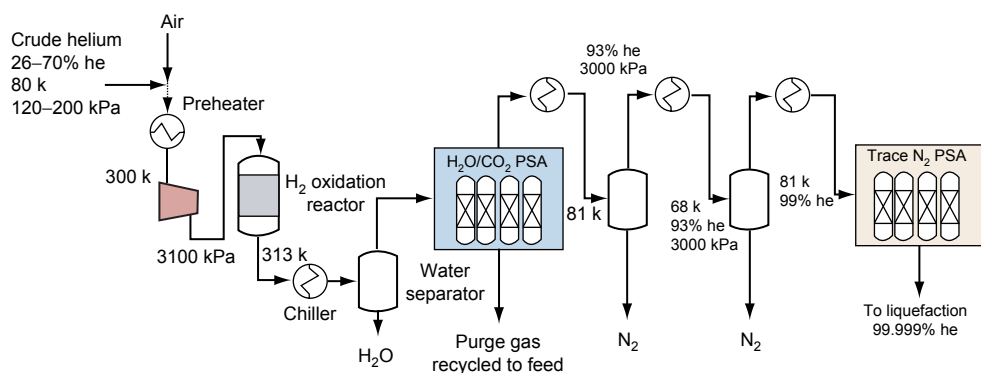
State-of-the-art modern cryogenic helium recovery processes are significantly more complicated than the simplified single-column and double-column systems described. The dual-column cycle shares many common features with the double-column process, but has a higher level of integration between process and refrigeration streams. Depending on the local feed gas composition, and available product markets, the complete, integrated cryogenic process may include the recovery of  $\text{C}_{2+}$  hydrocarbons, fuel gas fractions, and a nitrogen fraction, in addition to the recovery of crude helium.

### 2.3. Helium Upgrade and Purification Processes

Before liquefaction, crude helium must be upgraded to more than 90% He to meet product specifications and prevent the freezing out of impurities in the liquefaction process. Downstream of the NRU, the impurities that are still in the crude helium gas are  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2$  and Ne. These impurities are removed in several stages by condensation of the bulk components, catalytic oxidation of any trace  $\text{H}_2$ , separation of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{O}_2$  from the reactor by condensation of the  $\text{H}_2\text{O}$  and then with in a PSA unit, and removal of the final traces of  $\text{N}_2$  in another PSA unit to obtain a product that can approach 99.995% He purity (Daly 2005).

Usually the bulk  $N_2$  is removed from the crude helium by further cryogenic distillation steps, at lower temperatures than the temperatures in the NRU. Crude helium, which may be combined with blowdown from the (downstream) PSA purifier, is cooled to around 80 K in a Perlite-filled cold-box heat exchanger, also known as the upgrader. Here it is partially condensed to provide an  $N_2$ -rich liquid stream and a vapour stream of upgraded He containing approximately 90% He (Agrawal *et al.* 2003). The  $N_2$ -rich liquid from the partial condensation is warmed and separated to provide a waste stream that can be used to regenerate the (downstream) driers (Agrawal *et al.* 2003).

A typical process used to purify upgraded He is shown in Figure 6. The upgraded He is mixed with air to provide combustion oxygen, pre-heated to above 300 K (Lindemann *et al.* 2010), and then passed through a catalyst bed to oxidize any trace  $H_2$  or remaining hydrocarbons. The reactor product is cooled to condense any water produced by combustion of the  $H_2$ . Molecular-sieve adsorption beds in a PSA unit may be used here for further dehydration,  $CO_2$  and  $O_2$  capture at this stage.



**Figure 6.** Schematic of helium purification process (based on system reported by Agrawal *et al.* 2003 and Lindemann *et al.* 2010).

To achieve a He purity of 99.995% the dry,  $H_2$ -free gas flows through additional cryogenic  $N_2$  condensation (Lindemann *et al.* 2010) and/or a low temperature PSA unit to remove  $N_2$  to less than 10 ppm (Agrawal *et al.* 2003). A typical PSA unit for this application is a four-bed unit containing a molecular sieve adsorbent such as zeolite 4A. Helium upgrade processes with PSA purification units using commercially available molecular sieves are available from Praxair, Linde, and Air Liquide. This PSA unit for trace  $N_2$  removal does not remove any Ne or unreacted  $H_2$  from the He stream. These light impurities must be removed after the gas has been cooled in the liquefaction process using more adsorption to remove  $H_2$  at 80 K and then Ne at 20 K. The  $N_2$ -rich blowdown gas from the PSA purification unit is compressed, dried and recycled to the inlet of the upgrader where it is combined with the crude He feed.

Detailed discussions and comparisons of He liquefaction processes are beyond the scope of the current review. Here we provide only a short description of common liquefaction processes; a more detailed review of He liquefaction processes is available in Häussinger *et al.* (2005). Most industrial processes for the liquefaction of helium are based around isenthalpic throttling of the purified He across a Joule–Thomson valve. Purified helium is compressed (usually to 2 MPa) and pre-cooled to 80 K with either liquid  $N_2$  or exhaust from the helium expander, then cooled to

below 80 K with exhaust from the helium expander, or to approximately 20 K with a H<sub>2</sub> refrigerant (Agrawal *et al.* 2003; Häussinger *et al.* 2005). The final cooling to liquefy the He is achieved by free expansion of the compressed gas.

## 2.4. Case Studies of Recent Helium Production Facilities

Conventional cryogenic-based helium recovery and purification systems are available from vendors including Air Products, Praxair, Air Liquide and Linde. Here we present two case studies on recently commissioned He production facilities in Qatar and Australia.

### 2.4.1. Ras Laffan, Qatar

The Ras Laffan Helium Plant in Qatar is an Air Liquide designed plant that started production in 2005. The plant was designed to treat gas from Qatar's North Field estimated to contain 0.04% He and to produce 8.65 t/d (1.808 MMscfd) of liquid He (Daly 2005). The construction of a second Qatari He plant is scheduled to begin in May 2011 and is expected to be in production by 2013 (Air Liquide 2010). The addition of the second Qatari He plant, which is also to be designed by Air Liquide, will make Ras Laffan the world's largest He production facility with a total helium production capacity of 38 million m<sup>3</sup> per year (17.7 t/d).

