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“Clean” Liquid Helium

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Abstract

Liquid helium is the coldest fluid that exists in nature. By virtue of this fact, any unwanted substance present in liquid helium, that is, any impurity, will be “frozen” and will be in solid form. In practice, these solid impurities can be easily eliminated to obtain “optically clean” liquid. However, even “optically clean” filtered liquid helium may contain a non-negligible quantity of molecular hydrogen. These minute traces of molecular hydrogen are the causes of a known problem worldwide: the blockage of capillary tubes in helium evaporation cryostats. This problem seriously affects a wide range of cryogenic equipment used in low-temperature physics research at a considerable operational cost increase. In this chapter, we propose an underlying mechanism for this effect and provide a definitive solution by means of production of hydrogen-free liquid helium, that is, not only “optically clean” liquid helium but completely “clean” liquid helium. Moreover, basic superfluidity research studies could benefit from the availability of “clean” liquid helium.

Keywords: helium liquefaction, helium cryogenics, small-scale helium liquefiers, hydrogen contamination, impedance blockage, helium purification

1. Introduction

It is well known that the performance of continuously operating ^4He evaporation cryostats is often degraded as a result of the blocking of fine capillary tubes used as flow impedances to achieve temperatures below 4.2 K. This effect has been generally attributed to nitrogen or air impurities entering the capillary tubes from the main bath. However, even the most thorough laboratory best practices adopted to maintain the helium bath clean and prevent impurities from entering the capillary tubes fail. The blocking problem often recurs with no apparent cause.

Many low-temperature research laboratories around the world have experienced this nuisance at a considerable financial cost because helium is boiled off when the equipment has to be warmed up to room temperature in order to unblock the capillary tube and thus, recover the low-temperature operation performance.

This chapter summarizes the work performed during the last 3 years to obtain “Clean” liquid helium and to solve the flow impedance blocking issue definitely. On the other hand, the availability of clean liquid helium opens the door for the preparation of finite H_2 concentrations in superfluid 4He . These $^4He-H_2$ liquid mixtures with known H_2 concentrations will be the key to experimentally study very interesting phenomena like the possible existence of a supercooled stable liquid phase of molecular hydrogen that could exhibit superfluidity [1].

After a detailed description of low-temperature production in 4He evaporation cryostats (Section 2), we describe the underlying physical mechanism responsible for the blockages (Section 3). This is based upon the freezing of molecular H_2 traces present in the liquid helium bath. Solid H_2 is accumulated at the impedance low-pressure side and, after some time, it produces a total impedance blockage.

Section 4 shows that the presence of H_2 traces in helium is unavoidable due to its occurrence in the natural gas wells where this fossil gas is harvested, forcing helium gas suppliers to specify a lower bound for impurity levels at about 100 ppb even in high-grade helium.

Finally, Section 5 describes a (small-scale) helium recovery plant capable of producing gas and liquid helium with ultra-high purity (H_2 molecular concentration $y_{H_2} < 10^{-14}$) named by us as “Clean helium.” Apart from other possible applications in which extreme pure rare gases may be needed, “Clean helium” reliably avoids the low-temperature flow impedance blocking issue.

Details, other than those given here, can be found in Gabal’s Ph.D. thesis [2].

2. Low-temperature production in 4He evaporation cryostats

The simplest way to reduce the temperature in a liquid helium bath is by pumping on it following the liquid–vapor coexistence curve of the 4He phase diagram. However, this method is very uneconomical since about 40% of the liquid must be evaporated to cool the remaining liquid from, for example, 4.2 to 1.3 K, due to the large change of its specific heat in this temperature range [3]. In practice, it is more efficient to leave the main bath at 4.2 K and 100 kPa (1 bar) and to cool only a small fraction of the fluid in a separate container to reach the lower temperature using a 4He evaporation cryostat design [4, 5]. Other advantages are the smaller vacuum required to achieve the lowest temperature and the absence of interruptions in the operation of the refrigerator: having the main bath at atmospheric pressure, the liquid helium refills can be done easily while the 4He main bath is pumped through the impedance.

Figure 1 shows a simple diagram of a continuously operating 4He evaporation cryostat. In such a refrigerator, a small fraction of the liquid from the main 4.2 K bath flows through a suitable flow impedance into a small vessel of several cubic centimeters often referred to as the

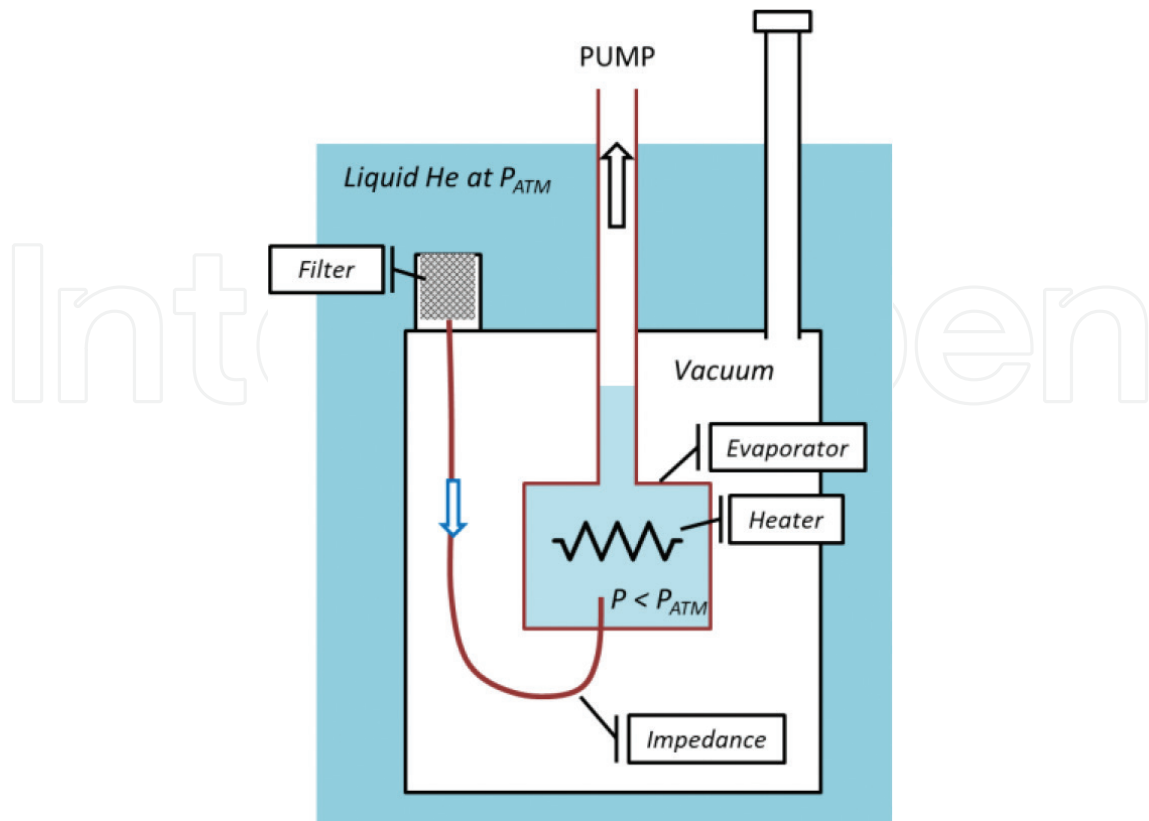


Figure 1. Schematic drawing of continuously operating ^4He refrigerator.

