Minor constituents

Nitrogen Rejection (Chapter 13)
Trace-Component Recovery or Removal (Chapter 14)

Based on presentation by Prof. Art Kidnay
Plant Block Schematic

Gas & liquids from wells
- Field liquids removal
  - Field acid gas removal
  - Field dehydration
  - Field compression
  - Inlet receiving
    - Water & solids
  - Inlet compression
  - Gas Treating
    - Hydrocarbon recovery
      - Nitrogen rejection
      - Dehydration
  - Helium recovery
    - Outlet compression
      - Liquifaction
      - LNG
    - Sales gas
  - Crude Helium
  - CO2
    - Sulfur recovery
      - Elemental Sulfur
    - Sales gas
      - LNG
      - NGLs
      - Natural gasoline
Topics

Nitrogen Rejection (NRU)
- Nitrogen Rejection for Gas Upgrading
- Nitrogen Rejection for EOR

Trace-Component Recovery or Removal
- $\text{H}_2$, $\text{O}_2$, NORM, As
- Helium
- Mercury
  - Amalgam Formation
  - Removal Processes
- BTEX
Nitrogen Rejection (NRU)
Nitrogen Removal / Rejection

Nitrogen rejection required to:

- Lower $N_2$ level to meet pipeline specifications
- Recover $N_2$ for use in enhanced oil recovery (EOR)
- Obtain raw $N_2$ / He stream for He recovery
Subquality gas and EOR

16% of the non-associated reserves (2000) were subquality in nitrogen and consequently require blending or processing to meet the 3 mol % total inerts specification for pipelines

In 1998 EOR methods contributed about 12% of the total US oil production.

- about 55% from thermal methods,
- 28% from carbon dioxide flooding,
- 12% from natural gas flooding,
- 4.5% was from nitrogen flooding.
## Removing N₂ from natural gas

<table>
<thead>
<tr>
<th>Process</th>
<th>Flow range MMscf/d (MSm³/d)</th>
<th>Complexity</th>
<th>Heavy hydrocarbon recovery</th>
<th>Stage of development</th>
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<tbody>
<tr>
<td>Distillation</td>
<td>&gt; 15</td>
<td>Complex</td>
<td>In product gas</td>
<td>Mature</td>
</tr>
<tr>
<td>Pressure Swing</td>
<td>2 – 15</td>
<td>Simple: batch operation</td>
<td>In regeneration gas</td>
<td>Early commercial</td>
</tr>
<tr>
<td>Adsorption (PSA)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane</td>
<td>0.5 – 2.5</td>
<td>Simple: continuous operation</td>
<td>In product gas</td>
<td>Early commercial</td>
</tr>
</tbody>
</table>
Conventional Cryo Process
Conventional Cryo Process
Distillation

Nitrogen + methane feed → VERY COLD

Nitrogen

N₂ -320 °F

CH₄ -259 °F

Methane
Two-column cryogenic distillation

-98% C₁
-200°F
10 psig

-160°F

-175°F
200 psig

Demethanizer
Overhead
15% N₂
-150°F, 250 psig

65% N₂ 35% C₁
-210°F

N₂ -260°F 10 psig

-300°F

-250°F

-240°F

-245°F
15 psig

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Adsorption – Modes of Regeneration

Temperature Swing Adsorption (TSA)
- Increase temperature for regeneration
- Good for trace impurities with high heat of adsorption

Pressure Swing Adsorption (PSA)
- Decrease pressure for regeneration
- Good for enriching streams
- Components have low heat of adsorption
- Rapid cycles (seconds to few minutes)
Adsorption

Four steps in one complete cycle
1> Bed 1 pressurized with feed, Bed 2 is depressurized
2> Feed flow started through Bed 1, Bed 2 purged with small product gas slipstream
3> Bed 2 pressurized with feed, Bed 1 is depressurized
4> Feed flow started through Bed 2, Bed 1 is purged with small product gas slipstream
**Adsorption**

Four steps in one complete cycle:
1> Bed 1 pressurized with feed, Bed 2 is depressurized
2> Feed flow started through Bed 1, Bed 2 purged with *small* product gas slipstream
3> Bed 2 pressurized with feed, Bed 1 is depressurized
4> Feed flow started through Bed 2, Bed 1 is purged with *small* product gas slipstream

Key:
- Closed
- Open
- Slipstream
- Main flow
Adsorption

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closed
open
slipstream
main flow
Adsorption

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- closed
- open
- slipstream
- main flow
Membranes

Composite membrane structure used to separate nitrogen from natural gas

membrane is a silicone rubber/polyetherimide (PEI) composite
Membranes

Membrane unit to treat gas containing 8 - 16% $N_2$ to bring it to Btu gas specifications and 5 to 10% $N_2$ in the treated stream.
Trace-Component Recovery or Removal
Possible trace components

Hydrogen
- Rare unless refinery cracked gas is fed to plant

Oxygen
- Not naturally occurring. Major source – leaks in sub-atmospheric gathering systems

Radon (NORM)
- Solids collect on pipe walls & inlet filters

Arsenic
- Toxic nonvolatile solid

Helium
- Valuable!

