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Helium contamination through polymeric walls

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Abstract

The concentration of impurities in helium gas is an important parameter for a recovery and liquefaction plant. A low level of impurities is necessary to maintain an optimum liquefaction rate in any kind of liquefier. The main origin of the impurities is the air contamination that enters into the helium mainstream at some point in the recovery cycle. In this work we have: i) identified the main sources for impurities in an experimental helium recovery plant, ii) quantified the contamination rate and iii) proposed a mitigation strategy. An analysis of the He impurities composition reveals a nitrogen/oxygen ratio different to the one existing in air. This observation is in accordance with the permeability values for nitrogen and oxygen through the polymer materials used in the plant. Experimental on line measurements for oxygen content in the He mainstream with sensitivity below 1 ppm, have been performed after recirculation through metal and polymeric pipelines, respectively, to validate our hypothesis. In addition, the dependence of the impurities concentration with the He retention time in the recovery gas bag has been evaluated. Finally some operational recommendations are given for practical applications.

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1. Introduction

During the last years, the low temperature community has suffered periods in which it has been difficult to get liquid helium from commercial suppliers. Indeed the worldwide supply of helium cannot be guaranteed because it is a scarce and fossil element with a small amount of sources around the planet [1]. Thus, liquefaction and reutilization of the helium once it evaporates emerge as one of the most adequate strategies for laboratory or industrial applications.

A typical configuration for a helium recovery plant is shown in Fig. 1. An undetermined number of cryostats and transport dewars are connected to the metallic pipes of the recovery line that could be extended over several labs located on different buildings. The evaporated helium flows through the recovery line into the gas bag that acts as a temporary storage buffer. The compressor enables the He pumping and storage on the gas cylinders at high pressure ($2 \cdot 10^7$ Pa). One of the main problems deals with the potential contamination of recovered He by other permanent gases existing in the atmosphere (namely nitrogen, oxygen,

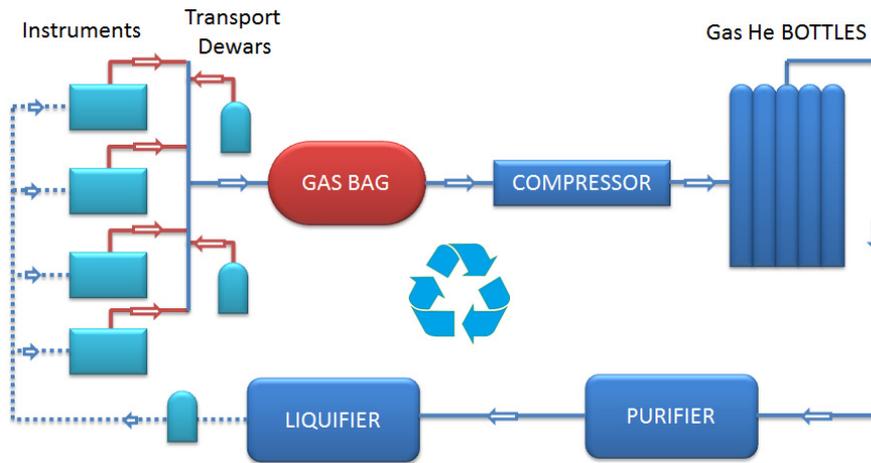


Fig. 1. Scheme of a general liquefaction-recovery helium plant. Blue lines: metallic pipes, blue dashed line: Liquid helium transfer, red line: helium gas connection pipes to recovery line, material in study at this report. Main elements: Transport dewars or instrument cryostats, gas bag, a compressor, high pressure storage bottles, a system to purify and a system to liquefy the helium.

water, or carbon dioxide) due to the permeability properties of the pipelines. Consequently, a purification step is mandatory due to the fact that He purity is the determining performance factor for any liquefier. In medium-pressure recovery systems without gas bag and with only metallic pipework, the total content of impurities can be lowered to tens of ppm. In those cases the helium gas can be cleansed by liquid nitrogen traps or heated getter systems [2]. In high-pressure recovery systems, with a compressor and gas bag, a more powerful purification step is needed. In fact, large-scale Collins liquefiers have internal purifiers; whereas small scale liquefiers based on cryocoolers require external counterparts [3].