"pot" located inside the cryostat [3]. The vacuum space allows to thermally isolate the small cold vessel from the main 4.2 K bath.

Thanks to the pumping action, the liquid from the main bath at atmospheric pressure, P_{ATM} is isenthalpically expanded through the impedance and reaches the pot at a lower temperature. Almost half of the heat of evaporation is used to cool the liquid, and thus, the other half can be used to cool the experiment.

In general, the impedance Z is given in terms of the flow through the capillary \dot{V} and the pressure drop across it, ΔP , (typically from 100 kPa to 100 Pa) by:

$$\dot{V} = \frac{\Delta P}{(\eta Z)} \quad (1)$$

where η is the viscosity of the liquid helium. Impedances in the range of 10^{10} – 10^{11} cm^{-3} are typically used in most cryogenic applications. Cooling power of the order of 5 mW or more is easily achievable at the impedance outlet once we consider the heat of evaporation of ^4He ($\approx 83 \text{ J/mol}$) and a typical flow rate of $\dot{V}=10^{-4} \text{ mol/s} = 0.13 \text{ sL/mn}$ that can be obtained with a mid-sized mechanical pump. In practice, the impedance is usually built with an appropriate length of fine CuNi capillary tube, usually with a short length of wire inside it to increase the impedance value.

If the impedance value (Z) is too large, there will be insufficient refrigeration and no liquid will accumulate in the evaporation vessel. If the impedance is too small, more liquid than required will flow, with the level rising higher at the vessel. This will not prevent the device from working but will result in higher helium consumption and a higher minimum temperature [5].

Historically, the appearance of a blockage in the capillary has been attributed to nitrogen or air impurities, for example, from [3]: *“During cooldown the refrigerator should be connected to a volume with pressurized very pure ^4He gas in order to prevent N_2 or air from entering and blocking the fill capillary. Sometimes problems arise because impurities in the main liquid helium bath (e.g. frozen air) block the fine capillary used for the impedance. One therefore has to put a filter in front of the capillary and keep the main ^4He clean.”*

During an initial cooldown of a cryostat, if the liquid helium transfer is not carefully carried out (e.g., forgetting to purge the Dewar with helium gas prior to transferring liquid helium), any residual air inside the cryostat can enter, freeze and block the impedance during the pre-cool process. But, if the system has been cooled very carefully with high-purity liquid helium, and, the correct flow through the impedance has been verified, there is only a substance capable to pass through the filter and to block the impedance. This is molecular hydrogen, as we demonstrate in the following section.

Other authors [4] recommended the impedance construction: *“Problems with plugged capillaries sometimes occurred when the impedance was increased using a fine wire, hence, longer capillaries without wires are favored. The filters, which were necessary to prevent plugging of the impedance by frozen air or other particulate matter, were disks of sintered copper felt compression fitted at both ends of the capillary.”*

As we see, the impedance geometry can affect the time necessary to produce the solid that blocks the impedance, but if the helium bath contains molecular hydrogen traces, sooner or later, the problem will occur.

3. Flow impedance blocking issue

3.1. Liquid helium purity

With a boiling point of 4.2 K at 100 KPa, liquid helium is the coldest fluid that exists in nature. Below its critical temperature ($T_c = 5.2$ K), any unwanted substance present in the liquid phase, that is, any impurity, will be in solid form, resulting in mist, snow, suspensions or particulates [6]. The vapor pressure of these solid impurities will be, in general, negligibly small ($\ll 10^{-9}$ Pa), except for the case of the hydrogen isotopes and their molecular combinations [7] for which this is of the order of 10^{-2} Pa and 10^{-5} Pa, at 5.2 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 [7]. But, even “optically clean” filtered liquid helium may contain a relevant quantity of non-solid hydrogen, that is, molecular hydrogen traces.

The He-H₂ gas mixture has attracted much interest in the scientific community because it is the simplest system for the study of intermolecular potentials [8–10]. The interaction potential of hydrogen and helium has been extensively studied by Silvera [11]. The Lennard-Jones wells for the weakly interacting He-He, He-H₂ and H₂-H₂ pairs are 10.8, 13.34 and 34.3 K, respectively. According to this study, H₂ molecules may have a bound state with He atoms, reside in liquid He surface states and penetrate the liquid helium. Thus, in addition to the possible presence of hydrogen molecules in the helium vapor, due to the non-negligible vapor pressure of solid hydrogen at 4.2 K, there may also exist a non-negligible amount of these hydrogen molecules "dissolved" in the liquid He phase.

In general, liquid helium in research laboratories is either delivered by a distributor of specialty gases or produced by liquefaction of both commercial grade and recovered gas. Liquid helium is subsequently stored and transferred to the application's cryostat requiring cryogenic cooling at atmospheric pressure and temperatures around 4.2 K. Since the triple point of H₂ is at 13.84 K and 7.04 kPa, the equilibrium vapor pressure of solid H₂ at those temperatures (≈ 4.2 K) is very small, of the order of $\approx 10^{-5}$ Pa. Therefore, if there is enough H₂ in the He gas being liquefied to produce a partial pressure higher than the equilibrium vapor pressure at 4.2 K, the H₂ molecules will directly nucleate into solid clusters. At atmospheric pressure (10^5 Pa), those solid clusters will be in equilibrium with a H₂ molar fraction in the vapor phase of the order 10^{-10} ($y_{\text{H}_2} = (10^{-5} \text{ Pa}/10^5 \text{ Pa}) = 10^{-10}$).

Even though there are no experimental reports about solubility of H₂ in liquid helium, theoretical calculations from classical solubility theory [12] indicate that the limiting solubility of solid hydrogen in liquid helium at 4.2 K would yield to molar fractions in the liquid phase, x_{H_2} , of the order of $\approx 10^{-10}$, that is, the same order of magnitude than the H₂ molar fraction in the vapor phase, y_{H_2} .

