

# Performance Of Adsorber At Different Operating Conditions At Low Temperature

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**Abstract:** To produce LHe, there must be used the pure helium. So, to produce that purity the helium separation & purification system can be used. As a rule, the partition of gases at cryogenic temperatures is the most efficient separation system for all; hence, industrially gas separation frameworks have been all around grown over the past half-century. An adsorbent material must have a high internal volume which is accessible to the constituents being removed from the fluid. The adsorbent must also have good mechanical properties such as strength and resistance to attrition and it must have good kinetic properties, that is, it must be capable of transferring adsorbing particles quickly to the adsorption sites. Activated carbon is widely used in industrial applications which include decolorizing sugar solutions, gas purification and water treatment. The aim of this paper is to study the different research article on charcoal particles and its performance effect with the temperature in different condition.

**Keywords – Helium Purification system, adsorption system, 80 K Purification**

## 1. Introduction

The Helium Refrigerator/Liquefier (HRL) is normally operated with helium gas having purity better than 99.999 % by volume which is equivalent to having 10 PPM (parts per million) impure gas in the helium gas. Although sufficient precautions and impurity removal procedures are used, still, in the process of gas transfer or due to some other processes before reaching to liquefaction, impurity level sometimes can go as high as 100 PPM. These impurities consist of mainly gases present in the air, like N<sub>2</sub>, O<sub>2</sub>, Ar, H<sub>2</sub>O, CO, CO<sub>2</sub>, H<sub>2</sub> and traces of Ne. These gases condense at significantly higher temperature compared to the LHe temperature (4.5 K). If such high level of impurity enters the process equipment placed inside the cold box of the HRL, then it can condense and choke the pipe lines and valves leading to large pressure drop and inefficient liquefaction process. Some time, condensed and frozen impurity can destroy the blades of turbines of HRL. Hence, to be on safer side generally, internal purifiers are placed at two temperature levels inside the cold box to take care the operational problem due to impurities. One is at ~80 K to remove nitrogen, oxygen and other gases having normal boiling points above 77 K. Another one is at ~20 K to remove hydrogen and neon gases.

To produce LHe, there should be used the pure helium. So, to produce that purity the helium purification system is used. Helium purification system normally consists of heat exchangers and adsorber bed which is followed by filter. Here, filter is used to filter the gas, to remove adsorbent particles which might be come with the flow of the gas. As the helium gas passes through the heat exchanger where LN<sub>2</sub> is used to bring helium temperature down to ~80K. Thereafter the helium gas enters the adsorber (carbon) bed where the impurities like N<sub>2</sub>, O<sub>2</sub> and Ar are removed / adsorbed. A schematic of the mentioned process is shown in figure 1.1.

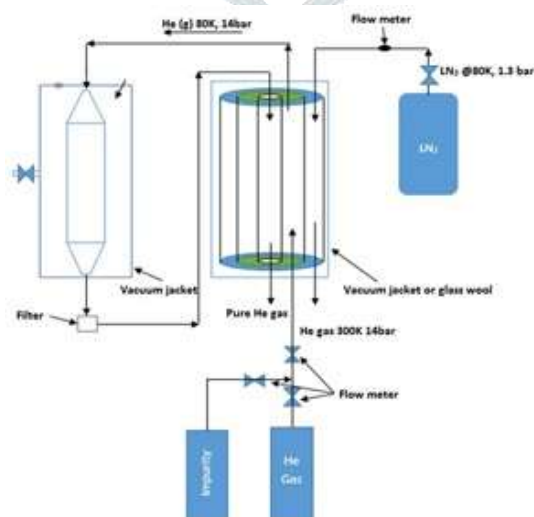


Figure 1.1 - Schematic of He Purification System

2. Literature Review

**Nitrogen Adsorption Isotherms for Zeolite and Activated Carbon** [1] by L.C. Yang, T.D. Vo, and H.H. Burris, cryogenics 1982

To select an appropriate adsorbent for nitrogen among zeolite and activated carbon an experiment was performed by L.C. Yang, T.D. Vo, and H.H. Burris to obtain the isotherms for two adsorbents.