The Ras Laffan plant collects He from seven LNG trains (three LNG trains of the Qatar gas plant and four LNG trains of the RasGas Plant) and processes the crude helium in a central upgrade facility. Each of the seven LNG trains has its own He recovery unit (HeXU) installed at the cold end of the LNG process. These He recovery units are cryogenic distillation systems (Perlite-filled cold boxes) designed and fabricated by Air Products and Chemicals (APCI; Daly 2005). The composition of the crude helium feed to the central He upgrade facility is 45% He with 55% N<sub>2</sub>.

The Ras Laffan He upgrade and purification section was designed by Air Liquide Engineering (Daly 2005). The bulk impurities, predominantly N<sub>2</sub>, are removed from the crude helium feed in a cryogenic fraction unit. The upgraded helium is warmed, then mixed with air and fed to the H<sub>2</sub> removal unit where any H<sub>2</sub> is catalytically oxidized and the stream cooled to condense the reactor product water. A four-bed PSA unit with molecular sieve adsorbents is used to remove trace N<sub>2</sub> to provide a purified helium product (99.9995% He). The blowdown gas from the PSA unit is dried and recycled to the front end of the helium upgrade plant.

### 2.4.2. Darwin, Australia

The BOC (subsidiary of the Linde Group) helium plant at the Darwin LNG facility was commissioned in March 2010 (James 2010). Engineering and fabrication of the plant was carried out by Linde Kryotechnik AG (Switzerland; Lindemann *et al.* 2010). The feed to the plant is the overhead product of the NRU, a 17.6 MMscfd stream at 120 kPa and 286 K containing 3% He and 93.6% N<sub>2</sub>. The plant produces 2.6 t/d of liquid He (860 l/hour, 99.999% purity).

The N<sub>2</sub>-rich feed (3% He) is compressed to 200 kPa and then upgraded by cooling to 80.5 K in the first N<sub>2</sub> removal stage, where part of the N<sub>2</sub> is condensed to give a He-enriched stream containing 26% He. The gas is warmed to ambient temperature, compressed to 3100 kPa and mixed with air to feed the H<sub>2</sub> oxidation unit. The water and CO<sub>2</sub> produced in the catalytic oxidation of H<sub>2</sub> are removed in a PSA unit. After H<sub>2</sub> removal, the He-enriched gas is cooled to 81 K in the second N<sub>2</sub> condensation stage, which produces a 93% He vapour stream. This

upgraded helium vapour is cooled further to 68 K to condense more N<sub>2</sub> and then flashed to provide a product containing 99% He. The final purification is performed by a cryogenic PSA unit, removing the trace N<sub>2</sub> not separated in the cryogenic flash units to less than 5 ppmv.

### 3. ADSORPTION-BASED PROCESSES FOR HELIUM RECOVERY

Adsorption-based separation processes are used to remove water, sulphur, mercury and carbon dioxide from NG (Tagliabue *et al.* 2009), and as described earlier to remove trace impurities in He purification. Gas separation using adsorption involves two primary steps, namely, *adsorption* and *desorption*. During adsorption, one gas component is selectively adsorbed on a porous solid to produce a gas stream enriched in the less strongly adsorbed gas component. Once the porous solid becomes, or approaches, saturation capacity the adsorbent must be regenerated. The gaseous product obtained during the desorption step is enriched in the strongly adsorbed component. To achieve a continuous gas separation process by adsorption several technologies have been developed. These technologies include temperature-swing adsorption (TSA), PSA, fluidized adsorbent beds and moving adsorbent beds. Fluidized and moving bed operations are less widely used in industrial gas separation than the cyclic-batch fixed bed operations of PSA and TSA (Seader and Henley 2006). In TSA processes, the external heat is supplied to increase the bed temperature for desorption, but in PSA the regeneration is carried out at low temperature by releasing pressure and purging the bed. Modern commercial PSA processes in operation range from small devices for oxygen production from air for medical use (300 scfd, approximately 90% O<sub>2</sub>; Tagliabue *et al.* 2009) to large-scale processes for production of high-purity H<sub>2</sub> from steam methane reformers (up to 200 MMscfd; Ritter and Ebner 2007).

The similarity in the molecular size of He (2.60 Å) and H<sub>2</sub> (2.89 Å) and the fact that both have very low boiling temperature means that PSA processes for helium purification potentially have many common features with H<sub>2</sub> purification processes. Sustained scientific and industrial interest in the purification of H<sub>2</sub> over recent times suggests that there could be several new technologies developed for that application, which may be applicable to helium purification. For example, H<sub>2</sub> purification PSA units have been built at large scales, including up to 200 MMscfd (Ritter and Ebner 2007; UOP 2010). Plants processing the largest gas flow rates for H<sub>2</sub> purification can have up to 12 adsorber beds (such as UOP's Polybed PSA; Sircar 2008). Commercial H<sub>2</sub> purification plants operate by selective adsorption of other components including CH<sub>4</sub>, CO<sub>2</sub>, CO and H<sub>2</sub>O. Similarly, helium purification PSA units operate by selective adsorption of the non-helium components. In general, modern PSA units for H<sub>2</sub> purification use layered adsorbent beds with three to four adsorbents (silica gel/alumina for H<sub>2</sub>O, activated carbon (AC) for CO<sub>2</sub>, and 5A zeolite for CH<sub>4</sub>, CO and N<sub>2</sub>; Ritter and Ebner 2007) and similar multi-layer bed designs are described in patents for He recovery processes (Baksh 2010).