Furthermore, the solid hydrogen vapor pressure and the theoretical limiting solubility of solid hydrogen in liquid helium decrease exponentially with temperature, both becoming very small ($\approx 10^{-9}$ Pa and $\approx 10^{-14}$, respectively) below 3 K. Thus, the maximum concentration of H₂ molecules present in liquid helium will be determined by the exact temperature and pressure conditions of the helium bath. For this chapter, the H₂ molar fractions in the vapor, y_{H_2} , and in the liquid, x_{H_2} , below 3 K, both being of the order of $\approx 10^{-14}$, will be considered negligible. Furthermore, at temperatures near or below 1 K, hydrogen may be regarded as being totally insoluble in He [12].

Thus, unless H₂ impurities are completely eliminated prior to He liquefaction, that is, its molar fraction is reduced from its typical values in the range $y_{\text{H}_2} = 10^{-6}$ – 10^{-5} down to $\approx 10^{-14}$, the liquid He, as produced, will have traces of H₂, up to a maximum concentration level determined by the temperature (e.g., $x_{\text{H}_2} \approx 10^{-10}$ at 4.2 K). If the temperature of liquid helium is further reduced, as it is the case in small capillary impedances, for attaining very low temperatures, $T < 3$ K, the excess H₂ will condense and accumulate at the impedance low-pressure side and, after some time, it will produce a total impedance blockage.

Many applications requiring liquid helium cooling are not sensitive to contaminants of any kind and consequently, do not require special provisions for helium cleanness and

precautions to avoid contamination during liquid helium refills. On the other hand, there are a considerable number of low-temperature applications that require achieving temperatures below 4 K [5], which are very sensitive to impurities present in the liquid and, therefore, those applications need extreme pure liquid helium for proper operation [13].

3.2. The impedance blocking problem

The impedance-blocking problem arises when liquid helium, containing traces of H_2 , is transferred to a cryostat in which the liquid is pumped through a very small capillary or impedance tube, to produce temperatures below 4.2 K using evaporation cooling.

To reduce any impedance blocking, a widespread and generally accepted “low-temperature best practice” is to stop any solid impurity at strategic locations along the helium supply chain with submicron metal-sintered filters. The first opportunity to stop solid impurities in a typical laboratory workflow is while transferring helium from a storage Dewar to the application cryostat for the first time, i.e. during initial cooldown. To this end, many laboratories incorporate a metal filter at the outlet “tip” of the helium transfer line so that the solid impurities are trapped in the line and not transferred into the application cryostat. Once the helium transfer is complete, the line is warmed up, the impurities are flushed away and the tip is ultrasonically cleaned. If any impurities should make it past the first filter, and, furthermore, to filter any other solid impurities already present in the application apparatus, a second “best practice” employed by cryostat designers is to incorporate a similar type of filter at the inlet of the impedance tube at the cold end of the apparatus cryostat.

It is important to appreciate, however, that mechanical filtering of this type is limited in its effectiveness and cannot selectively discriminate and separate H_2 molecules from their helium carrier flow (a two-phase liquid and vapor helium flow), neither during liquid transfer nor during pumping. This is because despite the relatively high binding energies reported for hydrogen with the surface of some solids [14, 15], which involve potentials of the order of several hundred K, the specific surface area per unit volume of the metal-sintered filters commonly used in this application is below $0.5 \text{ m}^2/\text{g}$. This is about three-to-four orders of magnitude smaller than the area per unit volume exhibited by state-of-the-art solid H_2 storage devices. Moreover, the porous size of media grade selected (0.5 microns) is also more than three orders of magnitude larger than the H_2 molecular radius. Based on these considerations, the contribution of H_2 physical sorption on the walls of the mechanical filter is estimated to be very small and, furthermore, limited by the very small vapor pressure of solid hydrogen at the temperature of liquid He.

Thus, in light of these considerations, we postulate that despite the adoption of these simple “best practices,” H_2 molecules will inevitably first enter the application cryostat during helium refills and then, the impedance fine capillary tubes during continuous operation below 4.2 K. As a result, part of the H_2 molecules, carried by the helium flow, will freeze (or precipitate) inside the capillary. This is a consequence of the reduction in temperature and total pressure of helium, which is accompanied by a sizable reduction in solid hydrogen vapor pressure and in the hydrogen limited solubility in liquid helium. So that, sooner or later, depending on the specific dimensions and helium flow rate pumped through the capillary, a blockage will appear. When this occurs, the whole set up has to be warmed up, at least up to about 14 K (hydrogen melting point) but more often to room temperature, with a dramatic loss of time and liquid helium.

Figure 2 illustrates molecular H_2 , present in the liquid helium bath, flowing through a sub-micron-sized metallic-sintered filter (e.g., 500 nm as average pore size) placed to stop solid impurities entering the fine capillary impedance tube. When the temperature in the capillary is reduced below 3 K by evaporation cooling, the H_2 vapor pressure, as well as the limiting solubility of H_2 in helium, becomes negligibly small ($x_{H_2} < 10^{-14}$). Therefore, all the H_2 present in the liquid helium heterogeneously nucleates along the walls of the impedance tube. A similar mechanism in a completely different working fluid and temperature range, for the freezing of water molecule impurities in nitrogen gas, has been proposed to explain blocking in micromachined Joule-Thomson coolers operating approximately at 100 K [16, 17].

As an example, a typical two-phase He flow of only 1 sL/min, having $x_{H_2} = 0.35$ ppb ($3.5 \cdot 10^{-10}$) of H_2 molecules [i.e., corresponding to the vapor pressure of solid hydrogen in liquid helium under typical laboratory conditions (4.2 K and 100 kPa)], pumped through a cylindrical tube impedance of 66- μm effective diameter [e.g., the low temperature impedance of a Quantum Design, Physical Properties Measurement System (PPMS)] [18], may produce a solid hydrogen cylinder block of 66- μm diameter that, in about 24 h, will have 132 μm of height. The exact time for the blocking to occur will depend on the exact solid hydrogen distribution in the impedance. Instead, several years would be necessary to produce the same effect when pumping helium with a lower concentration of H_2 molecules similar to the vapor pressure of solid hydrogen at 3 K, $x_{H_2} = 0.0075$ ppt ($7.5 \cdot 10^{-15}$). This is the reason why we consider the vapor pressure of solid hydrogen at 3 K negligibly small regarding impedance blockage.