The results are shown in fig. 2.1 and 2.2 for the Molecular sieves 13X and granular GI grade activated carbon, expressed in mass of nitrogen gas adsorbed per unit mass of adsorbent,  $\Delta m/M$ , i.e. the mass fraction, as a function of gas pressure. The series of curves have the shape of Type I adsorption isotherms described in literature. These runs showed charcoal to be 10 times more effective as an adsorbent for neon than molecular sieve and 70 times better than silica gel.

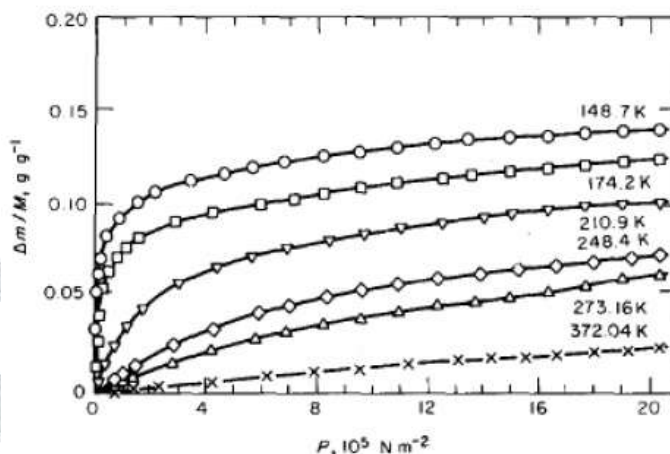


Figure 2.1 - Nitrogen adsorption isotherms in Molecular sieves 13X [1]

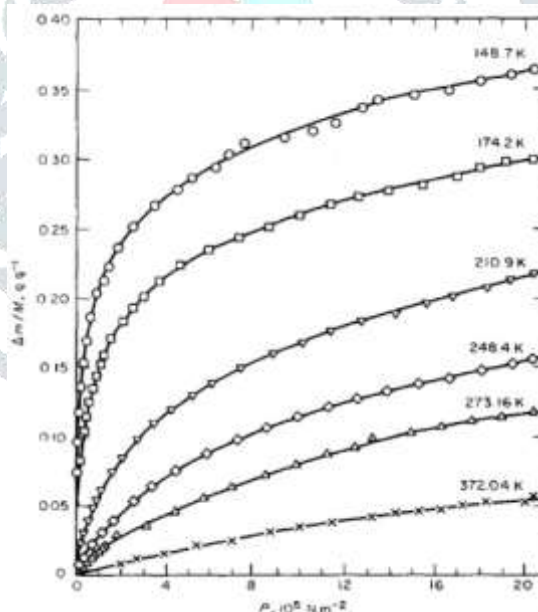


Figure 2.2 Nitrogen adsorption isotherms in granular GI grade activated carbon [1]

Table 2.1 Comparison between charcoal and zeolite [1]

N <sub>2</sub> (78.5 K)			
Charcoal		Zeolite	
Pressure (mm Hg)	Volume, cm <sup>3</sup> STP/g	Pressure (mm Hg)	Volume, cm <sup>3</sup> STP/g
0.187	116	0.200	108.1
0.210	123.8	0.870	124.3
0.340	145.6	3.190	131.3
1.730	175.5	3.300	130.5
8.030	195.6	8.440	134.4
22.5	214.8	22.3	137.3
42.3	224.1	41.5	139.9

**Porosity, Surface Area, Surface Energy, and Hydrogen Adsorption in Nanostructured Carbons**<sup>[2]</sup> by Alejandro Anson, Jacek Jagiello, Jose B. Parra, M. Luisa Sanjuan, Ana M. Benito, Wolfgang K. Maser, and M. Teresa Martinez, *J. Phys. Chem. B* 2004, 108, 15820-15826.

