Helium Recovery

Václav Chrz

Director of Technology Development, Chart Ferox, a.s.,
Helium discovery on the Sun

- Helium was discovered in the gaseous atmosphere surrounding the Sun by the French astronomer Pierre Janssen, who detected a bright yellow line in the spectrum of the solar chromosphere during an eclipse in 1868.

- The English astronomer Joseph Norman Lockyer concluded that that D3 line was caused by an element in the Sun that was unknown on Earth. Lockyer deduced the name of the new element using the greek name of the Sun, helios.

You may think, that it was very easy to discover helium?
Can you see any evidence of helium?
Someone had to come with an idea of studying the spectrum of sun chromosphere selectively and to organize measuring during a rare opportunity of eclipse.

This tells us something on importance of intuition in science.
Helium discovery
occurrence in the space

- In 1903 Ramsay and Frederick Soddy further determined that helium is a product of the spontaneous disintegration of radioactive substances.
- Helium is concentrated in stars, where it is synthesized from hydrogen by nuclear fusion.
- Helium constitutes about 23% of the mass of the universe and is thus second in abundance to hydrogen in the cosmos.
- This initiated search for helium on the Earth....
The helium that is present on Earth is not a primordial component of the Earth but has been generated by radioactive decay. Alpha particles, ejected from the nuclei of heavier radioactive substances, are nuclei of the isotope helium-4. Helium does not accumulate in large quantities in the atmosphere because Earth's gravity is not sufficient to prevent its gradual escape into space.

Consequently, the occurrence of helium on the Earth is just a result of dynamic equilibrium between the generation and the escape. This is why helium is a really RARE GAS.
Helium isotopes $^4\text{He}$ and $^3\text{He}$ and phase diagram of $^4\text{He}$

Helium-4 has two liquid forms. The **normal** liquid form is called **helium I** and exists at temperatures from its boiling point of 4.21 K (-268.9° C) down to about 2.18 K (-271° C). Below 2.18 K, helium-4 undergoes **superfluidity** (i.e., its viscosity, or resistance to flow, nearly vanishes) and its **thermal conductivity** becomes more than 1,000 times greater than that of copper. This liquid form is called **helium II**. (See the phase diagram in the left)

The isotope helium-3 (0.1 ppm in He; norm. boiling point 3.2 K) has even one more liquid phase.
Helium recovery

Resources by beginning of 20th century

• Much the best practical source of helium is *thorianite*, a mineral imported from *Ceylon* for the manufacture of thoria. It dissolves readily in strong *nitric acid*, and the helium contained is thus liberated.

• The gas contains also H₂, CO₂ and N₂. In order to get rid of hydrogen, some oxygen is added to the helium, and the mixture exploded by an electric spark. All remaining impurities, including the excess of oxygen, can then be taken out of the gas by Sir James Dewar's ingenious method of absorption with *charcoal* cooled in liquid *air*. Helium alone refuses to be absorbed, and it can be pumped off from the charcoal in a state of absolute purity.

• If thorianite cannot be obtained, *monazite*, which is more abundant, may be utilized. A part of the helium contained in minerals can be extracted by heat or by grinding


These were the only sources of helium when Kamerlingh Onnes liquefied helium first in July 1908. For recovery one m³ of helium 1 ton of monazite sand was needed.
Helium recovery
Resources by beginning of 20th century

Only after air separation developed during the same period, it offered a more economical way of recovery.

Even more important source of helium became natural gas (from 1917), Hamilton, Ontarion, Canada.

Finally, waste gases of ammonia synthesis are another important source.

Helium is an important industrial gas, today. The resources are of strategic importance.
Helium world consumption

75 tonne/day

27 375 tonne/year

Most of it is recovered from natural gas

Cai Z. et al., proceedings of the conference CryoPrague2006
Fig 2 The U.S. alone consumes more than half of the world’s supply of helium (2002)
Helium world consumption
by branch of industry

Metal Atmospheres 3%
Space Program 4%
Semiconductor 5%
Leak Detection 6%
Analytical 6%
Fiber Optics 7%
Welding 12%

Balloons & Airships 16%
Superconductors incl. MRI 29%
Other 10%
Diving 2%

Fig 3 Helium use in various applications
Helium world consumption by branch of industry

Highlighting applications important for cryogenics:

- Superconductors incl. MRI 29%
- Balloons & Airships 16%
- Welding 12%
- Fiber Optics 7%
- Analytical 6%
- Leak Detection 6%
- Semiconductor 5%
- Space Program 4%
- Diving 2%
- Other 10%
- Metal Atmospheres 3%
# Properties & Applications of Helium

