Better All Around…

*Heat Treaters are utilizing Air Products’ knowledge in the use and recycle of helium as a gas quenchant to realize significant economical and environmental benefits*

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Gas is an excellent quenching medium because of its unique environmental, economical and operational benefits. An environmentally-friendly quenching medium, gas eliminates the issue of quenching liquid disposal. Gas quenching also produces cleaner parts, eliminating the need for part washing after quenching. In addition, because gas quench provides more uniform cooling and therefore less part distortion compared to liquid quenching, there is a reduced need for post quench machining. Helium is a gas ideally suited for gas quenching.

**Helium Sourcing**

Although helium is the second most abundant molecule in the universe, it is not as readily available on earth because helium is lighter than the earth’s atmosphere and the vast majority dissipates into the atmosphere and eventually escapes. Helium is formed from the radioactive decay of uranium and thorium, producing an average concentration in air of 10 ppm. Larger concentrations of helium are found in natural gas reservoirs where the earth gases are trapped by impermeable rock. “Helium-rich” natural gas contains concentrations of helium in the range of 0.2%.

The world supply of helium is extracted from various natural gas fields throughout the world. The amount of helium extracted and purified at each site depends on the overall production rate of the wells, the helium concentration in the natural gas field and the supply and demand of helium.

*Figure 1* shows the world’s helium-rich natural gas fields and which of these are producing helium today.
Figure 1: Natural gas fields containing helium

To capture helium from the natural gas, crude natural gas is first purified to remove heavier-than-methane hydrocarbons such as ethane and propane. Next, most of the methane is removed and sent back to the natural gas pipeline. The resulting crude helium undergoes another stage of purification during which other gases, such as carbon dioxide (CO₂) and nitrogen, are removed. After this final purification, most of the helium is liquefied for efficient storage and transportation, while the balance of the pure helium gas is compressed into hydryl tubes and sent directly to customers, such as welding distributors, where it’s used in gaseous form.

After liquification, the liquid helium is shipped to transfill sites around the world, from which it is then shipped to local customers. Large liquid helium consumers, such as MRI manufacturers, receive helium directly in liquid tankers; most other customers receiving liquid helium in dewars or gaseous helium in cylinders or hydryl tubes.

Helium Thermal Properties
Helium has many unique properties that benefit or enable a variety of applications. Table 1 lists these properties and their importance to various industries.
<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><strong>Inert Atmosphere for metal processing</strong> Analytical, Semiconductor</td>
</tr>
<tr>
<td>Lowest boiling point; does not solidify at 0K 1 atm.</td>
<td>Liquid cooling: superconductors Purging/pressurizing liquid hydrogen: rockets</td>
</tr>
<tr>
<td>Very high specific heat &amp; thermal conductivities</td>
<td><strong>Metal Quenching</strong>, fiber optic cooling</td>
</tr>
<tr>
<td>Highest ionization potential</td>
<td>Metal arc welding: aluminum…. 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 (~1000 m/s)</td>
<td>Metal coating, demolition</td>
</tr>
<tr>
<td>Liquid becomes superfluid below 2.2K</td>
<td>Cooling of low-temperature superconductors</td>
</tr>
</tbody>
</table>

**Table 1  Unique properties of helium**

**Helium Gas Quenching**

As shown in Table 1, helium’s high thermal conductivity and inertness make it an ideal medium for metal quenching.

During gas quenching, parts are cooled as a result of the forced convective heat transfer between the part surface and gases. The cooling rate of the quenched part is proportional to the heat transfer coefficient (h) between the cooling gases and the surface of quenched parts. In general, the heat transfer coefficient can be expressed as