Pressure swing adsorption is used to remove trace N<sub>2</sub> from upgraded He (>90 mol%) in the final stages of industrial He purification processes to achieve 99.999% He product streams (Daly 2005; Lindemann *et al.* 2010). On a smaller scale, adsorption-based He purification and recycle units are available for conserving He in scientific and medical applications. In each of these cases, all the other components in the gas are adsorbed because He generally has the lowest affinity of any species for adsorption. For example, at ambient conditions (298 K, approximately 100 kPa), the He uptake on commercial zeolites 5A and 13X is less than  $2 \times 10^{-3}$  mmol/g (Malbrunot *et al.* 1997) while the adsorption capacity for N<sub>2</sub> on these materials is several hundred times greater (Cavenati *et al.* 2004; Saha *et al.* 2010), as shown in Table 3. Likewise, ACs have a very low

**TABLE 3.** Comparison of Adsorption Capacities of Zeolites 5A and 13X for He, N<sub>2</sub> and CH<sub>4</sub> at 298 K and 100 kPa

Adsorbent	He (mmol/g)	N <sub>2</sub> (mmol/g)	CH <sub>4</sub> (mmol/g)
Zeolite 5A	1.17 × 10 <sup>-3</sup> (Malbrunot <i>et al.</i> 1997)	0.56 (Saha <i>et al.</i> 2010)	0.84 (Saha <i>et al.</i> 2010)
Zeolite 13X	1.31 × 10 <sup>-3</sup> (Malbrunot <i>et al.</i> 1997)	0.28 (Cavenati <i>et al.</i> 2004)	0.59 (Cavenati <i>et al.</i> 2004)

capacity for He uptake at ambient conditions ( $1.15 \times 10^{-3}$  to  $2.27 \times 10^{-3}$  mmol/g reported by Maggs *et al.* (1960) for AC prepared from anthracite coal, nutshell or wood). At all scales, current commercial PSA units designed to treat He streams require that the feed stream is already upgraded (90%) because otherwise the adsorbent may be too readily saturated by non-helium components.

The upgrade and purification of helium from the NRU product (1–3% He) or crude helium (50–70% He) streams is predominantly a separation of N<sub>2</sub> from He. Commercially available zeolites and narrow pore-ACs with reasonable adsorption capacities for N<sub>2</sub> make suitable adsorbents for He purification. A list of potential commercial adsorbents used in industrial processes for the purification of H<sub>2</sub> and/or described in patents for PSA helium recovery processes, which could be used in a PSA processes to separate heavier components from He is provided in Table 4.

**TABLE 4.** List of Commercial Adsorbents (Vendor Listed in Brackets) with Potential for Selective Adsorption of N<sub>2</sub> and CH<sub>4</sub> from Helium

Adsorbent type	Trade names	Species adsorbed
Zeolites	ZSM-5 HISIV 3000 (UOP) Zeolite 5A (UOP, Sigma) Zeolite 13X (UOP)	CH <sub>4</sub> , CO <sub>2</sub> , N <sub>2</sub>
Wide pore-activated carbons	BAX-1100 (Westvaco) RB3, R2030, GAC 1240 (Norit) BPL 4 × 10 (Calgon) Acticarb EA1000 (Activated Carbon Technologies, Australia and New Zealand)	CH <sub>4</sub> , CO <sub>2</sub> , N <sub>2</sub>
Narrow-pore activated carbons	Maxsorb (Kansai Coke & Chemicals Co)	N <sub>2</sub> in final purification stage
Ca- and Li-exchanged 13X (Baksh 2010; Das <i>et al.</i> 2010)		N <sub>2</sub> in final purification stage

In the following section, examples of PSA processes for helium recovery published in patents and in the open literature are described. These include a commercial PSA helium extraction and purification plant in India described in a 2008 report by Das *et al.*, and processes claimed in patents assigned to Nitrotec (D'Amico *et al.* 1996) and Praxair (Baksh 2010). All three examples operate by the adsorption of heavy components from the helium flow.

### 3.1. Survey of Pilot Plant and Patented PSA Processes for Helium Recovery

#### 3.1.1. India's Oil and Natural Gas Corporation PSA Plant

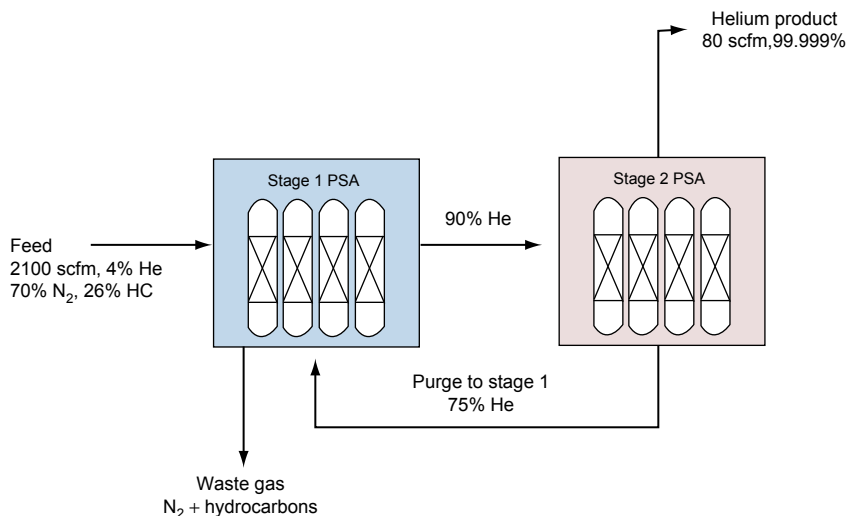
A pilot-scale PSA plant for the recovery and purification of He from a 0.04 MMscfd NG feed containing 0.06% He (88.5% CH<sub>4</sub>, 9.86% C<sub>2+</sub>, 1.18% N<sub>2</sub> and 0.4% CO<sub>2</sub>) was trialed in Tamil Nadu by India's Oil and Natural Gas Corporation (ONGC) in 2008 (Das *et al.* 2008). This pilot plant process had four process stages: (i) pre-treatment of the feed gas to remove C<sub>2+</sub> hydrocarbons and CO<sub>2</sub>, (ii) recovery of CH<sub>4</sub>, (iii) upgrade of He from N<sub>2</sub> and (iv) He purification. Each process stage has three adsorber beds and operated at ambient temperature.