<table>
<thead>
<tr>
<th>Property</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Second lightest element (after hydrogen)</td>
<td>Lifting – balloons, airships</td>
</tr>
<tr>
<td>Smallest molecular size</td>
<td>Leak detection</td>
</tr>
<tr>
<td>Chemically inert (essentially no tendency to react with other elements)</td>
<td>Carrier gas - analytical, semiconductor</td>
</tr>
<tr>
<td></td>
<td>Purging - semiconductor</td>
</tr>
<tr>
<td>Lowest boiling point; does not solidify at 0°C 1 atm.</td>
<td>Liquid cooling – Superconductors</td>
</tr>
<tr>
<td></td>
<td>Purging/pressurising LHY - rockets</td>
</tr>
<tr>
<td><strong>4.2 K at atm. pressure</strong></td>
<td></td>
</tr>
<tr>
<td>Very high specific heat &amp; thermal conductivities</td>
<td>Gaseous cooling – fiber optics</td>
</tr>
<tr>
<td>Highest ionisation potential</td>
<td>Metal arc welding – aluminium, ……</td>
</tr>
<tr>
<td></td>
<td>Plasma arc melting – titanium, ……</td>
</tr>
<tr>
<td>Very low solubility</td>
<td>Diving gases</td>
</tr>
<tr>
<td>Radiologically inert (no radioactive isotopes)</td>
<td>Heat transfer medium in nuclear reactors</td>
</tr>
<tr>
<td>Very high sonic velocity</td>
<td>Metal coatings</td>
</tr>
<tr>
<td>Liquid becomes superfluid below 2.2K</td>
<td>Cooling of LT superconductors</td>
</tr>
</tbody>
</table>
Helium recovery
from air - air separation industry

• Air separation is an important branch of industry, as it is a source of
  – **Oxygen** (welding, oxidation processes in metallurgy, chemistry, gas industry)
  – **Nitrogen** (synthesis of ammonia, inert atmospheres in metallurgy and petrochemical processes, plasma cutting of metals)
  – **Argon** (inert for semiconductor and microprocessor production, innertization of nuclear plants, welding of aluminum)
## Helium recovery

### Composition of air

<table>
<thead>
<tr>
<th>Component</th>
<th>Symbol</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>78.084%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td>20.947%</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>0.934%</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO₂</td>
<td>0.033%</td>
</tr>
<tr>
<td>Neon</td>
<td>Ne</td>
<td>18.2 parts per million</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>5.2 parts per million (ppm)</td>
</tr>
<tr>
<td>Krypton</td>
<td>Kr</td>
<td>1.1 parts per million</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>SO₂</td>
<td>1.0 parts per million</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>2.0 parts per million</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H₂</td>
<td>0.5 parts per million</td>
</tr>
<tr>
<td>Nitrosoe oxide</td>
<td>N₂O</td>
<td>0.5 parts per million</td>
</tr>
<tr>
<td>Xenon</td>
<td>Xe</td>
<td>0.09 parts per million</td>
</tr>
<tr>
<td>Ozone</td>
<td>O₃</td>
<td>0.07 parts per million</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>NO₂</td>
<td>0.02 parts per million</td>
</tr>
</tbody>
</table>

*and some other traces*
Helium recovery
from air - air separation industry

Fig. 1.4. Schematic process flowsheet of the high-pressure ASP of “AKAp” type
Helium recovery from air - air separation industry

Fig. 1.4. Schematic process flowsheet of the high-pressure ASP of “AKAp” type
Helium recovery
from air - air rectification
double column system

2 – UPPER COLUMN
pressure: top: N2 at 1.28 bar abs
bottom: O2 at 1.45 bar
T = 93.7 K

3 – CONDENSER - VAPORIZER
O2 in tubes T = 93.7 K
DT = 2 K
N2 in the shell T = 95.7 K

1 – LOWER COLUMN
top: temperature T = 95.7 K
condensation of N2 at p = 5.70 bar
bottom: gaseous air at 5.82 bar abs
(compressor air: 6.2 barg – ENERGY)
Helium recovery
from air - air rectification
double column system

Accumulation of non-condensable gases Ne + He reduces partial pressure of nitrogen.

For achieving the same temperature, the total condensation pressure is increasing. (ENERGY!)