Hydrogen adsorption isotherms at 77, 87, and 298 K have been measured on three samples of single-wall carbon nanotubes. The highest adsorption capacity (1.58 wt. % at 77 K, 1.15 wt. % at 87 K, and 0.02 wt. % at 298 K) at atmospheric pressure has been observed in a chemically activated sample (activated with KOH), which has hybrid porosity between a carbon nanotube material and a microporous activated carbon. According to CO<sub>2</sub> adsorption at 273 K and density functional theory pore size distributions from N<sub>2</sub> adsorption, it is deduced that pores up to approximately 0.5-0.7 nm can adsorb hydrogen at ambient conditions. Isothermic heat of hydrogen adsorption has been calculated for the three samples, having initial values around 7-7.5 kJmol<sup>-1</sup>. It is concluded that the hydrogen adsorption capacity of carbon nanotubes depends both on the extent of their surface area and on the adsorption energy of the surface sites.

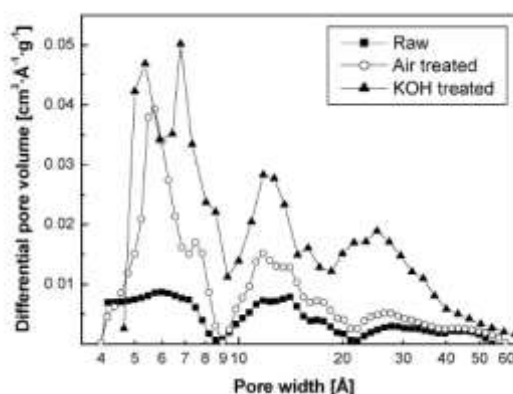


Figure 2.3 DFT pore size distributions from the N<sub>2</sub> isotherms at 77 K. [2]

The calculated pore size distributions (Figure 2.4) allow explanation of adsorption isotherms in relation to pore sizes taking into account that narrow pores represent the high energy adsorption sites that can adsorb gas molecules at very low equilibrium pressures. The distribution for the KOH-treated sample crosses that for the air-treated sample at about 0.5 nm. According to this calculation, the air-treated sample has more pores smaller than 0.5 nm width than the KOH-treated sample, although this sample has much higher total micropore volume. The raw sample has also smaller micropores (less than 0.5 nm) than the KOH-treated sample and possibly smaller micropores (less than 0.45 nm) than the air-treated sample. The DFT shows shift of the average micropore diameter toward larger values with the KOH activation.