In Stage 1 the heavy components (CO<sub>2</sub> and C<sub>2+</sub>) are selectively adsorbed at 450 kPa on a silica gel (196 kg/bed). In Stage 2, the CH<sub>4</sub> is recovered by adsorption at 225 kPa onto an AC bed (38 kg/bed), allowing N<sub>2</sub> and He to be concentrated to 16.1% and 1.4%, respectively, in the feed to Stage 3. In the regeneration of the Stage 2 beds, a CH<sub>4</sub>-rich gas is recovered and part of this CH<sub>4</sub>-rich heavy product is recycled for use as a purge gas to regenerate Stage 1. The feed to Stage 3 still contains a significant concentration of CH<sub>4</sub> (82.5%) and in Stage 3 most of this CH<sub>4</sub> is adsorbed along with N<sub>2</sub> on zeolite 13X (3 kg/bed). The Stage 4 beds also contain 3 kg each of zeolite 13X, which adsorbs the remaining CH<sub>4</sub> and N<sub>2</sub> at a pressure of 150 kPa, such that a 99% He product can be produced. Regeneration of each of the adsorption stages is performed by evacuating the beds to 6–7.5 kPa and by purging.

This pilot plant demonstrates the technical feasibility of using PSA processes to recover He from NG streams. However, the ONGC process recovers only 65% of the He in the feed gas, which is much lower than the typical He recovery rate achieved in most conventional cryogenic distillation processes (>95% recovery of He in feed gas). There are considerably opportunities to improve the efficiency of PSA processes for He recovery through using improved cycle designs; optimized processing conditions by operation at, for example, cryogenic temperatures; and improvements in adsorbent materials. One approach to improve adsorbent performance is to develop adsorbents with higher capacities for N<sub>2</sub> and, less critical here, CH<sub>4</sub>: for example Li-exchanged X-type zeolites with narrow pores around 9 Å wide (Das *et al.* 2010). A more challenging approach is to develop a He-selective adsorbent; this would also have more impact because it would greatly reduce the size and energy requirements of resulting PSA beds and the cryogenic distillation towers. Currently, there are no commercial adsorbents available with sufficient He capacity and selectivity to realize such an industrial application. However, recent advances in the development of adsorbents selective for H<sub>2</sub> over N<sub>2</sub>, for example certain metal-organic frameworks (MOFs; Mallick *et al.* 2010), provide a new opportunity for developing He-selective adsorbents because He and H<sub>2</sub> have comparable molecular sizes and boiling points. Novel, helium-selective adsorbents are discussed further in the "Helium-Selective Microporous Adsorbents" section.

#### 3.1.2. Nitrotec Two-Stage PSA Process

A two-stage PSA process for the recovery of He from feed gases containing less than 10% He is described in US patent no. 5542966 assigned to Nitrotec Corporation (D'Amico *et al.* 1996). Figure 7 shows a schematic of the example described in the patent. The example process treats 2100 scfm (3 MMscfd) feed gas at a pressure of 50 psia containing 4% He, 26% hydrocarbons (CH<sub>4</sub> and C<sub>2+</sub>) and 70% N<sub>2</sub> to recover 80 scfm (0.55 t/d) of He product (99.999%). The first stage consists of four adsorbent beds each filled with 11 m<sup>3</sup> of AC, such as those with a specific surface



**Figure 7.** Schematic of two-stage pressure-swing adsorption process for helium recovery described in US patent no. 5542966 (D'Amico *et al.* 1996).

area of  $1150 \text{ m}^2/\text{g}$  and density of  $0.45 \text{ g}/\text{cm}^3$ . The hydrocarbons and most of the  $\text{N}_2$  are adsorbed on the AC in this stage and the 90% He product gas flows to the second stage. The second stage consists of four beds each filled with  $1 \text{ m}^3$  of AC. The light product from the second stage has a purity of 99.999% He and the waste gas from this stage (47 scfm, 75% He) is recycled as a purge gas in the first stage. This two-stage design and He-rich recycle stream is claimed to achieve He recovery rates of 95%, which is approaching those of cryogenic distillation processes.

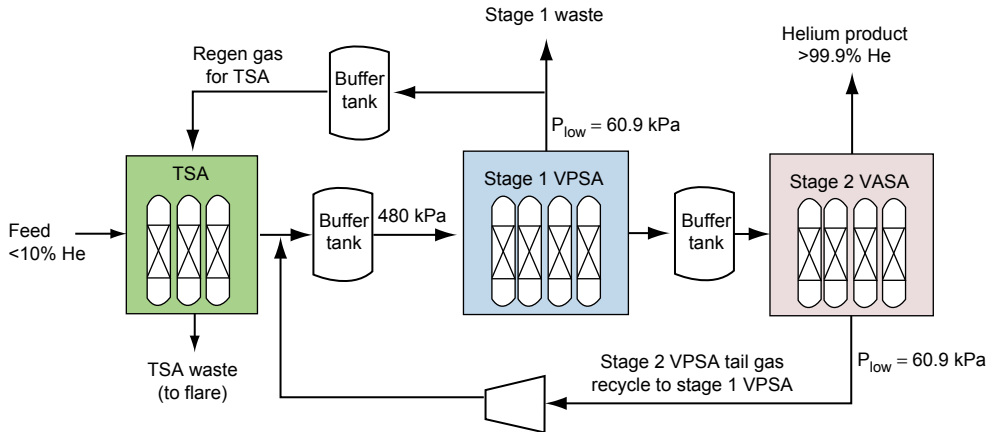
There are six cycle steps in the first PSA stage, namely, (i) adsorption, (ii) recycle, (iii) depressurization, (iv) evacuation to less than 10 kPa (absolute), (v) He pressurization with the recycle from the second stage, and (vi) recycle feed pressurization. The entire cycle duration is typically 480 seconds. There are five cycle steps in the second PSA stage, namely, (i) adsorption, (ii) depressurization, (iii) evacuation to less than 10 kPa (absolute), (iv) purge and (v) helium product pressurization. The total cycle duration for Stage 2 is typically 360 seconds.