Mercury
- Mechanical damage to brazed aluminum exchangers

BTEX (benzene, toluene, ethylbenzene, and xylene)
- Aromatic emissions from TEG & amine vents
Oxygen

Oxygen issues

- Enhances pipeline corrosion
- Forms heat stable salts (HSS) with amines
- Forms corrosive acidic compounds with glycols
- Forms water with heavy hydrocarbons during reactivation of adsorbent beds

Oxygen removal techniques

- Non-regenerative scavengers
- Catalytic reaction to form water and CO₂ (H₂O removed in dehydration process)
  - Sulfur compounds poison oxidation catalysts
Radon (NORM)

Naturally Occurring Radioactive Material

Natural gas contains Radon (Ra$_{222}$) at low concentrations

- gas is rarely health problem
- half-life of about 3.8 days

Radon gas $\rightarrow$ radioactive solids

\[
\begin{align*}
\text{Ra}_{222} & \rightarrow \text{Po}_{218} & \rightarrow \text{Pb}_{214} & \rightarrow \text{Bi}_{214} & \rightarrow \text{Po}_{214} & \rightarrow \text{Pb}_{210} & \rightarrow \text{Bi}_{210} & \rightarrow \text{Po}_{210} & \rightarrow \text{Pb}_{206} \\
3.8 \text{ d} & & 3.0 \text{ m} & & 27 \text{ m} & & 20 \text{ m} & & 164 \text{ ms} & & 22.3 \text{ yr} & & 5.0 \text{ d} & & 138 \text{ d}
\end{align*}
\]

Solids collect on pipe walls & inlet filters

Scale generates large quantities of low level radioactive waste which must be discarded in disposal wells.
Arsenic

Toxic nonvolatile solid
Predominately trimethylarsine (As(CH₃)₃)
Typically collects as fine grey dust

Removed from gas using nonregenerative adsorption
Facilities reduce concentrations in sweet raw gas from 1,000 to less than 1 μg/m³
Helium

Valuable!

Natural gas most viable source

“Helium-rich” gas > 0.3 vol% helium
  - Rarely > 5 vol%

United States (2003) produced 84% of world production of Grade-A helium (99.995% purity)
  - Remainder from Algeria, Poland & Russia.

New large helium plants:
  - Qatar (2005)
  - Darwin, Australia (2007)
Feed compositions to Ladder Creek (mol %)

<table>
<thead>
<tr>
<th></th>
<th>He-Rich Gas</th>
<th>He-Lean Gas</th>
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</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>61.92</td>
<td>31.58</td>
</tr>
<tr>
<td>Helium</td>
<td>3.54</td>
<td>1.81</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.98</td>
<td>0.91</td>
</tr>
<tr>
<td>Methane</td>
<td>26.65</td>
<td>52.84</td>
</tr>
<tr>
<td>Ethane</td>
<td>2.60</td>
<td>6.40</td>
</tr>
<tr>
<td>C3+</td>
<td>4.30</td>
<td>6.46</td>
</tr>
</tbody>
</table>

N\textsubscript{2}/He ratio  17.49  17.45
Helium recovery plant (Ladder Creek)

1. Feed Gas
   - CO₂ Removal
   - Waste Gas Recycle Compressor
   - Mole Sieve Dehydration
   - Nitrogen To Vent or Liquid Storage
   - NGL/NRU/HRU Cold Box

2. PSA Helium Purifier
   - Crude Helium Pretreatment
   - Helium Liquefier

3. Liquid Nitrogen Storage
   - High Pressure Storage
   - Truck Filling Station
   - Tube Trailer Filling Station

4. Helium Product Compressor
   - Helium Product
   - Residue Gas
   - NGL Product
Mercury

Two major problems of mercury in natural gas

- amalgam formation with aluminum
- environmental pollution - compounds readily absorbed by most biological systems

May be present as

- elemental mercury
  - Majority will condense in cryogenic section
- organometallic compounds, CH$_3$HgCH$_3$ (dimethylmercury), CH$_3$HgC$_2$H$_5$ (methylethylmercury), C$_2$H$_5$HgC$_2$H$_5$ (diethylmercury)
  - Will concentrate in hydrocarbon liquids
- inorganic compounds such as HgCl$_2$
## Typical mercury levels

<table>
<thead>
<tr>
<th>Location</th>
<th>Elemental Mercury Concentration in micrograms/Nm3 (ppbv)</th>
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<tbody>
<tr>
<td>South America</td>
<td>69 – 119 (8 to 13)</td>
</tr>
<tr>
<td>Far East</td>
<td>58 – 93 (6 to 10)</td>
</tr>
<tr>
<td>North Africa</td>
<td>0.3 – 130 (0.03 to 15)</td>
</tr>
<tr>
<td>Gronigen (Germany)</td>
<td>180 (20)</td>
</tr>
<tr>
<td>Middle East</td>
<td>1 – 9 (0.1 to 1)</td>
</tr>
<tr>
<td>Eastern US Pipeline</td>
<td>0.019 - 0.44 (0.002 to 0.05)</td>
</tr>
<tr>
<td>Midwest US Pipeline</td>
<td>0.001 - 0.10 (0.0001 to 0.01)</td>
</tr>
<tr>
<td>North America</td>
<td>0.005 - 0.040 (0.0005 to 0.004)</td>
</tr>
</tbody>
</table>
Mercury removal processes