The case of the liquefaction-recovery plant of Universidad de Zaragoza analysed in this work has a 487 STPm^3 of total helium capacity, the gas bag has a volume of 10 m^3 , the compressor has a pumpability of $5.56 \cdot 10^{-3} \text{ STPm}^3 \text{ s}^{-1}$ at $1.5 \cdot 10^7$ Pa, the storage cylinders have a volume of 1.6 m^3 , the purifier is an ATP30, and the liquefiers are 2 ATLs [4].

The amount of impurities that enter into the helium recovery circuit has to be controlled and maintain at the minimum level, to ensure the liquefaction rate. Otherwise, the purifier will be rapidly saturated. The gas permeation through polymeric membranes is identified as the main source of He contamination in a recovery plant. The major contamination focus is the gas bag used as storage flexible tank with tunable capacity (i.e. up to several cubic meters). Less notorious is the contribution of the polymeric tubes used for the connection of the instruments or

transport dewars to the metallic recovery line. Due to the harmful effects on vacuum technology, previous studies have been devoted to the study of gas permeation through different materials [5], [6].

2. Experimental measurements

2.1. First considerations

We have measured the purity of the helium in our recovery plant when it arrives to the storage bottles using a gas chromatography instrument from GOW-MAC, Model 295R DID. The result shows that the helium in the storage bottles is typically 99.92 % pure, and the main impurities are in fact nitrogen and oxygen from the atmosphere. The impurities composition is 63.01 % nitrogen, 36.95 % oxygen and 0.05 % carbon dioxide. As it was expected, the $N_2:O_2$ molar ratio notably differs from the air value, 1.7 versus 3.7. This observation agrees with the differences in permeation behavior of nitrogen and oxygen through polymers [7].

The mechanism of gas permeation through polymeric films could be described by the solution-diffusion model, in which permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient. The permeants are separated because of the differences in the solubilities of the materials in the membrane and the differences in the rates at which the materials diffuse through the membrane. Accordingly, the permeation flow rate of component i , F_i , through the membrane (expressed in $STPm^3 \cdot s^{-1}$) can be calculated as follows [8]:

$$F = K \frac{A \cdot \Delta P}{d} \quad (1)$$

Where K is the membrane permeability, and is a measure of the membrane's ability to permeate gas, A is the permeation area (expressed in m^2), d is the membrane thickness (expressed in m) and ΔP is the driving force for component i permeation (expressed in hPa). The membrane permeability can be written as:

$$K = D \cdot S \quad (2)$$

Where D is the concentration-independent, diffusion coefficient (expressed in m^2/s) which reflects the mobility of the individual molecules in the membrane material and S is the gas sorption coefficient (expressed in $STPm^{-3} \cdot hPa^{-1}$) which reflects the number of molecules dissolved in the membrane material.

This work is mostly focused on the analysis of the O_2 concentration in the helium mainstream. The N_2 concentration from the results above is assumed to be 1.7 folds the encountered O_2 values. The concentration of other impurities is practically negligible. Continuous oxygen monitoring is carried out by means of a Zirconia based sensor (SERVOMEX: Servopro Multiexact) that operates with 0.4 slpm as flow rate with a detection limit below 1 ppm.

Our simple model for the study of oxygen contamination in the He recovery plant is depicted in Fig. 2. As it can be observed, a pure He stream is pumped via stainless-steel and polymeric pipelines and the O_2 concentration is continuously measured downstream.