### 3.1.3. Praxair TSA and Vacuum PSA Process

A patent assigned to Praxair (US patent no. 2010/0251892 A1) describes processes and systems for the recovery of He from feed gas containing less than 10% He using TSA and multiple vacuum PSA (VPSA) stages (Baksh 2010). A schematic of the system is shown in Figure 8. In each adsorption stage the non-helium components are adsorbed from the gas. The VPSA stages operate at ambient temperature and at an adsorption pressure of 480 kPa. Baksh claims He recovery rates of up to 95% using this process.

In this process design, the TSA stage protects the VPSA stage beds from rapid degradation and saturation by removing  $\text{CH}_4$  and heavier components from feed. This guard bed strategy allows more efficient, smaller VPSA systems to be designed and reportedly achieves better He recovery rates. The selection of adsorbents for the TSA stage is dependent on the composition of heavy hydrocarbons and other impurities such as  $\text{H}_2\text{S}$  in the feed gas. If a TSA stage were required,





**Figure 8.** Schematic of a He recovery process using a temperature-swing adsorption unit upstream of two vacuum pressure-swing adsorption systems described by Baksh in a patent assigned to Praxair (Baksh 2010).

adsorbents in this stage may include aluminosilicates such as HISIV 3000 (UOP), zeolite ZSM-5 supported on gamma alumina and AC such as BAX-1100 (Westvaco Corporation).

Baksh proposes four adsorber beds in each of the VPSA stages. Each bed in the VPSA stages may contain three layers of adsorbents including bed loading plans with a top layer of alumina, a second layer of an adsorbent for removal of the heaviest components (e.g.  $\text{CH}_4$ ), and a bottom layer of a high-capacity adsorbent such as zeolite CaX or LiX (Ca- and Li-exchanged 13X, respectively) chosen for optimum  $\text{N}_2$  adsorption. Commercial adsorbents suitable for the VPSA stages are ACs for the removal of  $\text{CH}_4$  and  $\text{CO}_2$ , and zeolites such as 5A, Ca-X or Li-X to remove  $\text{N}_2$  and any  $\text{O}_2$  or argon contained in the feed gas.

#### 4. MEMBRANE SEPARATION PROCESSES FOR HELIUM RECOVERY

Gas permeation through a homogeneous membrane is a solution-diffusion phenomenon and the permeation coefficient  $P_i$  for a component gas is a product of the solubility coefficient  $S_i$  and the diffusivity coefficient  $D_i$ . The ability of a membrane to separate components of a gas mixture can be described by the ratio of the permeation coefficients as shown in equation (1), where  $\alpha$  is the selectivity or separation factor of gaseous components  $i$  and  $j$  (Häussinger *et al.* 2005)

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{D_i S_i}{D_j S_j} \quad (1)$$

As the He molecule is smaller in diameter than the other components of the NG, its diffusivity coefficient in most homogeneous membranes will be greater than those of the other components. Thus, most homogeneous membranes exhibit a high permeability for He compared with  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$  and other components of NG.

The extraction of helium from NG using membranes has been discussed for more than 40 years (Stern *et al.* 1965; Häussinger *et al.* 2005). Helium extraction plants using membrane separation have reportedly been used since 1985 (Häussinger *et al.* 2005). At least one vendor (Ube



Industries) lists an example of a membrane process for He recovery from an N<sub>2</sub>-rich stream. Lavery and O’Hair (1990) report a membrane process for He recovery in Alberta, Canada. However, no data on the performance or operating experiences of these membrane-based He recovery plants have been published in the open literature. By contrast, the use of H<sub>2</sub>-permeable membranes in the production and purification of H<sub>2</sub> has been described in the literature [e.g. Ritter and Ebner’s review of H<sub>2</sub> purification technologies (2007)].

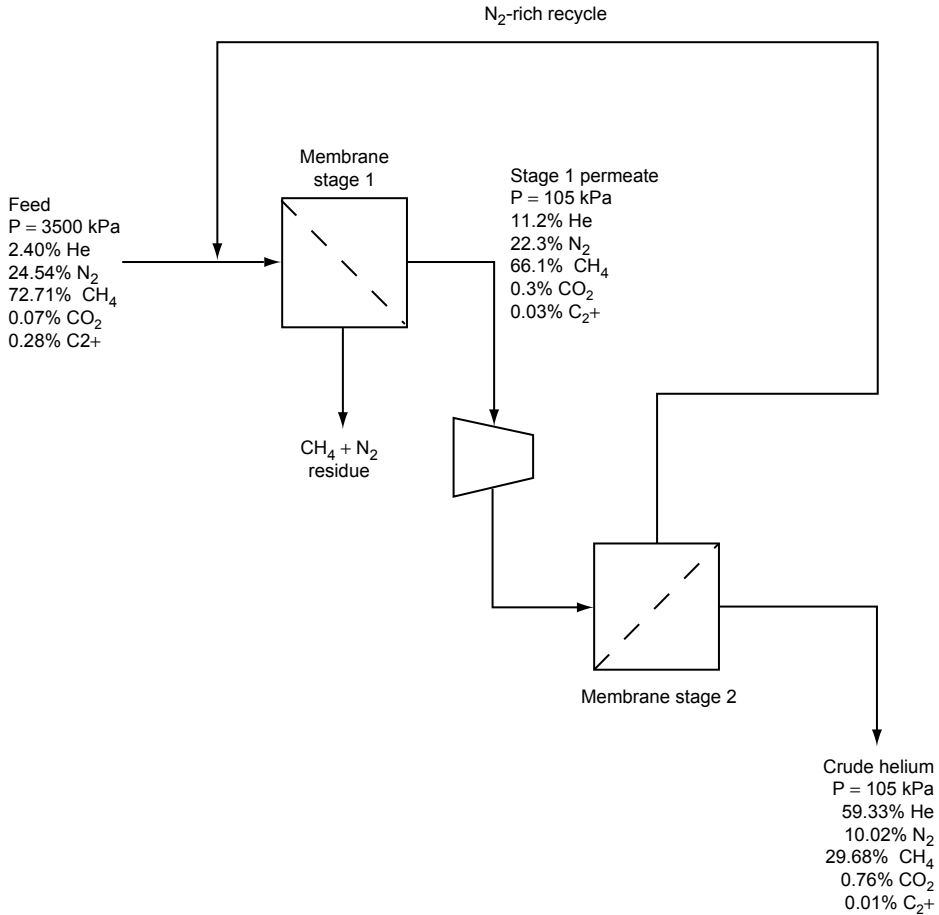
The first helium extraction membranes included tubular silicate and quartz glass membranes and, later, permeable polymeric membranes. Recently reported membranes suitable for He separation from N<sub>2</sub> and CH<sub>4</sub> include those constructed from ultra-microporous silica (Barboiu *et al.* 2006), molecular sieve carbons, porous graphene (Schrier 2010), titanium silicates (Li *et al.* 2011), polyimides and mixed matrix membranes of polyimides and zeolitic imidizolate frameworks (ZIFs; Bernado *et al.* 2009). Many of these membranes have been successfully applied in the separation of H<sub>2</sub> from CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub> and N<sub>2</sub>. Table 5 lists the selectivity for He over N<sub>2</sub> and CH<sub>4</sub> for several membranes. From the available literature on membrane materials performance, and in combination with reports of industrial H<sub>2</sub>-selective membranes, the most promising membranes for achieving a high selectivity for He over H<sub>2</sub> appear to be ultra-microporous inorganic membranes and glassy polymeric membranes (polymers with glass transition temperatures above the operating temperature). The aromatic polyimide membrane listed in Table 5 is an example of a glassy polymeric membrane.