Ne+He mixture withdrawal

3 – CONDENSER - VAPORIZER
O2 in tubes \( T = 93.7 \text{ K} \)

\( DT = 2 \text{ K} \)

N2 in the shell \( T = 95.7 \text{ K} \)

1 – LOWER COLUMN

top: temperature \( T = 95.7 \text{ K} \)
condensation of N2 at \( p = 5.70 \text{ bar} \)

bottom: gaseous air at 5.82 bar abs
(compressor air: 6.2 barg – ENERGY)
Helium recovery from air - air rectification double column system

1% (Ne+He) ..... 1% pressure more

Energy consumption on the compressor

\[ N = nRT \ln\left(\frac{P_{komp}}{P_{atm}}\right) \]
\[ \frac{dN}{dP_{komp}} = nRT\left(\frac{P_{atm}}{P_{komp}}\right) \cdot \frac{1}{P_{atm}} \]
\[ dN = \frac{nRT}{P_{komp}} \times dP_{komp} \]
\[ \frac{dN}{N} = \frac{dP_{komp}}{P_{komp} \cdot \ln(\frac{P_{komp}}{P_{atm}})} \]

Exercise 2:

\[ P_{komp} = 6 \text{ bar}, \quad P_{atm} = 1 \text{ bar} \]
\[ 1\% (\text{Ne+He}) \]
\[ dP_{komp} = ..................? \text{ bar} \]
\[ \frac{dN}{N} = ..............? \% \text{ energy on the compressor?} \]
Helium recovery
from air - air rectification
double column system

1% (Ne+He) ..... 1% pressure more

Energy consumption on the compressor

\[ N = nRT \ln(P_{komp}/P_{atm}) \]

\[ \frac{dN}{dP_{komp}} = nRT(P_{atm}/P_{komp}) \frac{1}{P_{atm}} \]

\[ dN = nRT/P_{komp} \times dP_{komp} \]

\[ \frac{dN}{N} = \frac{dP_{komp}}{P_{komp} \ln(P_{komp}/P_{atm})} \]

Exercise 2 (results):

\[ P_{komp} = 6 \text{ bar}, \ P_{atm} = 1 \text{ bar} \]

1% (Ne+He)

\[ dP_{komp} = 0.06 \text{ bar} \]

\[ \frac{dN}{N} = 0.56\% \text{ energy on the compressor} \]

Ne+He mixture withdrawal
Helium recovery from air - air rectification double column system

Deflegmator of Ne+He mixture
Cooled by boiling liquid nitrogen at 1.3 bar, 79.3K
DT = 0.5 K

Main condensers cascade.
Nearly no concentration (Ne+He) in the core 3

Condensing temperature 79.8 K
Concentration of neon in returning liquid phase and the withdrawn gaseous phase influence the condensation pressure.
They must be in accordance with mass balance
Condensing temperature 79.8 K
Concentration of neon in returning liquid phase and the withdrawn gaseous phase influence the condensation pressure.

They must be in accordance with mass balance between large liquid return with small concentration of Ne and small vapor flow with large concentrations of inerts.

Phase Equilibrium at NHM condensation
K = y(% in vapor)/x(% in liquid)

He/N2 at 77.3 K ... K = 800
Ne/N2 at 77.3 K ... K = 60

Typical composition of NHM:
40% N2, 60% of inerts
(44% Ne, 15% He, 1% H2)

Typical flowrate:
0.003% of inlet air of the plant
Helium recovery from air - air rectification
Crude Neon Helium Mixture

Deflegmator for purification of the condenser vent
M (z = 2% Ne+He)
to crude Neon-Helium mixture D (yd = 50% Ne+He)
Helium recovery
from air - He + Ne crude concentrate separation

Figure 1 Neon purifier system showing de-oxo, absorber and distillation steps (courtesy BOC)
Helium recovery
from air - air separation industry

78% Nitrogen
21% Oxygen
1% Argon

Air Separation - Cryogenic

Liquefaction

Cylinders

Liquid Storage

Cryogenic Tanker

Gas Pipeline
To Customers

Customer Liquid Storage And Vaporizer

Gas To Customer Operation
Helium recovery from air - air separation industry

Unavoidable by-product: a concentrate of Neon + Helium (3:1) in variable percentage with N₂
Helium recovery from air - air separation industry

**Unavoidable by-product:** a concentrate of Neon + Helium (3:1) in variable percentage with N\textsubscript{2}

**Single large plant**
20 000 Nm\textsuperscript{3} O\textsubscript{2}/hour
consumes
112 000 Nm\textsuperscript{3}/h air/hour

**Theoretical maximum production of helium?**
Nm\textsuperscript{3}/day .......................?
pressure cylinders/day?
Helium recovery
from air - air separation plant

**Exercise 1:**

Single plant: \(112\,000\,\text{Nm}^3/\text{h}\)