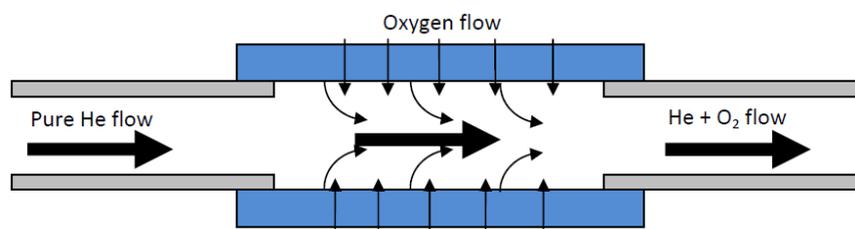


Fig. 2. Schematic representation of how the oxygen contamination enters the helium flow. Gray parts: metallic pipe, blue parts: polymeric pipe. The atmosphere is the source of the oxygen flow

These, experimental values are correlated with the permeation flow of oxygen through the polymeric wall, F_{O_2} , and the total helium flow in the main stream, F_{He} according to the equation (3) in which we assume that $F_{O_2} \ll F_{He}$

$$ppm[O_2] = \frac{F_{O_2}}{F_{He}} \cdot 10^6 \quad (3)$$

2.2. Polymeric pipelines characterization

Usually, the connection of instruments and dewars to the recovery line is made via inexpensive and easy to handle polymeric tubing. In this work, silicone and natural rubber based pipelines have been studied due to they are among the most commonly used.

For the experiments, a bundle of bottles containing high purity helium (99.999%) have been connected to a forward pressure controller to ensure 1448 mbar as absolute pressure upstream. Different pipelines, varying length, diameter and wall thickness and polymer nature have been tested at helium flow rate of 0.4 slpm; a typical value for the evaporation rate in a transport Dewar. Table 1 shows the so obtained permeability values where literature data for similar polymers have been also included for comparison purposes. The results reveal a reasonable agreement between our experimental permeability data and those already published. This observation underlines the goodness of our hypothesis about helium contamination sources.

As it can be observed, natural rubber and polyurethane based polymer tubes are the most adequate among the tested to reduce the O_2 impurities content, but the polyurethane, due to its stiffness, is inadequate for an easy connection. It is worthwhile to mention the relative high stabilization periods to attain stationary values for the oxygen concentration in the He main stream, up to 18 hours for natural rubber 6 mm thick. A possible explanation relies on the pipelines storage conditions rendering to O_2 saturation levels of the polymers corresponding to equilibrium at atmospheric conditions. In fact, additional experiments to study the oxygen contamination dependence with the helium flow were performed (see Fig. 3) with a silicone pipeline (2 m length, 3 mm thick and 16 mm as internal diameter). As it was expected, the stabilization period decreases monotonically with the He flow rate due to the sweep effect on the adsorbed species on the internal polymeric walls. From the linear fitting and equation 3, an average O_2 permeation flow rate through the silicone membrane 3 mm thick of $1.53 \cdot 10^{-9}$ STPm³s⁻¹, has been obtained. Similarly, the experimental O_2 permeability value is $215 \cdot 10^{-15}$ (STPm³ms⁻¹m⁻² hPa⁻¹) in reasonable agreement with published data ($76\text{-}460 \cdot 10^{-15}$ (STPm³ms⁻¹m⁻² hPa⁻¹) reported in [10], $375 \cdot 10^{-15}$ (STPm³ms⁻¹m⁻² hPa⁻¹) reported in [7].

Table 1. O_2 concentration measurements in the helium mainstream due to air permeation through the connection pipes to recovery line at room temperature. Obtained permeability values literature data (*Sources are:[7], [9]).