**TABLE 5.** Permeability Selectivity of Helium, Nitrogen and Methane in Inorganic and Organic Membrane Materials (Häussinger *et al.* 2005)

Membrane material	Temperature, °C	Selectivity $\alpha$	
		P <sub>He</sub> /P <sub>N<sub>2</sub></sub>	P <sub>He</sub> /P <sub>CH<sub>4</sub></sub>
<i>Inorganic membranes</i>			
Porous glass, Vycor type	25	2.5	1.8
Molecular sieve carbon (3–5 Å)	25	20	–
<i>Organic membrane materials</i>			
Ethyl cellulose	20	11	2.8
Polytetrafluoroethylene	20	31	42
Polycarbonate	20	14.3	18.6
Aromatic polyimide	35	74	165

#### 4.1.1. Industrial and Patented Membrane Systems for Helium Recovery

Most membrane processes cannot achieve simultaneously a high product purity and high product yield (throughput). To increase the purity of the product (i.e. He), several membrane stages can be operated in series as shown in the two-stage process in Figure 9. However, due to the large pressure drop (often 1500–3000 kPa) of the He-rich permeate across the membrane unit, multi-stage membrane processes require inter-stage compressors. The recompression between membrane stages increases both capital and operating costs of membrane systems. Thus, membrane processes may be more suitable for the coarse separation of bulk N<sub>2</sub> and He followed by an adsorption-based He purification process. Several hybrid membrane-cryogenic or membrane-cryogenic-adsorption processes have been reported (Häussinger *et al.* 2005).



**Figure 9.** Process schematic of a two-stage membrane helium recovery system (Häussinger *et al.* 2005).

In the example two-stage membrane system shown in Figure 9, each membrane separation stage consists of a row of separators with each containing a hollow fibre bundle (Häussinger *et al.* 2005). An aromatic polyimide polymer membrane with an effective area of 9000 m<sup>2</sup>/m<sup>3</sup> of volume is used in each membrane stage. This membrane material is suitable for operation at temperatures from -80 to 150 °C and tolerates NG impurities such as water, H<sub>2</sub>S and C<sub>5+</sub> hydrocarbons. Although this membrane process is reported to recover 95% of the He in the feed gas and reduces the N<sub>2</sub> concentration to less than half of the feed, the crude helium product still contains a significant concentration of CH<sub>4</sub>. The membrane is also CO<sub>2</sub> permeable. Clearly this example shows that with a membrane process alone it would be difficult to achieve the required product purity of 99% He from an NG feed. The case of recovering He from the NRU overhead product should be less intensive than from the NG feed gas, but the data in Table 5 show that the selectivity of the membrane process for He from N<sub>2</sub> is still too low to achieve the desired separation performance in two stages. Several membrane stages with inter-stage recompression would be required to achieve a high-purity He product.

Membrane Technology and Research Inc. describe in US patent no. 2005/0217479 A1 membrane systems for the recovery of He from reject streams in gas processing, which may include vent streams, fuel gas streams and purge streams (Hale and Lokhandwala 2005). This patent claims that the process may use any type of membrane that can provide an adequate He flux and a high selectivity for He over the other principle components of the reject gas ( $N_2$ ,  $CH_4$ ,  $CO_2$ ). Fluorinated, glassy polymer membranes are the preferred embodiment. This patent provides selectivity data for several commercial polymeric membrane materials including Hyflon AD60 (Solvay Plastics) and Cytop (Asahi Glass).

Another Membrane Technology and Research Inc patent, US patent no. 6630011 B1, describes a process for the removal of  $N_2$  from NG using two or more membrane stages (Baker *et al.* 2003). An example including the concentration of He in the  $N_2$ -rich product is also described in this patent. The process uses a  $CH_4$ -selective membrane operating at  $-40$  to  $0$  °C in the first stage followed by an  $N_2$ -selective membrane in the second stage. This patent is not specific to separation of He from an  $N_2$ -rich stream but does demonstrate the potential application of membranes at flow scales and operating conditions (low temperature and high pressure) characteristic of an LNG facility.

Shoji and Moriya describe a He purification method based on hollow glass fibre membranes in US patent no. 2003/0221448 A1 (Shoji and Moriya 2003). The glass fibre membrane walls have pores of 1.5 nm, which were created by the incorporation and the subsequent leaching of alkali metal ions in the wall surfaces. The selective permeation rate of these hollow glass fibre membranes for He over  $N_2$  is claimed to be 1800–2000. An example system to recover He from a 120,000  $Nm^3/h$  feed gas containing 60%  $CH_4$ , 1.5% He and the balance  $N_2$  is described in this patent. The membrane module consisted of 16 basic membrane units of 20 cm diameter and 3.5 m length each having a bundle of 70- $\mu m$  diameter glass hollow fibres. The feed gas is supplied at 1.27 MPa and the low-pressure He permeate is obtained at 120 kPa.

