# Cryocooler-Based Helium Recovery Plant for Applications Requiring Gas or Liquid with Extreme Purity

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## ABSTRACT

A cryocooler based helium recovery plant designed to store, compress and purify helium gas collected from one or more helium-using instruments, as well as to liquefy and redistribute the purified gas within a closed system, is presented. The recovery plant is composed to match the purification and liquefaction rate of the system with the consumption rate of the coupled instruments in an attempt to achieve zero loss. In addition, extreme purity helium (gas and liquid) is obtained by the combination of cryo-condensation of impurities and further chemical adsorption by a getter. Problems like clogging of low temperature impedances by impurities normally present in helium have been definitely solved using this plant concept.

## INTRODUCTION

Although helium (He) is the second most abundant element in the universe, on earth it is scarce and only extracted with difficulty. Helium is found underground, in a gaseous state, as a byproduct of natural radioactive disintegrations.

Liquid-phase helium is generally obtained from high power industrial liquefaction plants, referred to herein as "Class XL" liquefiers, which produce liquefied helium in quantities greater than 1000 1iters/hour, and require more than 1000 kW of power. These Class XL plants generally yield a liquefaction efficiency of around one liter/hour/kW. Within these Class XL liquefiers, the helium gas undergoes one or more cyclical thermodynamic processes and the gas is then cooled until it reaches its liquefaction temperature. The technology of these liquefaction plants dates from the last century, and can be referred to as "Collins Technology" [1].

Moreover, in view of the Class XL liquefiers specified above, various other liquefaction classes may be referred to herein. For example, Class L liquefiers will refer to those liquefiers which produce greater than 100 liters/hour; and Class M liquefiers will refer to those liquefiers which produce greater than 20 liters/hour. All of these large-scale liquefiers typically achieve a liquefaction efficiency of about 10 liters/day/kilowatt of input power.

The scientific and industrial applications of helium gas are numerous. In a gas-phase, helium under ambient temperature is useful for welding and as a means for floating balloons; at the highest purity levels is used as a carrier gas in gas chromatography. Moreover, in a liquid-phase, helium at atmospheric pressure is at or near -269 $^{0}$C, and thus is commonly used for refrigeration

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of medical and scientific equipment, among other things. Helium is therefore considered to be a valuable resource, lending interest to advancements in helium gas recovery and reuse, especially such recovery and reuse as might be accomplished with negligible or zero loss.

In modern recovery plants, helium gas is generally processed throughout multiple stages, that is, stage 1: recovery; stage 2: storage under pressure; stage 3: purification; stage 4: liquefaction; and stage 5: distribution. These modern plants are generally known to suffer losses in each and every stage as outlined above. Furthermore, even where the loss is very small at one or more stages, when aggregated together the total loss can be significant and often exceeds 10% per cycle. Furthermore, these plants require complex facilities for the storage of vast volumes of highly pressurized gas, regardless of the liquid consumption rate at the particular facility, since the liquefaction rate generally cannot be coordinated, regulated, or adapted for consumption. Finally, without the capability to adjust the liquefaction rate, the liquefied helium is produced in volumes that exceed consumption, which necessitates the use of very large storage dewars, and consequently requires smaller transportation dewars to distribute the liquid to end users of liquid helium.

With the advent of closed-cycle refrigerators capable of achieving temperatures below that of liquid helium, such as those based on known Gifford McMahon (GM) and pulse tube technologies, liquefiers having lower liquefaction rates and lower maintenance requirements have been developed [2-3]. In such liquefiers, the gas to be liquefied does not undergo complex thermodynamic cycles, but rather condenses by convection and direct thermal exchange with the different stages of the cryogenic refrigerator and is subsequently stored in a dewar. However, at present there has yet to be developed such a helium recovery plant based on GM or pulse tube technologies which is designed to yield liquefaction efficiencies comparable to the class XL liquefaction plants described above; that is, one liter/hour/kW.

In an attempt to solve the problem for an individual medical or scientific instrument, that is, providing liquefied helium as needed, liquefaction systems have been developed which incorporate a closed-cycle refrigerator adapted to collect and re-condense helium that is evaporated by the medical or scientific instrument using helium. However, these systems are constructed to use one refrigerator per instrument, and thus underutilize the refrigerator's capacity. For installations in which the direct installation of a refrigerator is technically not feasible, these closed-cycle refrigerator systems do not solve the problem of providing helium as and when required. Moreover, when a large number of instruments require refrigeration, the acquisition and maintenance costs associated with the corresponding number of refrigerators make this solution impractical.