Material	Dimensions [Length (m); Diameter (mm); Thickness (mm)]	Steady State O_2 concentration (ppm)	Permeability K (10^{-15} STPm ³ ms ⁻¹ m ⁻² hPa ⁻¹)	Average Permeability K (10^{-15} STPm ³ ms ⁻¹ m ⁻² hPa ⁻¹)	Literature Permeability K (10^{-15} STPm ³ ms ⁻¹ m ⁻² hPa ⁻¹)*
Silicone Rubber	[0.5; 16; 3]	62.5	234.4	240.2 ± 6.6	375
Silicone Rubber	[2; 16; 3]	266	249.4		
Silicone Rubber	[5; 16; 3]	631	236.7		
Natural Rubber	[2; 22; 6]	2.13	2.90	2.5 ± 0.4	17.2
Natural Rubber	[4; 22; 6]	3.07	2.09		
Polyurethane	[2.6; 8; 1]	1.07	0.51	0.51	25.1
Stainless Steel Flexible	[2; 28; 1]	0.5	-		

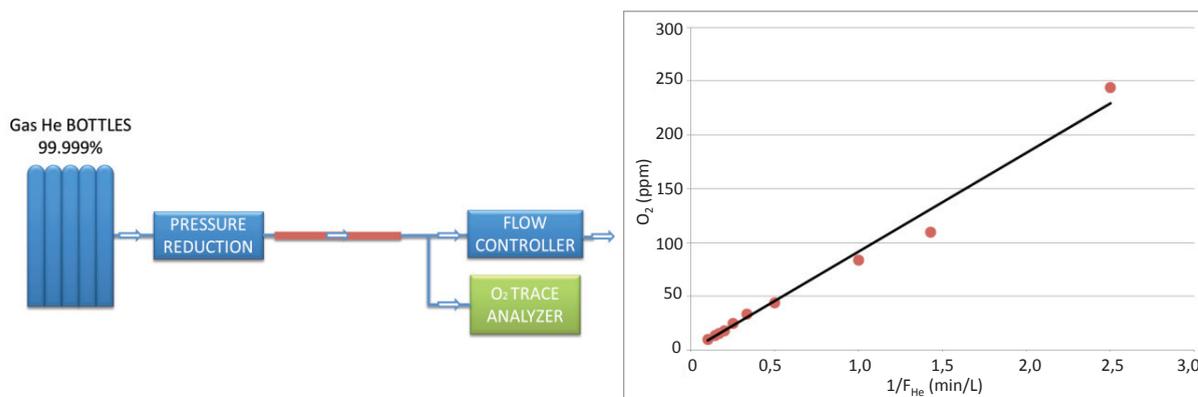


Fig. 3. Evaluation of O₂ contamination due to polymeric pipelines as a function of the helium flow rate: left) experimental set-up; right) experimental results.

Moreover, to validate the O₂ contamination source, a blank experiment was also performed with stainless steel pipelines (see table 1). In this particular case, the registered O₂ concentration values were always below the detection limit of the SERVOMEX. Accordingly, stainless steel non porous flexible tubing seems the most adequate to avoid He contamination in the recovery line at the expense of higher unitary cost compared to polymeric counterparts.

2.3. Gas bag characterization.

The gas bag in our recovery system is fabricated in J-22 material, a modified vinyl based polymer, including up to 3% wt. polyvinylidene chloride, and polymeric non-migrating plasticizers (<http://www.flexi-liner.com/SpecsheetJ22.pdf>). According to the supplier specifications, the He permeability in J-22 is $644,7 \cdot 10^{-15}$ (STPm³ms⁻¹m⁻²hPa⁻¹) at 340 K. Thus, the estimated He flow rate permeating through J-22 is $7.83 \cdot 10^{-6}$ (STPm³s⁻¹), circa 250 (STPm³) of He losses per year.