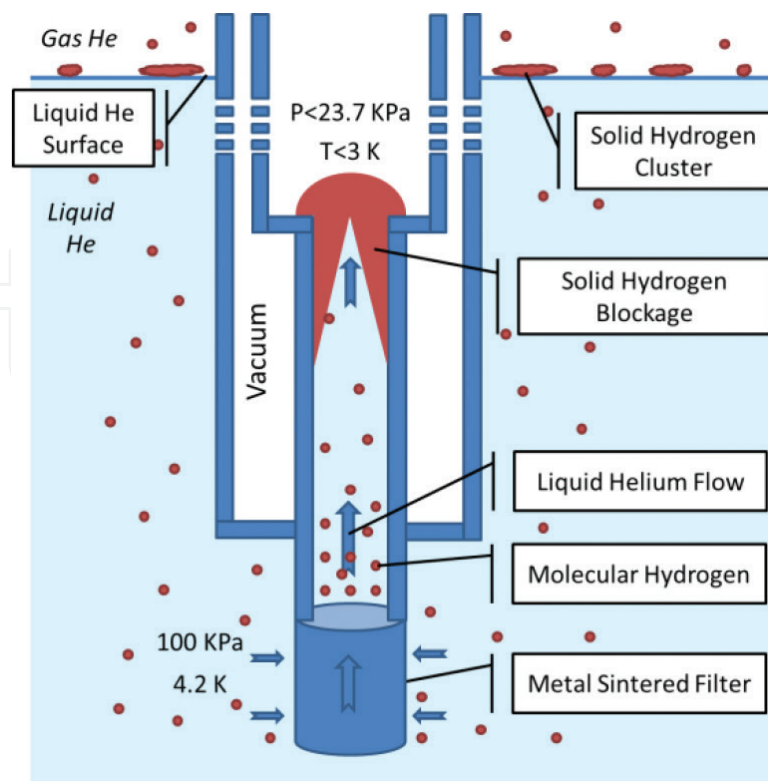


Figure 2. Schematic description of low-temperature impedance blockage by molecular H_2 present in liquid He.

3.3. Pumping two-phase liquid: vapor helium through a capillary impedance tube

When two-phase liquid–vapor He is pumped from a bath at 4.2 K and 100 kPa (10^5 Pa), through a capillary impedance tube, the He stream cools down through its P–T vapor–liquid equilibrium saturation line, $\pi_{\text{He}}(T)$. Thus, if there is enough hydrogen to form solid clusters, the saturation molar fraction of molecular H_2 in the vapor phase will be the starting concentration, $y_{\text{H}_2}(T)|_{eq}$. This can be calculated from cryocondensation theory (see Section 5.1), in this case, the vapor pressure saturation line of hydrogen, $\pi_{\text{H}_2}(T)$:

$$y_{\text{H}_2}(T)|_{eq} = \frac{\pi_{\text{H}_2}(T)}{\pi_{\text{He}}(T)} \quad T \leq 4.2\text{K} \quad (2)$$

On the other hand, at the very low concentration levels under discussion, solid hydrogen may dissolve in the liquid [12]. In that case, the molar fraction of solid H_2 dissolved in the liquid phase, $x_{\text{H}_2}(T)$, may be estimated from classical solubility theory.

Figure 3 shows the saturation molar fraction of H_2 in the vapor phase, $y_{\text{H}_2}(T)|_{eq}$, calculated using expression [Eq. (2)] in the interval 3–4.2 K (solid line). Similarly, the molar fraction of H_2 obtained from its theoretical limiting solubility in the liquid phase, $x_{\text{H}_2}(T)|_{eq}$, obtained from expression (1) in the work of Jewel and McClintock [12] (dashed line), is also shown. Both are very similar.

Thus, a well-defined lower limit for H_2 concentration as a function of temperature in helium vapor phase is obtained from the vapor pressure of solid hydrogen. Since solid hydrogen can be considered as a volatile solute (i.e., the solute vapor pressure is not negligible) for $T > 3$ K, there is a well-defined minimum solubility in the liquid phase for each temperature. This minimum solubility is also obtained from the vapor pressure. Furthermore, to know whether the actual value of the solubility of H_2 in the liquid phase is higher than the minimum value is not relevant because this already justifies the experimentally observed blockage times. In fact, if it is higher, it will just reduce the blockage time of the impedance.

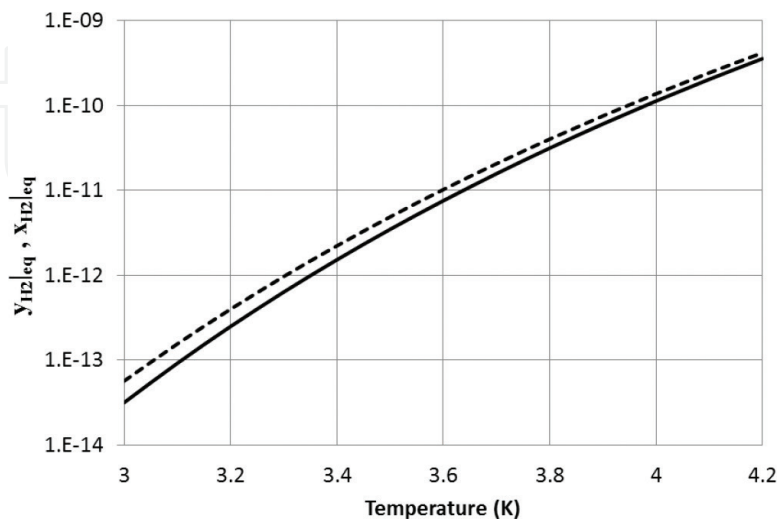


Figure 3. Low-temperature H_2 saturation molar fraction in helium, obtained from the limiting solubility of H_2 in He (dashed line, $x_{\text{H}_2}(T)|_{eq}$ [12]), and, from the H_2 equilibrium-saturation vapor pressure (solid line, $y_{\text{H}_2}(T)|_{eq}$ [19]), as a function of T in the range 3–4.2 K, at $\pi_{\text{He}}(T)$.

Thus, when the pumped helium stream expands and cools down inside the capillary impedance, from 4.2 to 3 K, the H_2 molar fraction in the two-phase liquid–vapor helium flowing through the impedance decreases by four orders of magnitude (from $\approx 10^{-10}$ to $\approx 10^{-14}$), and, consequently, the excess H_2 freezes or precipitates and blocks the capillary.