Accordingly, helium-gas recovery and purification plants, based on closed-cycle refrigerator technologies, are of immediate and significant interest. With such plants, helium gas being employed as a trace gas in leak detection processes, or as a cooling medium, can be recovered and reutilized over several cycles with little or no loss, thereby reducing of the need to acquire virgin helium gas. Moreover, the recovery of helium would provide an economic advantage for processes that require pressurized helium gas. During the last years, in order to implement efficient solutions, we have developed a new technology for helium liquefiers and purifiers based on cryocoolers (ATL 'Advanced Technology Liquefiers', ATP 'Advanced Technology Purifiers' [4-7]).

Below its critical temperature ($T_c$ = 5.2 K) any unwanted substance present in the liquid phase, i.e. any impurity, will be in solid form, resulting in mist, snow, suspensions or particulates. The vapor pressure of these solid impurities will be in general negligible small ($<<10^{-9}$ Pa), except for the case of the hydrogen isotopes and their molecular combinations [8] for which this is of the order of $10^{-2}$ Pa and $10^{-5}$ Pa, at 5.2 K and 4.2 K, respectively. The solid impurities are usually charged and can be easily eliminated by electrostatic precipitation using Petryanov filters to obtain "optically clean" liquid, as demonstrated by Abrikosova and Shal'nikov [8]. But, even "optically clean" filtered liquid helium may contain a relevant quantity of non-solid hydrogen, i.e. molecular hydrogen traces. These small quantities are eventually the cause for blockages in small capillaries used in instruments to produce temperatures below

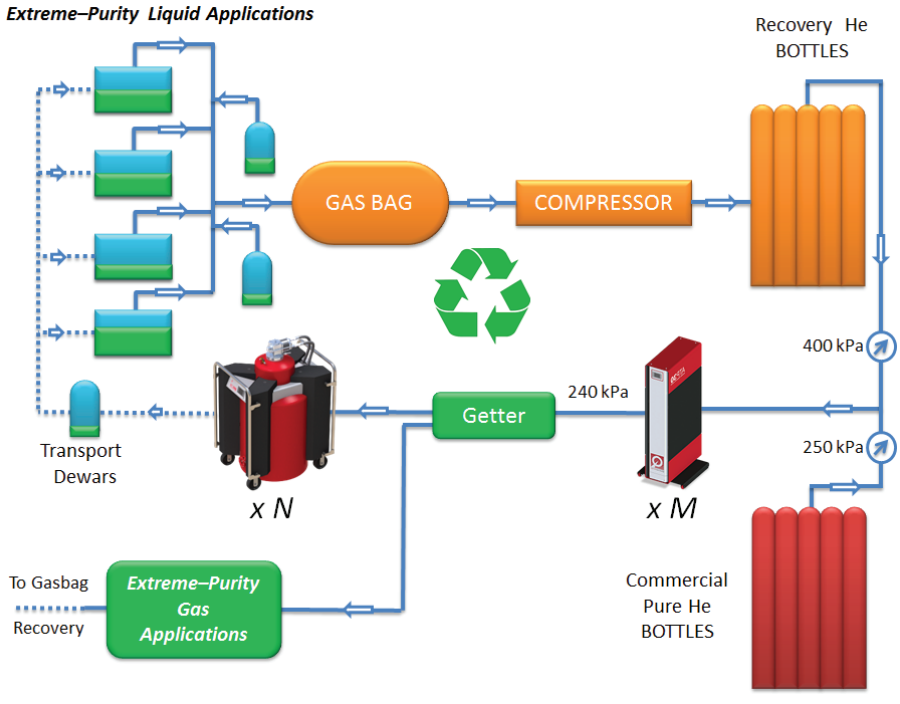


**Figure 1**. Schematic view of a helium recovery plant for the production of helium with extreme purity.

4.2 K. Therefore, the complete elimination of hydrogen has to be ensured in a helium recovery plant to produce high extreme purity helium either in liquid or gas form. This is a concept plant that we called ¨Green Helium¨ recovery plant.