$$ h = a \frac{k}{D} (Re)^{\alpha} Pr^{\beta} $$

**Equation 1**

Where $Re = \frac{\rho V_{\text{max}} D}{\mu}$ and $Pr = \frac{C_p \mu}{k}$

In the above equations $D = \text{diameter of cylinder (metal part)}$, $k = \text{gas thermal conductivity}$, $Re$ is the dimensionless Reynolds number and $Pr = \text{Prandtl number}$, $V_{\text{max}} = \text{gas maximum velocity}$, $\rho = \text{gas density}$, $\mu = \text{gas viscosity}$, $C_p = \text{gas specific heat}$. According to equation (1), the heat transfer coefficient is proportional to the gas thermal conductivity ($k$), gas flow rate (velocity), gas density, and specific heat capacity ($C_p$). The constants $a$, $\alpha$ and $\beta$ are functions of the furnace and part geometry, layout of parts in the furnace and type and number of gas nozzles.
The Grimson equation\(^1\) for systems where the quenching gas flows perpendicular to parts is given by:

\[
h = 0.52 \frac{k}{D} \frac{\text{Re}^{0.562}}{\text{Pr}^{1/3}}
\]

This equation is plotted in Figure 2 for a set of parameters for various industrial gases.

**Helium Recycle**

Helium is a non-renewable natural resource because once helium is exposed to the earth’s atmosphere, it dissipates. Therefore, in many cases it makes good business and environmental sense to recycle it. As the world’s leading producer and supplier of helium, Air Products focuses our efforts on helping heat treaters lower their operating costs while protecting and conserving this valuable resource through the use of recycle and recovery technologies.

\(^1\)“Handbook of Quenchants and Quenching Technology”, G.E. Totten, C.E. Bates and N.A. Clinton; ASM International, OH 1993
There are three parts to a recycling process. The first part is the capture of helium from the customer’s application. Conditions that affect the ease (and cost) of helium capture are:

- Batch versus continuous processes—some batch systems may require low-pressure storage.
- Low pressure applications—should minimize air ingress, also some applications require vacuum pumps.
- Open versus closed systems—closed systems are easy to capture without ingressing air.

The second part is the purification process. To do this, an assessment is conducted to understand the customer’s needs and to determine the scope, including:

- What impurities are in the captured gas
- Which of these impurities are harmful to the customer’s process
- Which impurities are considered inert and just need build-up prevention
- What concentration of each impurity can be tolerated in the return gas

Part three is the final storage. The purified recycle gas, which may require compression, is integrated with the make-up and back-up gas supply system.

**Helium Purification**

As the world leader in the production and purification of helium, Air Products is extremely qualified to identify an optimal purification method for each recycle opportunity by considering the amount and type of impurities and the desired purity of the return gas. There are four main technologies used in gas purification: 1) adsorption, which exploits the differential adsorption characteristics of gases; 2) membrane, which uses the differential permeabilities of gases; 3) cryogenic distillation, which exploits the differential boiling points of gases; and 4) combustion and getter systems, which utilizes the differential chemical reactivities of gases. For any purification system, however, there is a balance (and therefore an optimization) between return purity, percentage of gas recovery, power requirement and capital expenditure. Air Products works with our customers to optimize these variables within the customer’s constraints.

Helium recycle systems primarily utilize adsorption and membrane systems in the purification processes. For this reason an overview of each technology is given below.

** ADSORPTION SYSTEMS**

In adsorption systems, the feed gas (captured gas in recycle applications) is passed through a bed of adsorbent, see Figure 3. As the impure process gas flows through the bed, the impurities (adsorbates) are adsorbed onto the adsorbent and purified process gas flows from the bed. Once the bed is saturated with adsorbates, the feed is routed to another clean bed and the saturated bed is regenerated. The use of multiple beds helps maintain a constant product flow.
The adsorbents are chosen based on the types of impurities to be removed. Silica gel or alumina may be used to remove water, activated carbon is used to remove various types of hydro-carbons and zeolites are used to remove the components of air. Some systems require layering of adsorbent due to the variety of impurities. The capacity of an adsorbent to “capture” each adsorbate increases with increasing pressure and decreasing temperature.