5.2 ppm He

Molecular mass of He \(4\)

Helium \(112\,000 \times 5.2 \times 10^{-6} = 0.58\,\text{Nm}^3/\text{h}\)

\[= 14.0\,\text{Nm}^3/\text{day}\]

(in a case of 100% recovery)

Normal volume of one kilomole \(22.4\,\text{m}^3\)

Molecular mass of He \(4\)

\[14 / 22.4 \times 4 = 2.5\,\text{kg/day}\]

(0.0035 of the world production)

High pressure cylinders (50 liters, 200 bar) 1.4 cylinder/day

*This process is not effective any more. It is used for neon recovery only.*
Helium from Natural Gas

History and content in the crude gas resources

- First found in 1905 by H.P. Cady in Dexter, Kansas, USA: 1,5% He. His student C. Siebel analyzed helium content in many other natural gases, but he thought still in 1917, that it has „regrettably no practical application.“

- First helium recoveries:
  1917, Hamilton, Ontario, Canada, British army for airships, WW I.
  1921-1927, Fort Worth, Texas, USA

  Helium Conservation Act 1960 – governmental purchase of crude helium 130 Mill. m3/year, storage in the Cliffside gas field
  Helium Privatization Act 1996 – Sale of USA national reserves
Helium from Natural Gas

History and content in the crude gas resources

U.S. Helium Recovery/Storage
Helium from Natural Gas

History and content in the crude gas resources

- Europe: Odolanow, Poland: 0.2% He
  Production since 1975 (?),
  the most important source in Europe
  446 ton/year
- Orenburg, Russia, 0.05% He
  helium deliveries from 1990
  3200 ton/year
- Qatar North Field: 0.04% He
  3 500 ton/year of LHe from 2006
- Qatar 2
  6 500 ton/year of LHe from

Estimated energy costs of helium recovery from gases containing 0.02, 0.05, 0.35% of helium are 250, 100, 18 kWh/Nm3, respectively.
Helium from Natural Gas

World resources

Fig 1 Helium can be extracted from only a few natural gas fields around the world. The richest field is in the state of Utah in the U.S.
Crude He from an NRU (Nitrogen rejection from the raw natural gas)

World largest Nitrogen rejection unit.

Reduction of nitrogen content in the natural gas from 15% to 3% and crude He recovery.

One train with a two-column Nitrogen rejection process operates 8600 ton of natural gas/day.

Crude helium is recovered from the gas at Amoco plants, designed by Chart, in Hugoton, KS.
Qatar is the largest exporter of liquefied natural gas in the world.

Helium rich mixture is recovered in the process of liquefaction of natural gas (condensation point -162°C). Helium remains as non-condensing gas and can be vented from the process condenser.
Helium from Natural Gas
Example Qatar

Table 1. Impure helium feed gas from both Qatar gas and Ras Gas sources

<table>
<thead>
<tr>
<th>Feed gas</th>
<th>Qatar Gas</th>
<th>Ras Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>55.2118</td>
<td>41.2501</td>
</tr>
<tr>
<td>N₂</td>
<td>41.4547</td>
<td>55.3319</td>
</tr>
<tr>
<td>CH₄</td>
<td>2.3216</td>
<td>2.3686</td>
</tr>
<tr>
<td>H₂</td>
<td>0.9963</td>
<td>1.0320</td>
</tr>
<tr>
<td>CO</td>
<td>0.0026</td>
<td>0.0038</td>
</tr>
<tr>
<td>Ne</td>
<td>0.0017</td>
<td>0.0013</td>
</tr>
<tr>
<td>Pressure</td>
<td>bara</td>
<td>2</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>ambient</td>
</tr>
<tr>
<td>Total flow</td>
<td>Nm³/h</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Composition of crude helium concentrate from two Qatar natural gas base load liquefaction plants
Block scheme of pure liquid helium recovery from the crude
Crude gas composition:
60% CH4, 38% N2, 0,3% CO2, 0,3% H2O, 0,25% He, rest C2+

Basic process:
- Crude gas purification from condensing and freezing impurities
- Separation of nitrogen from methane by low temperature distillation
- Compression of liquid methane in pumps
- Vaporization of methane in the main heat exchanger and delivery to pipeline

Plant capacity: 200 000 Nm3/hour = 3460 ton/day

Side production of 50 ton/day liquefied methane (LNG),
To be increased to 150 ton/day in 2009
446 ton/year
1.6% of world consumption

from ICEC 2010 website

Low-methane gas purification

Low temperature distillation of natural gas

Helium purification, liquefaction and storage
Helium from Natural Gas

KRIIO Odolanow *(visited by students, when the course is in Wroclaw)*

Crude gas purification:
- from CO2 with absorption on methylamine
- from CO2 with adsorption on molesieve (synthetic zeolite)
- from C5+ hydrocarbons on charcoal (activated carbon)
Helium from Natural Gas
KRIO Odolanow