## 5. FUTURE RESEARCH AND DEVELOPMENT NEEDS

The literature survey identified that cryogenic distillation is the most commonly used process technology for He recovery from NG. Much of the helium recovery literature on process advances in new plants describes the optimization of the cryogenic refrigeration processes. Although the bulk of the separation is performed by cryogenic distillation, adsorption processes are already used in the helium upgrading and purification stages of conventional processes to remove any remnant contaminant species, such as  $N_2$  and  $H_2$ .

The literature survey identified that improvements in He recovery technologies may be achieved through developments or major breakthroughs in adsorption or membrane separation process. Helium recovery and purification processes are comparable in many ways with systems designed for hydrogen purification. Thus, many of recent technological advances for  $H_2$  separation from  $CH_4$ ,  $N_2$  and  $CO_2$  may be applicable to a He recovery process, which could allow quicker deployment of the technology. Key areas identified that require further research and development are helium-selective adsorbents, helium-selective membrane processes, and flow sheet development of integrated cryogenic-membrane-adsorption systems.

### 5.1. Helium-Selective Microporous Adsorbents

Helium recovery by selective adsorption of the He from the  $N_2$  may allow process designs with smaller adsorbent bed sizes. The small molecule size of He (kinetic diameter 2.60 Å; Tagliabue

*et al.* 2009) can be taken advantage by size or kinetic exclusion of larger  $N_2$  (3.64 Å) and  $CH_4$  (3.8 Å) molecules in narrow-pore adsorbents or permeable membranes. Kinetically selective adsorption processes have been successfully applied in air separation units, and for  $N_2$  rejection from NG in the Molecular Gate PSA process (Molecular Gate Adsorption Technology 2010). The kinetic or steric separation of He from  $N_2$  would require adsorbents with pore openings of 4 Å or narrower. In addition, the pore volume and/or surface area accessible to He but not  $N_2$  would need to be sufficiently high to allow practical adsorber bed sizes. Potential adsorbents for use in a He-selective PSA process may include carbon molecular sieves, small-pore commercial/synthetic zeolites 3A and 4A (Zeochem Molecular Sieves 2010), small-pore natural zeolites such as Natrolite (Breck 1974), novel zeolites such as PTS-1 (Shin *et al.* 2010), ZIFs and novel MOF adsorbents such as Mg-MOFs (Mallick *et al.* 2010).

The entrapment of He in carbon molecular sieve fibres and Type A zeolites at low pressures and temperatures from 77 K to room temperature has been reported by a research group (Finkelstein *et al.* 2003; Saig *et al.* 2003, 2005). Although the absolute volume of He adsorbed at low pressures was small, the materials did adsorb some He at low pressures, and reasonable He uptakes were observed at higher pressures. For example, at 2000 kPa and 77 K they reported an uptake of 0.9 mmol/g He on 5A zeolite.

Small-pore MOFs such as Mg-MOFs have shown potential for the selective adsorption of  $H_2$  from gases with larger molecules such as  $N_2$  and  $CO_2$  (Li *et al.* 2009; Mallick *et al.* 2010). The similarity in the molecular size of He and  $H_2$  (2.89 Å), and the fact that both have very low boiling temperature, suggests that these small-pore adsorbents may also be selective for He. For example, Mallick *et al.* (2010) report a chiral hexagonal Mg-MOF-1 with pore apertures of 4 Å. In gravimetric measurements with pure gases at 77 K and a pressure of 100 kPa this Mg-MOF-1 exhibited higher uptakes of  $H_2$  (3.07 mmol/g) than  $CO_2$  or  $N_2$  (0.57 and 0.08 mmol/g, respectively).

A synthetic small-pore zeolite that selectively adsorbs He and  $H_2$  from argon and  $CO_2$  was reported by Shin *et al.* (2010). This adsorbent known as PST-1 is a potassium gallosilicate natrolite with a high Ga content (Si/Ga = 1.28). The uptake of He on PST-1 at 101.3 kPa was 0.02 mmol/g at 303 K and 0.082 mmol/g at 77 K. The fast kinetics for He and  $H_2$  uptake reported by Shin *et al.* (2010) suggest this material could have potential as an adsorbent for a PSA-based He purification process, or as a material to be incorporated into a membrane separation process.

These published results demonstrate that reasonable He uptakes can be obtained on some microporous adsorbents at certain conditions and suggest that the development of a He-selective PSA process may be possible. Further experimental studies with materials such as PST-1, narrow pore zeolites and MOFs are required to confirm the potential of He-selective PSA processes. However, understanding the sorption kinetics and equilibria of He,  $N_2$ ,  $CH_4$  and their mixtures in microporous adsorbents at low temperatures and high pressures is essential to the design of industrial gas separation processes.

Crucial to assessing the He selectivity of any of the novel adsorbents is making accurate measurements of He uptake. Helium pycnometry is a standard method for determining void volumes and skeletal densities of porous materials (Rouquerol *et al.* 1994). Central to this standard method is that He adsorption is often erroneously assumed to be negligible (Malbrunot *et al.* 1997); this assumption is only the case at elevated temperatures. The challenge of such measurements may be addressed first with careful adsorbent density measurements with a pycnometer at elevated temperatures and operation of a commercial volumetric adsorption apparatus in an absolute volume mode (manual mode). This approach allows independent calibration of the adsorption sample cell and the adsorbent void volume (Maggs *et al.* 1960; Malbrunot *et al.* 1997).