4. Sources of hydrogen in helium

Helium is a nonrenewable and scarce resource on Earth. It is formed by natural radioactive decay from some thorium and uranium minerals. Today, commercial helium is predominantly extracted from natural gas sources. Alternative sources of helium production have been investigated over the years such as the ability of extracting helium from non-hydrocarbon sources. In 2016, scientists from the United Kingdom reported the discovery of a large helium reserve, 54 BCN (1.53×10^{12} sL, i.e., 2.7×10^5 Tm) in Tanzania, trapped in ancient rocks and not intermixed with natural gas [20]. Additionally, the possibilities of helium extraction from the atmosphere [21] or from CO_2 stream [22] are being studied. Despite these future opportunities, helium is still a nonrenewable resource that must be used responsibly by mankind. This implies recycling helium when it is possible.

The present commercial helium production is extracted from a few natural gas fields around the world (located in Canada, the USA, Algeria, Poland, Qatar, China, Russia, Australia and Indonesia). These sources have a considerable amount of helium-rich gas (around 1%) to make extraction economically feasible.

Let us consider the Linde Group helium extraction facility in Darwin, Australia [23]. In this facility, the raw feed gas flow is 20,730 Nm^3/h with up to 3 mol% helium. The purification process of the feed gas consists of partial condensation of nitrogen in two stages, cryogenic adsorption and finally, catalytic oxidation of hydrogen followed by a dryer system.

After the purification, the refined helium is liquefied using a Bryton process and stored for further distribution. The raw gas has 0.1 mol% of hydrogen (1000 ppm), and the final processed 99.999% helium has up to 1 ppm.

Therefore, molecular H_2 is naturally present in helium gas as obtained from natural gas sources [24], and, in general, different methods are used to eliminate it, prior to large-scale helium liquefaction, for worldwide distribution [23, 25]. However, despite the effort to eliminate it completely, very precise analytical methods indicate that even ultra-high pure commercial grade He gas, 99.9999% pure, thus, containing less than 1000 ppb in volume of total impurities, may contain up to 500 ppb in volume of H_2 (i.e., a hydrogen molar fraction $y_{H_2} = 5 \cdot 10^{-7}$ in He gas) [21, 26–28].

If the purified helium gas has a molar fraction of $y_{H_2} = 500$ ppb ($5 \cdot 10^{-7}$), after the liquefaction of this gas, the liquid helium will contain solid hydrogen in equilibrium with a molar fraction of H_2 molecules given by $x_{H_2} = 0.35$ ppb ($3.5 \cdot 10^{-10}$) (i.e., corresponding to the vapor pressure of solid hydrogen in liquid helium under typical laboratory conditions [4.2 K and 100 kPa]), and, as we have seen in the previous section, this small amount of hydrogen may produce blockages in thin impedances in only a few hours.

Apart from natural gas sources, there are other possibilities to introduce small amounts of hydrogen in the helium recovery system. These include oil degradation in high-pressure compressors or pumps, outgassing of metallic pipes or diffusion of naturally present atmospheric H_2 [29] through plastic pipes and gas bags [30]. Thus, the presence of traces of H_2 in laboratory Helium Recovery Plants: Large Scale (LS-HRP) or Small Scale (SS-HRP), up to the ppm range ($y_{H_2} = 10^{-6}$), seems to be unavoidable.

5. Clean helium recovery plant

Up to this point, we have described the impedance blocking problem, and we have shown how a small amount of H_2 ($y_{H_2} < 10^{-10}$) is enough to produce the blocking of fine capillary tubes used to achieve temperatures below 4.2 K in helium-pumped cryostats. We have seen that hydrogen is naturally present in raw helium sources. Therefore, the production of hydrogen-free “Clean” helium is necessary to reliably operate cryostats with small impedances for long periods without interruptions. In the following paragraphs, we present a helium recovery plant capable of producing “Clean” helium.

We propose a helium purification and liquefaction system layout using small-scale helium liquefiers based on closed-cycle refrigerators (cryocoolers). The commercial Advanced technology liquefiers (ATLs) [31, 32] have a liquefaction rate of 30 L/Day with a performance of 0.16 (L/h)/kW, close to the performance of industrial size Collins liquefiers (0.5–1.2 (L/h)/kW) [33]. This technology adapts the liquefaction rate to the consumption, it is modular and scalable and it covers needs of consumption from a few liters per day up to liquefaction rates of the Collins industrial technology >240 L/Day.

The purification stage of the “Clean helium” recovery plant proposed is based on a combination of two purification techniques:

- the cryocondensation, performed with an advanced technology purifier (ATP) [34], for the elimination of all the impurities present in the recovered helium, except hydrogen and
- the chemisorption of hydrogen by a non-evaporable getter alloy.

5.1. Cryocondensation by advanced technology purifier

Purification by cryocondensation [35] is a method to separate undesired components (impurities) from a given mixture, by freezing them. The effectiveness of this method depends on the working temperature of the purifier; it must be low enough to ensure that the vapor pressure of the impurities is negligible. The cryocondensation method can provide high levels of purification at low temperatures, even at high-input gas flows and without the need of consumable items.

For this first stage, we use the advanced technology purifiers (ATPs) [34]. These purifiers are equipped with a 10 K class cryocooler (Sumitomo CH-208R) as the refrigerator element.

The gas input flows into the Dewar neck at room temperature, and it is cooled in direct contact with the cold head and the output heat exchanger while it descends through the neck down to the Dewar bottom.

When the gas reaches the condensation temperature for the component "j" (see **Figure 4**), at some point, near the cold head first stage, the component "j" will start to solidify by impingement on the metallic cold surfaces of the cold head cylinder and heat exchanger walls. Below the cold head, the gas temperature decreases further, and the molar fraction in the vapor phase of the component "j" will decrease rapidly with T, as $\pi_j(T)$:

$$y_j(T) = \frac{\pi_j(T)}{p_T}, \quad T \leq T_j \quad (3)$$

When a region of temperature of ≈ 15 K is reached, the helium can be considered pure from all impurities except for hydrogen and neon. At this point, the gas passes through a mechanical filter with a passage in the micron range, which will avoid the possible dragging of solid particle impurities toward the output.

After the filter, to be energy efficient, the clean and cold helium is forced to exchange the enthalpy from 15 to 300 K with the warm and dirty helium that enters the purifier. To do that, the helium output path consists of a heat exchanger in the form of a thin-walled stainless-steel tube coiled with the form of a solenoid around the cold head.

Thanks to the heat exchange, the cold outgoing gas cools the warm incoming gas, and therefore, the required power of the cold head is minimized. So, the system can manage high flows. In addition, the coldhead excess power during purification will counteract the growing inefficiencies caused by the solid impurities' coating around the cold surfaces.