There are three basic techniques for regenerating a saturated bed. In temperature swing adsorption (TSA), regeneration gas (most often a slip stream of product gas) is heated and passed through the bed. The heat lowers the sieve capacity and the adsorbate desorbs into the regeneration gas. In pressure swing adsorption (PSA), the bed pressure is lowered, reducing the sieve capacity and the adsorbates desorb into the regeneration gas. Vacuum swing adsorption (VSA) uses a vacuum to bring the system pressure below atmospheric level to remove the adsorbate.

Adsorption systems can be tailored to remove a variety of impurities and can remove impurities to low levels. For helium systems, the purified helium is produced at the adsorption pressure and post compression may not be required.
A picture of a mid-size adsorption system for helium recycle is given in Figure 4.

Figure 4: Mid-size adsorption system for helium recycle

**Membrane Systems**

Membrane systems for helium separation utilize membranes that are manufactured in hollow fiber form, as shown in Figure 5. These membranes are bundled together (Figure 6) with a distribution header and an outlet header. The impure process gas is compressed and then passed through the bore side of the fibers. The helium preferentially permeates through the membrane into the low pressure shell side where it is collected.²,³

The mechanism for gas transport through the membrane begins with the components first dissolving into, then diffusing through, the membrane. Therefore, the permeability of a gas is dependent on two factors – gas solubility and gas diffusion. The selectivity is the relative permeability between two components. The solubility selectivity of two gases in a given membrane depends on the interaction of the gases with membrane materials, whereas diffusion selectivity is dependent on the size of the gas molecules. Roughly, the overall selectivity of a pair of gases is a multiple of the solubility selectivity and the diffusion selectivity. For example, the overall selectivity of water and helium is such that membranes cannot be used to dry helium.

When helium is purified at a low pressure from the membrane, post purification compression may be needed. Membrane systems are useful in a narrower range than adsorption systems but are generally less expensive.


³ Puri, P. S., "Gas Separation Membranes- Current Status, La Chimica e l'industria 1996, 78( 815-821)
Economic Study
Gas quenching applications are ideal for helium recycle systems because the gas can be easily captured, the captured gas is relatively pure and the volumes are usually amenable. Table 2 gives an economic analysis of three cases: once-through helium use; helium recycle in which the gas is not purified; and helium recycle, where purification is used. As shown in Table 2, helium recycle offers approximately 45 to 60% annual savings over once through usage.

<table>
<thead>
<tr>
<th></th>
<th>Once-Through</th>
<th>Recycle</th>
<th>Recycle with Purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monthly Volume</td>
<td>200k SCF</td>
<td>200k SCF</td>
<td>200k SCF</td>
</tr>
<tr>
<td>Recovery</td>
<td>--</td>
<td>85%</td>
<td>80%</td>
</tr>
</tbody>
</table>

Figure 5: Micro-graph of hollow fiber membrane

Figure 6: Schematic of a fiber bundle
<table>
<thead>
<tr>
<th></th>
<th>Once-Through</th>
<th>Recycle</th>
<th>Recycle with Purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Make-Up Volume</td>
<td>200k SCF</td>
<td>30k SCF</td>
<td>40k SCF</td>
</tr>
<tr>
<td>Helium Cost $/100 SCF</td>
<td>$20</td>
<td>$20</td>
<td>$20</td>
</tr>
<tr>
<td>Monthly Lease Fee*</td>
<td>--</td>
<td>$10,000</td>
<td>$14,000</td>
</tr>
<tr>
<td>Added Power Costs</td>
<td>$300</td>
<td>$400</td>
<td></td>
</tr>
<tr>
<td>Total Monthly Cost</td>
<td>$40,000</td>
<td>$16,300</td>
<td>$22,400</td>
</tr>
<tr>
<td>Annual Savings</td>
<td>--</td>
<td>$284,400</td>
<td>$211,200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59%</td>
<td>44%</td>
</tr>
</tbody>
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**Summary**

Helium recovery and recycling provides numerous benefits for heat treaters. As helium supplies remain fixed, the economics of installing recycle systems become increasingly attractive. While many factors must be taken into account in deciding the most effective helium recycle solution for a given situation, the economics of recycling improve with increased usage volume.

**For More Information**

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