## 5.2. Advanced Helium-Selective Membranes

There already exists a large body of published data for pure gas permeability coefficients of  $N_2$ ,  $CH_4$ ,  $CO_2$ ,  $H_2$  and He in membranes, because a common technique for measuring membrane selectivity is relative He permeation. Many of these studies were motivated by separation of  $CH_4/N_2$ ,  $CO_2/N_2$  or  $H_2/CO_2$  mixtures and only a few studies have specifically targeted the development of membranes to recover He from  $CH_4$  or  $N_2$ . A detailed analysis of the available pure gas permeability data could help to identify the best membranes for He recovery applications. However, for real gas mixtures, such as NG streams and the overhead vapours from the NRU, the separation performance of the membrane will be affected by the interactions between gas components as well as the interaction between the components and membrane material. The measurement of membrane performance with representative gas mixtures of the industrial application, that is low-concentration  $N_2$ - or  $CH_4$ -rich streams, at a range of temperature and pressures is required to assess the true ability of membrane units to recover or purify helium from NG.

There remain critical challenges in the fabrication of membranes with high selectivities for helium. For example, the fabrication of inorganic membranes from materials such as MOFs and ZIF-8 requires the membranes to be defect free—a defect such as a crack or gap between MOF particles would significantly affect the membrane selectivity. However, the control of the initial seeding steps in MOF synthesis on a membrane support substrate (Dumée *et al.* 2013), for example, is challenging and the development of new techniques for fabrication of membrane is required if the most promising He-selective membranes are to be translated from the laboratory to industrial-scale processes.

## 5.3. Integrated Cryogenic Distillation Membrane and Adsorption Systems

Several hybrid membrane-cryogenic distillation or membrane-adsorption processes for the recovery of He from NG and/or the rejection of  $N_2$ -rich streams from NG have been suggested in the open and patent literature (Behling *et al.* 2001; Häussinger *et al.* 2005). These hybrid processes are those described in patents assigned to Advanced Extraction Technologies (Mehra 1993; AET-Technology 2010) and Nitrotec Corporation (Stoner *et al.* 1997). In their US Patent 2003/0221448 A1 reporting the use of a glass fibre membrane, Shoji and Moriya (2003) also refer to an unexamined Japanese patent no. JP-A-54-110193 that describes a method to obtain a high-purity 99.95% He product from a gas mixture of 70% He and 30%  $N_2$  by a combination of cryogenic separation and gas separation membrane units based on cellulose acetate. According to Shoji and Moriya in the method of JP-A-54-110193, five membrane separation units are required to achieve a He purity of 99.95%.

Mehra describes in US patent no. 5224350 (Mehra 1993), assigned to Advanced Extraction Technologies, a process for the recovery of He from an  $N_2$ -rich NG stream using a  $CH_4$  absorber column, a membrane separation unit and a PSA unit. The  $N_2$ -rich feed gas containing more than 0.1% He is contacted with a lean physical solvent to remove  $CH_4$  and heavier hydrocarbons (in the so-called *Mehra* absorption process). The  $CH_4$ -rich solvent bottom product is flashed two times to recover a  $CH_4$  product gas and regenerate the solvent. The  $N_2$ -rich overheads product of the contactor is fed to a membrane unit, which provides a low-pressure crude helium stream (50% He) and rejects the  $N_2$ . The crude helium can be compressed to 200-3000 psig for direct sale or fed to a PSA unit which produces an  $N_2$  waste stream and a purified 99.99% He product. The membrane material is selected for maximum He permeability and examples of Li- and Na-exchanged perfluorosulphonic acid polymers are suggested. The patent does not prescribe any

particular adsorbents for the PSA unit, but any adsorbent suitable for adsorption of  $N_2$  and  $CH_4$  could be selected (such as an AC, aluminosilicate, or silica gel).

In US patent no. 5632803 assigned to Nitrotec Corporation, Stoner *et al.* (1997) describe a hybrid process consisting of a membrane separation unit and two PSA units in series to produce a He product stream of more than 98% purity from feed containing 1.6% He, 26% hydrocarbons and 72.2%  $N_2$  (5250 scfm, inlet pressure of approximately 1000 psig). The membrane unit contains polyimide hollow fibres that are permeably selective for He from  $N_2$ ,  $CO_2$ ,  $CH_4$  and other hydrocarbons. The concentration of He is enriched in the membrane unit by two to ten times and this low-pressure product (65–100 psia) flows to the first PSA stage. In each PSA stage, there may be three to five adsorbent beds filled with an adsorbent such as AC, aluminosilicate or silica gel, which have little affinity for He. The first PSA stage can contain 11 m<sup>3</sup> of AC to adsorb most of the hydrocarbons and  $N_2$  from the gas and provide a 90% He product. This He-rich gas flows to the second PSA stage, which contains 1 m<sup>3</sup> of AC and produces a He product of more than 98% purity. The waste gas from the first PSA stage is mixed with the residue of the membrane unit. The waste gas of the second PSA stage (47 scfm, 73% He) is recycled to the feed of the first PSA stage.

There remains scope for the development and optimization of various He recovery process layouts featuring cryogenic distillation, membrane separation and PSA modules. The technical feasibility, energy requirements and process economics of these integrated system designs need to be assessed. Such an integrated process design, for example, may comprise cryogenic distillation of the 1% He feed to a crude helium stream, then coarse separation of the crude helium stream by a membrane system, and then final He upgrading in a PSA unit. In addition, the performance of membrane and adsorbents at low-temperature conditions needs to be assessed for integrated systems, which operate at cryogenic conditions.

## STANDARD GAS VOLUMES AND CONVERSIONS FOR HELIUM PRODUCT RATES

In this paper the basis for standard cubic feet (scf) is 14.969 psi and 60 °F (101.325 kPa, 288.75 K). The condition for Nm<sup>3</sup> is defined at 101.325 kPa and 298.15 K.

The equivalent gas volume and mass flow rates of 1 t/d liquid He product in other commonly used units of measures are as follows:

Mass flow	1 t/d
Liquid volume	5.557 slpm
Molar flow	249.837 kmol/d
Gas volume	254.678 Nm <sup>3</sup> /hour
Gas volume	0.209 MMscfd
Gas volume	2.231 million Nm <sup>3</sup> /year
Gas volume	76.302 MMscf/year

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