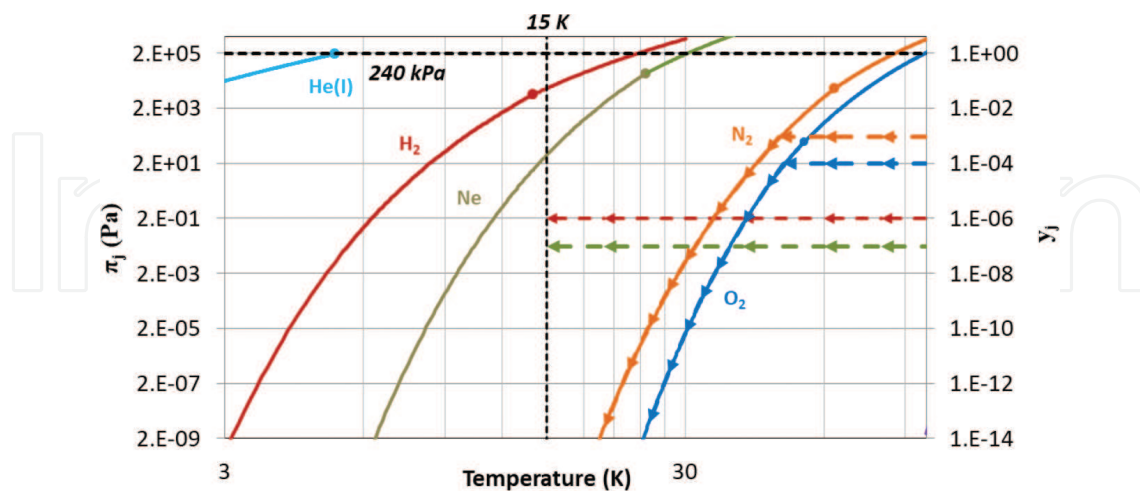


Figure 4. Partial pressures $\pi_j(T)$ and molar fractions $y_j(T)$ of H_2 , Ne , N_2 and O_2 in a gas mixture at 240 kPa [19]. The arrow lines indicate examples of impurities cooldown paths [e.g., initial impurities concentration in the mixture: H_2 (1 ppm), Ne (0.1 ppm), O_2 (100 ppm) and (N_2 1000 ppm)]. Starting from the high temperature side, the molar fraction of each impurity is constant until its vapor pressure line is reached, after which it decreases exponentially. Black dashed lines indicate the working point of the purifier filter, at 240 kPa and 15 K.

This system can purify gas flows up to 30 sL/min with 10,000 ppm of impurities. The output flow quality is about six orders of magnitude better for the main contaminants (i.e., air in the case of recovered helium).

The purifier can operate without interruptions during, at least, 1 month, and can purify more than 1 million sL of recovered helium (with a typical average impurity volume concentration of 300 ppms in total). The regeneration procedure is totally automated and it takes 7 h. Thus, the operational down-time ratio is only 1.25%.

Once the main contaminants have been removed, the second purification stage needs only to eliminate the remaining hydrogen via chemisorption by the non-evaporable getter (NEG) material.

5.2. Chemisorption by non-evaporable getter materials

Getters are solid materials, usually metallic alloys, which can chemisorb gas molecules in its surface; they can be considered as chemical pumps. They are widely used for a variety of applications such as vacuum systems, electronic devices, sensors and MEMS, energy devices, gas purification, and so on. [36]

For a proper absorption of gas molecules, the surface of the getter material must be clean. The surface cleaning process, also called getter activation, is done in two different ways, depending on the type of getter:

- For evaporable getters, the active surface is obtained by sublimation under vacuum of a fresh metallic film.
- For non-evaporable getters (NEGs), the active surface is produced by thermal diffusion of the surface contaminants into the bulk of the NEG material itself. After air exposure, the main contaminant is oxygen present in the passivating oxide layer.

For gas purification systems, NEGs are generally used, and from now on, we focus on them.

NEGs are typically based on zirconium alloys. Examples of these alloys are Zr(84%)-Al(16%) and Zr(70%)-V(24.6%)-Fe(5.4%). Zirconium-based systems are very reactive for a wide variety of gas molecules such as H_2 , H_2O , O_2 , N_2 , CO , CO_2 , and so on.

For active gases such as N_2 , O_2 , CO , CO_2 , and so on, the reactions proceed by dissociative chemisorption followed by a reaction to form oxides, carbides or nitrides [37]. If the concentration of these gases is high, the getter surface is quickly passivated. To maintain active state of the getter surface, the material can be maintained at high temperature (e.g., 400°C), thus avoiding the formation of a passivation layer. In this way, the surface contaminants diffuse into the bulk of the NEG material.

Hydrogen sorption is governed by a different reaction. Hydrogen easily diffuses into a getter because it dissociates on the getter surface into atomic hydrogen. The hydrogen atoms easily slip into the atomic lattice of the metal grains [37]. As Rameshan explains, hydrogen in the interior of a NEG forms a solid solution that exhibits an equilibrium pressure, which

depends on the concentration of the hydrogen and the temperature of the material. Sieverts' law describes this relationship:

$$\log P = A + 2 \log Q - B/T \quad (4)$$

where P is the H_2 equilibrium pressure in torr, Q is the H_2 concentration in the NEG alloy in torr·L/g, T is the temperature of the getter in K and A and B are constants for different NEG alloys (e.g., $A = 4.8$, $B = 6116$ for Zr(70%)-V(24.6%)-Fe(5.4%), commercialized under the name St707 [38]). When the hydrogen concentration exceeds 20 torr·L/g, a phenomenon called "hydrogen embrittlement" occurs due to the change of the lattice parameters [37]. With enough time under these conditions, the getter alloy becomes a fine powder that can cause problems in the getter application.

An NEG material working at ambient temperature is an ideal candidate for the elimination of the remaining molecular hydrogen in helium that has been purified by cryosorption in the ATP. **Figure 5** shows that the hydrogen concentration in helium after passing through the getter will be better than grade 14 ($y_{H_2} \ll 10^{-14}$), that is, several orders of magnitude lower than at 400°C. Even more, the hydrogen capacity of the getter is higher, and the sorption speed is still reasonably high [38].

5.3. Clean helium recovery plant configuration

Our "Clean helium" (extreme pure helium free of molecular H_2) low-pressure ($P < P_c$) SS-HRP concept is depicted in **Figure 6**. The plant is initially fed with commercial grade 5 (99.999% pure) helium gas that may contain up to a H_2 molar fraction of 10^{-6} [25]. The gas is further purified by cryocondensation by one or more cryo-refrigerator-based purifiers (ATPs), each with a total effective volume to store solid impurities of several liters and a maximum purification flow rate of around 30 sL/min at 20 K.