Crude gas purification:
- from CO2 with absorption on methylamine (similar flow scheme)
Helium from Natural Gas
KRIO Odolanow

Crude gas purification:
- from CO2 with adsorption on molesieve (synthetic zeolite) (similar flow scheme)
Helium from Natural Gas

KRIO Odolanow

Cold box:
- Heat exchanger
- Distillation column
Helium from Natural Gas

KRIO Odolanow

Diagram of a process for extracting helium from natural gas.
Helium from Natural Gas
KRIO Odolanow

Helium compressor
Helium from Natural Gas

KRIODolanow

Helium liquefier
Helium from Natural Gas

KRIO Odolanow

Helium liquefier

upper part (closer look)
Helium from Natural Gas

KRIIO Odolanow

Helium storage tank 500 m³ on the roof of the liquefier building
Helium from Natural Gas
KRIO Odolanow

Helium storage tank 500 m3 on the roof of the liquefier building

Front end of the storage tank
Helium from Natural Gas
KRIO Odolanow

Liquid helium shipping in Dewar vessels
Helium from Natural Gas
KRIO Odolanow

Compressed gas helium shipping in cylinder packs
Helium from Natural Gas

KRIO Odolanow

Liquid helium shipping in road trailers
Helium from waste gases of ammonia synthesis

Basic process

Air separation

Air separation → N2 (Ar, Ne, He)

Partial oxidation

Partial oxidation → CO2 + H2 (CH4, Kr, Xe)

Air separation

CO2 liquefaction

CO2 liquefaction → H2 (Kr, Xe)

NH3 synthesis

NH3 synthesis → NH3 liquefaction

NH3 synthesis

NH3 liquefaction

NH3 liquefaction → LC02 (sale)

H2, N2, CH4, Ar, Ne, He, Kr, Xe

WASTE GAS

LNH3 (sale or direct use for nitrose acid, urea or ammonium nitrate synthesis)
Helium from waste gases of ammonia synthesis

Examples of waste gase composition

<table>
<thead>
<tr>
<th>ENTERPRISE</th>
<th>NH₃</th>
<th>Xe+Kr</th>
<th>CH₄</th>
<th>Ar</th>
<th>N₂</th>
<th>Ne</th>
<th>H₂</th>
<th>He</th>
</tr>
</thead>
<tbody>
<tr>
<td>«Azot» enterprise, Severodonetsk, Ukraine</td>
<td>1,7</td>
<td>&lt;0,001</td>
<td>13,0</td>
<td>5,3</td>
<td>20,7</td>
<td>0,01</td>
<td>59</td>
<td>0,3</td>
</tr>
<tr>
<td>Priportovy Zavod, Odessa, Ukraine</td>
<td>2</td>
<td></td>
<td>8,6</td>
<td>5,6</td>
<td>19</td>
<td>0,01</td>
<td>64,4</td>
<td>0,4</td>
</tr>
</tbody>
</table>

**Table 1:** Volume content of the components in the waste flows, %

[This and further slides from: Bondarenko, Losyakov, Simonenko O., Conference Cryogenics 2008]
Helium from waste gases of ammonia synthesis

Stages of separation

Figure 1: The preferable sequence of complex waste flow processing
Figure 2: Phase equilibrium isotherms of the systems $\text{H}_2-\text{N}_2$ (a) and $\text{He}-\text{H}_2$ (b) in the vapor phase. $1^V-2^V-3$ - enrichment and purification of $\text{H}_2$-fraction in the additional reflux condenser RCl and the freezer Fr (Figure 3); $6^V-12'-12''$ - helium concentration process under different phase equilibrium conditions.
HELIUM CONCENTRATE RECOVERY

SPS- Prelim. separation
RC1- N2 reflux condenser
Fr – N2 Freezer (two of)
NA – Neon adsorber
HC – He column
RC1- He reflux condenser
HR – He refrigerator
Conclusions on He recovery

- Helium is found in some gas mixtures like natural gas or some by-products of gaseous processes in concentrations 0.005 to 2%.
- The separation methods are high-tech and energy consuming, mostly cryogenic methods.
- He is an important industrial gas with unique properties, which makes it irreplaceable in many processes.
- Global resources are limited and consumption is growing, which initiated administrative actions to prevent wasting.