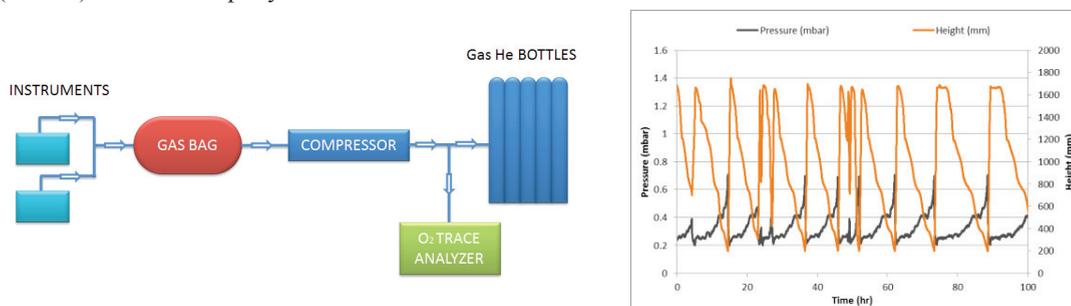


Fig. 4. Evaluation of O₂ contamination due to the gas bag during filling-evacuation cycles: left) experimental configuration note that the instruments are connected to the recovery line using metallic pipes; right) overpressure (black line) and height (red line) of the gas bag with time on stream, note that the compressor turns on for He pumping to the gas cylinders at 1700 mm and 0.75 mbarg as height of the bag and gas overpressure, respectively.

The experimental set up used to evaluate He contamination in the gas bag is shown in Fig. 4. The parameter used to control the process of bag filling is the height of the bag. For such purposes, a non-contact ultrasonic distance measurement sensor is deployed. The high-pressure compressor ($2 \cdot 10^7$ Pa) and the O₂ analyzer turn on simultaneously when the height of the bag reaches the upper limit (1700mm) (Fig. 4 right) In this work, several experimental conditions have been tested to simulate different He recovery rates. Fig. 5 shows the oxygen concentration values as a function of He flow rate from the instruments; that means, as a function of He retention time in the gas bag. The obtained data follow the expected linear trend from equation (3), with an average O₂ flow

rate permeating through J-22 of $2.38 \cdot 10^{-8}$ (STPm³s⁻¹). This constant source of He contamination by O₂ depends on the gas bag material, dimensions (total area and thickness) and pressure driving force. Therefore, the proper design for a recovery plant implies a gas storage buffer with minimum dimensions but large enough to handle with the high flow rate occurring during helium transfers.

From the average O₂ flow rate, F_{O₂}, and using equation (1), an O₂ permeability in J-22 material of $9.20 \cdot 10^{-15}$ (STPm³ms⁻¹m⁻² hPa⁻¹) has been estimated, rather similar to the evaluated for natural rubber (see table 1).

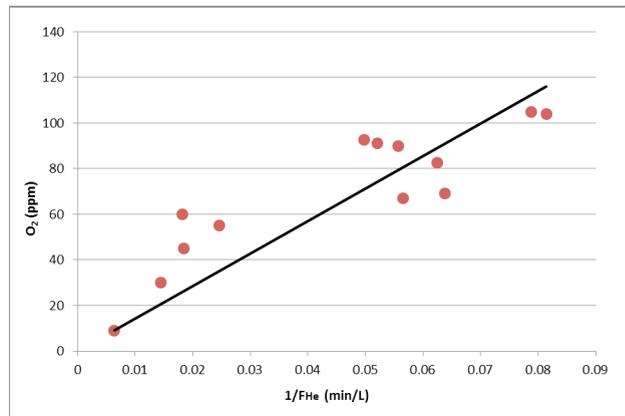


Fig. 5. Evaluation of O₂ contamination due to storage in the gas J-22 bag as a function of retention time.

3. Conclusions

The gas permeation through polymeric walls is the main source for contamination in a helium recovery plant. Firstly, the gas bag, used as temporary storage buffer, plays a critical role in the high-pressure recovery system. This work demonstrates that its design (size and material) is controlling the purity of the recovered helium. Thus, the size should be the lowest as possible, once the plant requirements are fulfilled, to minimize the exposed area for air permeation. Secondly, the air permeation through polymeric pipelines used as connectors between dewars/instruments and the recovery line is also responsible for He contamination by O₂. Among the polymer type tubing tested, natural rubber provides the best results, but still is insufficient to preserve He purity. On the other hand, stainless-steel flexible tubing is the most adequate to avoid contamination in the recovery circuit at the expense of higher cost.

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