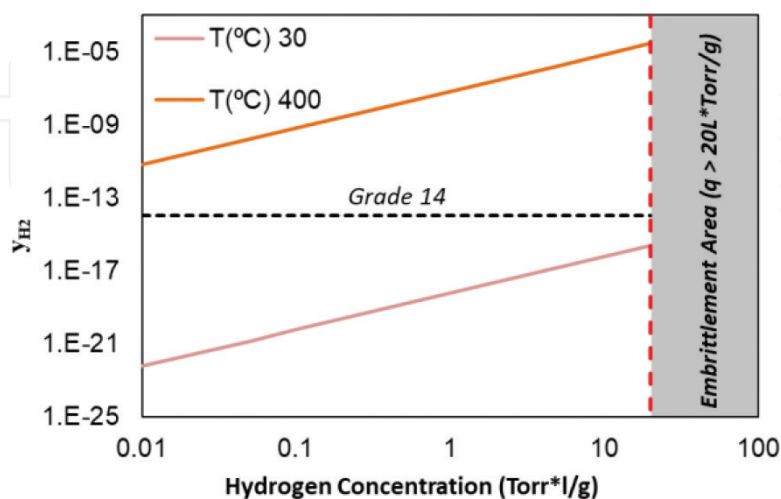


Figure 5. Hydrogen molar fraction, y_{H_2} , calculated from equilibrium isotherms of the St 707 getter alloy obtained from Sievert's law. y_{H_2} increases accordingly when the material captures hydrogen molecules until it reaches the embrittlement area.

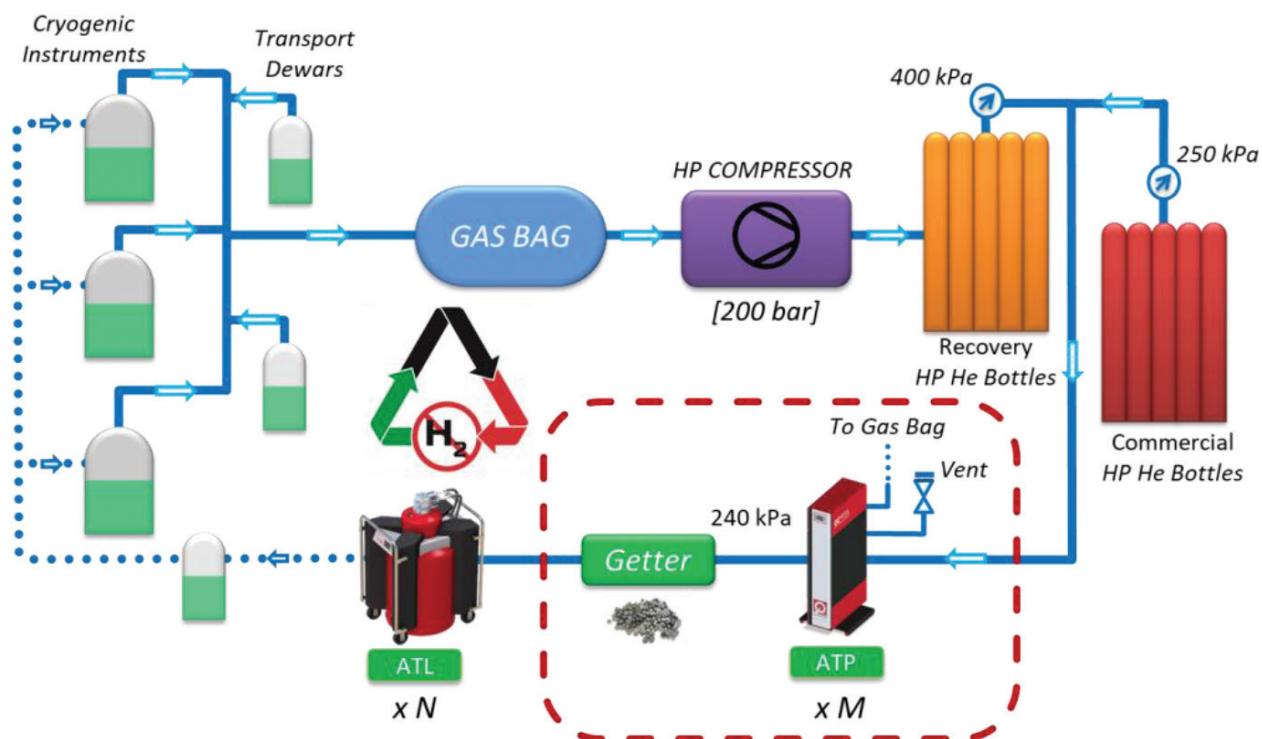


Figure 6. Schematic configuration of a small-scale “Clean Helium” recovery plant (free of hydrogen). Gas bag, compressor and recovery helium bottles are not completely free of H_2 (orange). The commercial He bottles are the main source of contamination (red). The bypass is closed when the ATP operation temperature is $T > 3$ K.

The purification temperature in the coldest zone of the ATP Dewar will be in the range between 10 and 30 K, and this does not guarantee a negligible vapor pressure of solid H_2 nor a negligible solubility in liquid He. Thus, the purified gas will contain H_2 molecules that need to be eliminated before liquefaction. A solution tested in our plant consists of the chemisorption of the remaining H_2 molecules in the ATP output gas by a getter material at room temperature (**Figure 6**). The non-evaporable getter (NEG) materials used in this study are:

- thermally activated media-based [Zr(70%)-V(24.6%)-Fe(5.4%)] St707 [38] and
- Ni(31%)-NiO(32%)-SiO₂(24%)-MgO(13%)-based oxides working at room temperature.

This solution is extremely efficient since there are no helium losses at all. On the other hand, in this configuration, the St707 getter only traps hydrogen, and it does in a reversible way. Therefore, once it is near saturation, typically, every two years, it can be regenerated by heating it up to a specific H_2 desorption temperature (typically $>500^\circ\text{C}$).

The H_2 -free He from the double purification stage (cryocondensation + chemisorption) is then fed a parallel network of advanced technology liquefiers (ATLs) [31] that produce H_2 -free ultra-pure liquid helium (named by us as “Clean Helium”). The instruments are always filled with ATL “Clean Liquid Helium.” Obviously, commercial liquid helium should never be transferred to hydrogen-sensitive instruments because the absence of H_2 is not guaranteed. In this small-scale HP-HRP, helium boil-off from the cryogenic instruments is collected in a gas

bag and compressed in the recovery bottles at 2×10^4 kPa (200 bar). A H₂O dryer, plumbed in the series after the compressor, not shown in the scheme of **Figure 6**, should always be used.