Nonregenerative chemisorption
- Removes elemental mercury to < 0.01 μg/Nm\(^3\)
- Typical bed capacities > 10%
- Most use sulfur impregnated on high surface area support

Regenerative chemisorption (1 process)
- Silver on mole sieve chemisorbs elemental mercury and dehydrates at the same time
- Can be added to existing dehydration unit
- Generates mercury waste stream
Mercury Recovery
No Treatment of Regeneration Gas

545 MMscfd, 70°F, 845 psia
27.67 lb H₂O/MMscf
2.5 micrograms Hg/Nm³

H₂O + regeneration gas and 34.45 g/day Hg

H₂O + 0.154 g/day of Hg

34.4 MMscfd regeneration gas

dry, Hg - free gas

Hg_removal_ENG
Mercury Recovery
Treatment of Regeneration Gas

545 MMscfd, 70°F, 845 psia
27.67 lb H₂O/MMscfd
2.5 micrograms Hg/Nm³

Nonregenerated Hg bed
34.39 g/day accumulation

H₂O + 0.206 g/day of Hg

34.4 MMscfd regeneration gas
dry, Hg-free gas
BTEX: Benzene, Toluene, Ethylbenzene, Xylenes

Possible problems:

- Freeze out and plugging in cryogenic units
- Excessive aromatic hydrocarbon emissions
  - Venting from TEG regenerator largest source
  - Venting from amine regenerators lesser source
  - Recovery systems eliminate problem
BTEX Absorption in glycol dehydrators

TEG absorbs aromatic (BTEX) hydrocarbons

- Absorption enhanced at low temperatures, high TEG concentrations, and higher circulation rates
- Most of the absorbed BTEX vented with steam at top of regeneration column

BTEX Emission Control Methods

- Adjusting glycol unit operating conditions to minimize the quantity of BTEX absorbed
- Burning glycol still offgases prior to venting
- Condensing glycol offgases and recovering BTEX as a liquid product
- Adsorbing BTEX on a carbon adsorbent
Summary
Summary

Nitrogen removal to improve calorific value of gas and/or use for EOR gas injection
  - Large scale removal by cryogenic distillation

Trace component removal
  - Mercury removal upstream of brazed aluminum exchangers in cryogenic sections
  - Control of BTEX in gas emissions – air quality concerns
  - Helium recovery by cryogenic distillation
    - Even small concentrations could make the helium more valuable than the remaining natural gas & NGLs
Supplemental Slides
Commercial unit sold to Towne Exploration for treating gas containing 8-16% nitrogen.

<table>
<thead>
<tr>
<th>Feed Gas (Btu/scf)</th>
<th>Product Gas</th>
<th>Vent Gas</th>
<th>Recycle Gas</th>
</tr>
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<tbody>
<tr>
<td>Design</td>
<td>Actual</td>
<td></td>
<td></td>
</tr>
<tr>
<td>908.000</td>
<td>908.05</td>
<td>988</td>
<td>300</td>
</tr>
<tr>
<td>976.957</td>
<td>821.000</td>
<td>421.361</td>
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<td>881.425</td>
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<table>
<thead>
<tr>
<th>Operating Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (psig)</td>
</tr>
<tr>
<td>Design</td>
</tr>
<tr>
<td>960.000</td>
</tr>
<tr>
<td>795.000</td>
</tr>
<tr>
<td>952.000</td>
</tr>
<tr>
<td>970.000</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Temp (°F)</th>
<th>Design</th>
<th>Actual</th>
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<tbody>
<tr>
<td>104</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>86.8</td>
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</tr>
<tr>
<td>90</td>
<td>63</td>
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<tr>
<td>104</td>
<td>104</td>
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</table>

<table>
<thead>
<tr>
<th>Volume (MMscfd)</th>
<th>Design</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>1.738</td>
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<tr>
<td>1.65</td>
<td>1.423</td>
<td>0.21</td>
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<tr>
<td>1.483</td>
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<td>0.188</td>
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<tr>
<td>5.37</td>
<td>2.711</td>
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<table>
<thead>
<tr>
<th>Stream Compositions (daily average mol%)</th>
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<tbody>
<tr>
<td>CO₂</td>
</tr>
<tr>
<td>Methane</td>
</tr>
<tr>
<td>Ethane</td>
</tr>
<tr>
<td>Propane</td>
</tr>
<tr>
<td>n-Butane</td>
</tr>
<tr>
<td>Isobutane</td>
</tr>
<tr>
<td>n-Pentane</td>
</tr>
<tr>
<td>Isopentane</td>
</tr>
<tr>
<td>n-Hexane</td>
</tr>
<tr>
<td>C₇+ Hydrocarbons</td>
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