## CRYOCOOLER-BASED HELIUM RECOVERY PLANT

A closed-cycle, high-efficiency, automated helium recovery plant is herein described. This high-efficiency helium recovery plant is designed for computerized control and switching between a liquefaction mode and a standby mode, and is further adapted to collect, re-liquefy, and redistribute recovered helium amongst a plurality of medical or scientific instruments or other equipment. As helium gas is utilized among several instruments within the closed system, it is recovered and subsequently liquefied before being re-introduced to the equipment. As a finite supply of helium is continuously recycled, with no or minimal loss within this closed system, thus reducing the cost associated with resupply of virgin helium gas.

The helium recovery plant presented here covers a liquefaction range of zero liters/hour when operated in standby mode, and 1.25 x N liters/hour when operating in liquefaction mode. In this regard, this helium recovery plant yields liquefaction rates generally comparable to the prior art Class M plants. Additionally, the performance efficiency of the helium liquefaction is around 4 liters/day/kW, nearly matching the production and performance attributes associated with Class L plants, but with simplified operating and maintenance procedures.

The recovery plant shown in figure 1 comprises several parts:

(i) a recovery module for collecting and storing helium gas from one or more helium using instruments;

(ii) a gas collection and storage module adapted to collect gas under atmospheric pressure in a balloon or a container, filter the gas through one or more filters, pressurize the gas to an

absolute pressure above 200 bar by means of a purge-free compressor, and store the gas in a gas storage container at the compressor output pressure;

(iii) a purification module ATP based on a cryocooler, which allows the removal of low vapor pressure impurities such as water, nitrogen, oxygen;

(iv) a non-evaporable getter purifier dedicated to the elimination of hydrogen;

(v) a liquefaction module ATL by means of a closed-cycle based refrigerator, the liquefaction module being adapted to vary the liquefaction rate to closely match the gas recovery rate, and therefore to match the consumption of liquefied gas of the connected equipment;

Maximum efficiency in the liquefaction of helium gas within this helium recovery plant is accomplished with an electronic control adapted to provide precise regulation of the vapor pressure within the dewar. Each pressure value "P" at which liquefaction is performed within the helium recovery plant has a corresponding liquefaction rate "T1," expressed in liters/hour, whereas "T1" is an increasing function of "P" [6].

This helium recovery plant is adapted to adjust the liquefaction rate of helium gas and thus minimizes the storage time lapse of the evaporated gas and therefore reduces the acquired impurities therein. The volume of the stored gas prior to liquefaction is also minimized which simplifies the plant. Furthermore, the liquefier allows permanent storage of the produced liquid within its own thermally insulated dewar, during which the system is operated in a standby mode with a zero liters/hour liquefaction rate and a loss of 0%, thus providing a reserve of liquefied helium for its immediate on-demand use.

This helium recovery plant is scalable by increasing the number of liquefaction (N) and purification (M) units (with $M \approx N/2$ because one ATP can handle enough gas flow to feed two ATLs), resulting in a simplified procedure. Moreover, as the available power of closed-cycle refrigerators continues to increase, fewer refrigerators will be required in each liquefaction unit within the plant.

## HELIUM WITH EXTREME PURITY

The purity of helium is important to be maintained at the highest level, either in liquid phase to avoid blockage produced by impurities in small capillaries, and in gas phase for applications like gas chromatography where any impurity will jeopardize the ultimate sensitivity of the analysis.

In order to obtain helium with extreme purity with the above recovery plant, the gas is purified by passing it through the purifier ATP. The ATP cools down the helium to $T<30$ K, and thus all the relevant impurities having very low vapor pressures at 30 K (nitrogen, oxygen) are eliminated by cryo-condensation, except hydrogen.

The main impurities in the recovered helium, i.e. nitrogen and oxygen, come from the atmosphere by gas diffusion processes through polymeric materials (e.g. gasbag and/or polymeric pipes) [9]. Meanwhile, hydrogen traces can come from the helium sources, since molecular $H_2$ is naturally present in helium gas as obtained from natural gas sources [10], or from oil degradation in the recovered helium compression stage.

The elimination of hydrogen is performed afterwards by passing the helium through a non-evaporable, thermally activatable getter (e.g. Zr-V-Fe) where the hydrogen becomes trapped. It diffuses easily into the bulk because it dissociates on the getter surface into atomic hydrogen. The hydrogen atoms slip into the atomic lattice of the metal grains. The process is represented by the following reaction [11]:

$$H_2(gas) + M \leftrightarrow 2H(adsorbed) + M \leftrightarrow 2H(Mbulk) \quad (1)$$

Where M represents the metal constituents of the getter alloy.