When a pressure drop develops between the input and the output of one of the ATPs, due to the accumulation of solid impurities (H₂, N₂, O₂), an ATP regeneration process is automatically initiated. The input and the output gas ports of the given ATP are closed, so that this ATP is now isolated and the entire ATP Dewar volume is heated up to around 130 K so that all the low-vapor pressure impurities, collected in solid form, for example, H₂, N₂ and O₂, are sublimated and released to the atmosphere through a vent valve. Before restarting a new purification cycle, the ATP cools down again to the temperature of normal operation at 10 K.

Nevertheless, as we have seen in Section 5.2, some getter materials are capable of eliminating other impurities besides hydrogen; the chemical reactions are competitive. Therefore, if the input gas contains other impurities (e.g., some ppms of O₂, N₂, H₂O, etc.), the getter duration until the saturation is reduced significantly.

In the first version of the "Clean Helium" plant, we used a getter placed after the commercial pure helium (99.999%, less than $y_j < 10^{-5}$ in total) bottles (**Figure 7**). With this configuration, we were able to produce hydrogen-free liquid helium in 3 months. From that moment, impedance blockages start to appear due to the saturation of the NEG produced by the presence of different impurities (N₂, O₂, CO, CO₂, etc).

The purified helium at the ATP output, with a working temperature < 20 K, has a negligible concentration of molecular content ($y_j < 10^{-14}$) of all impurity constituents (i.e., N₂, O₂, H₂O,

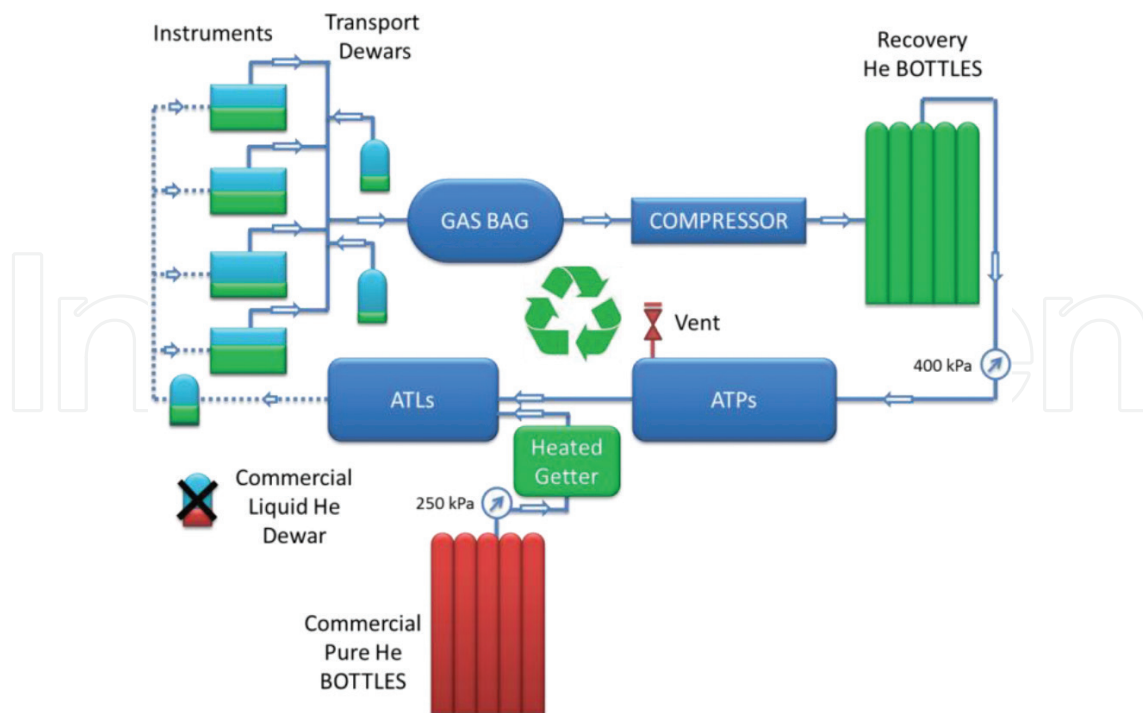


Figure 7. Schematic configuration of a first-generation small-scale helium recovery plant . The commercial He bottles are the main source of H₂ contamination (red), and it is purified with a heated getter before helium enters in the recovery plant.

CO₂, etc.) except for the neon and hydrogen case (see **Figure 4**). The neon is not a problematic substance for the impedance clogging issue, since at liquid helium temperature (4.2 K at P_{atm}), the vapor pressure is negligible; besides, if there exists a molecular concentration at higher temperatures, it is not affected by the getter material because it is a noble gas like helium. Therefore, the best place to put the hydrogen grabber is at the ATP output (**Figure 6**), when the helium is extremely pure. In fact $y_j < 10^{-14}$ for all the substances except for the H₂; thus, the unique function of the getter is to capture H₂. In this way, the process is optimized and the life of the getter material extends.

The “Clean helium” gas produced by the Clean Helium Recovery Plant (**Figure 6**) is ultimately liquefied in a commercial ATL and transferred directly or by intermediate transport Dewars into the application instruments. The evaporated gas from non-H₂ sensitive instruments, that could be initially filled with commercial non-“Clean” liquid (e.g., NMRs, MEGs, high field magnet cryostats, etc.), and can have a hydrogen quantity equal or below that corresponding to the vapor pressure of the hydrogen at 4.2 K and 100 kPa (i.e., $y_{H_2} = 3.5 \cdot 10^{-10}$), is also collected in the gas bag, compressed and injected again in the ATPs for purification and complete elimination of the H₂ impurities.

The validity of the “Clean helium” plant concept is demonstrated by the fact that impedance blockages have been completely eliminated for more than 3 years, when the plant configuration was implemented in the Cryogenic Liquids Service at the University of Zaragoza [39]. Furthermore, the efficiency of the double purification method presented in this chapter was verified by extra-sensitive H₂ detection techniques presented in [2], for both gas and liquid phases.

6. Conclusions

We have proposed a plausible mechanism for explaining the capillary blocking issue that occurs in many laboratories using helium evaporation cryostats. The unavoidable presence of traces of molecular hydrogen is at the heart of the problem. Molecular hydrogen condenses in the low-pressure side of the fine capillary tubes when helium is pumped to obtain temperatures below 4.2 K. Finally, we have found a solution to produce hydrogen-free liquid helium in two steps: (1) cryocondensation of the air components and (2) chemical adsorption of hydrogen molecular traces that are not solidified in step (1). We have already demonstrated the validity of this solution for more than 3 years.

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