This is a reversible process that allows regeneration of the getter material by thermal activation. Regeneration can be performed every 20,000 hours, taking profit of cryocooler maintenance, to minimize the impact on the operation of the plant.

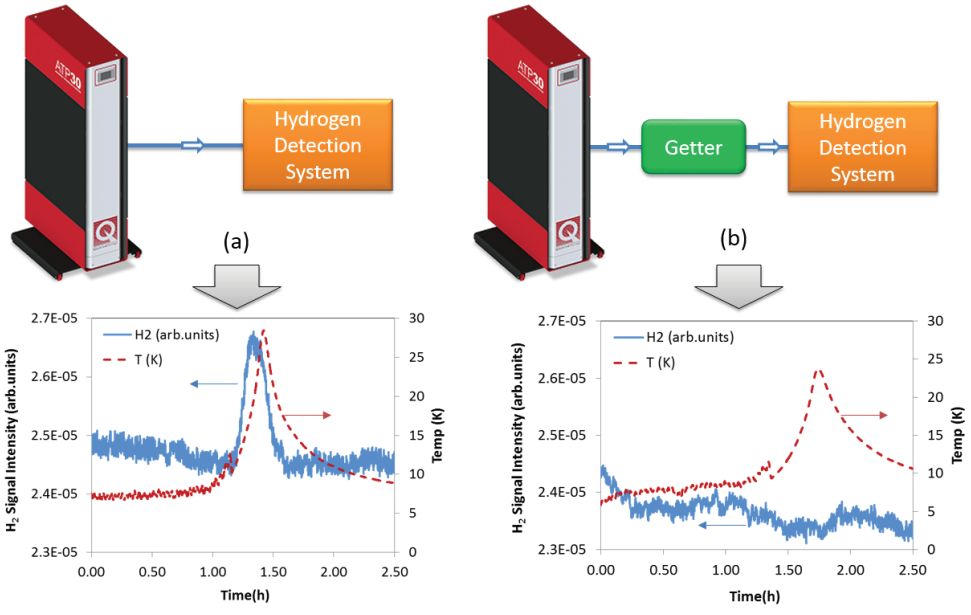


**Figure 2**. Experimental verification for the elimination of hydrogen with a getter. (a) After purification of 100,000 sL of He gas, the ATP is slowly warmed up and a peak of hydrogen is detected (blue continuous line) when the temperature (red dashed line) is close to 14 K. (b) No peak of hydrogen is detected after purification of the same amount of He gas when a getter is connected at the output.

The validity of the "Green Helium" plant concept is demonstrated by the fact that impedance blockages in small capillaries have been completely eliminated for more than one year, when the plant configuration was implemented in the Cryogenic Liquids Service at the University of Zaragoza and in Quantum Design Inc. Furthermore, the efficiency of the thermally activated getter media in trapping $H_2$, was verified by the continuous on line $H_2$ monitoring described below. The $O_2$ content was also verified to be well below 0.1 ppm using a Servomex Multiexact 5400 $O_2$ trace analyzer. Since the $N_2$ content is known to be of the same order of magnitude than the $O_2$ content, the gas purity will be > 99.99999 %. The graphs in Figures 2a and 2b show the filter temperature of the ATP as a function of time. During the test this temperature is varied from the base temperature of the purifier up to about 25 K, and back to the base temperature, in about 2.5 hrs. The hydrogen concentration in the helium purified carrier gas is monitored using a mass spectrometer (helium leak detector QualyTest HLT260 from Pfeiffer Vacuum with hydrogen mass selected). During the test, the ATP collected solid $H_2$ sublimates. The getter effectivity capturing $H_2$ molecules is very well demonstrated by placing the $H_2$ detector to analyze the helium gas at the output of the ATP (Figure 2a) and at the output of the heated getter (Figure 2b), respectively.

## CONCLUSIONS

A helium recovery plant has been presented that utilizes liquefiers and purifiers based on cryocoolers. Special care has been given to the purity of the helium produced by the plant. The purification of helium is performed by a combination of the cryocondensation of all the relevant impurities (except hydrogen) at T<30 K, and the subsequent elimination of hydrogen with a (heated) getter. With this plant concept we obtain extreme purity helium (purity > 99.99999 %) liquid, from recovered helium with impurity levels up to 1%, that has completely eliminated the occurrence blockages of liquid helium small flow impedances.

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