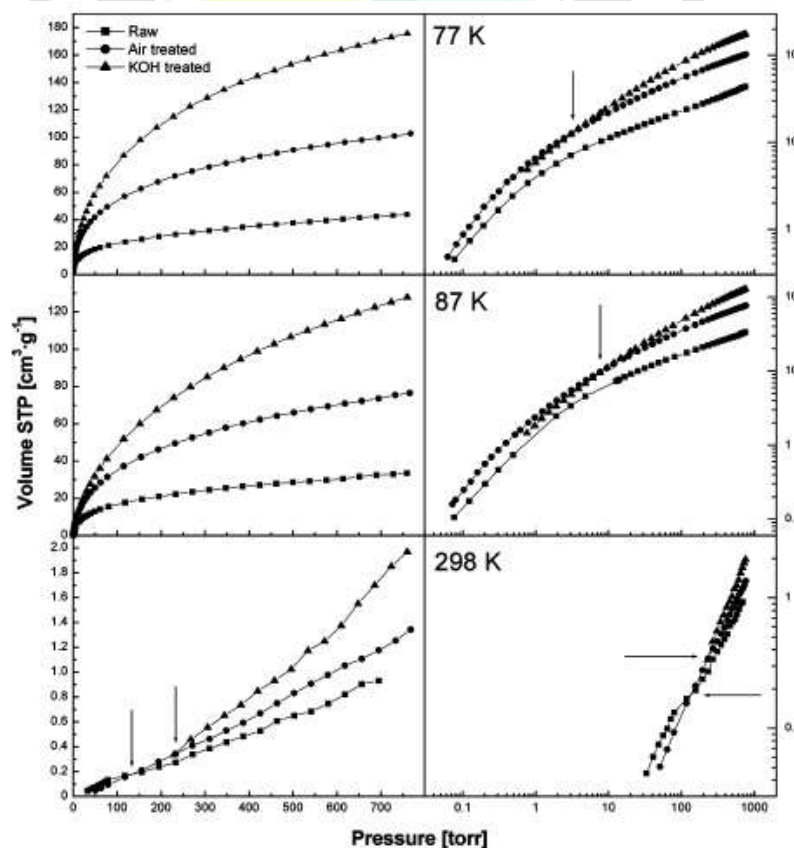


Figure 2.4 - Experimental adsorption isotherms of hydrogen on raw, air-treated, and KOH-treated samples at 77, 87 & 298 K [2]

Isotherms are plotted in linear scale (left) and double-logarithmic scale (right) in order to show clearly the whole range of the measurements. Lines between experimental points are drawn to guide the eye. Arrows point to sites where the isotherms cross. Figure 2.4 is a comparison of the hydrogen isotherms obtained for the three samples at the same temperatures. The KOH treated sample adsorbs more H<sub>2</sub> than the air-treated sample, and this one adsorbs more than the raw sample. However, when the isotherms are plotted in a double-logarithmic scale, the low-pressure region is magnified and the relative positions of the isotherms vary. At about 2-3 Torr, the isotherm for the KOH treated sample crosses that for the air-treated sample. This sample adsorbs more H<sub>2</sub> than the others at pressures less than 2-3 Torr. For N<sub>2</sub> adsorption at 77 K, the crossing occurs at absolute pressures much lower than in the case of H<sub>2</sub> at 77 K. The crossing between the isotherms for the KOH-treated sample and the air-treated sample can be interpreted as pressure points in which the adsorption potential is equal for both samples. This has also an interpretation according to the pore size distributions shown in Figure 2.3, where the KOH-treated line crosses the air-treated line at about 0.5 nm: pores of about 0.5 nm width start adsorbing hydrogen at 77 K at a minimum pressure of approximately 2-3 Torr.

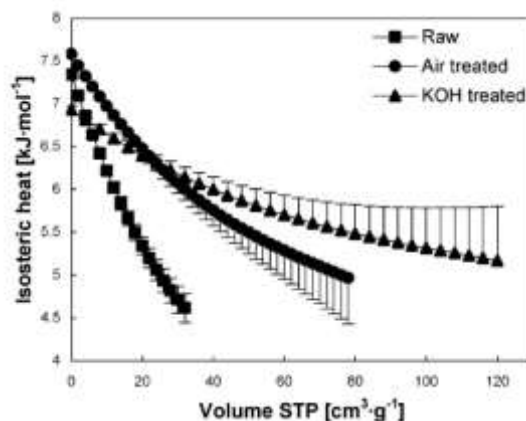


Figure 2.5 - Variation of the hydrogen isosteric heat of adsorption with the coverage for the raw, air-treated, and KOH-treated samples [2]

The air-treated sample has the highest initial isosteric heat of hydrogen adsorption (7.58 kJ mol<sup>-1</sup>), while the KOH treated sample has the lowest (6.93 kJ mol<sup>-1</sup>). The raw sample has an intermediate value (7.34 kJ mol<sup>-1</sup>) Nevertheless, at higher coverages the KOH-treated sample has the highest values of heat of adsorption. The crossing tendencies in the heat of adsorption for the samples are related to a change in the energy site distribution, that is, a change in the pore size distribution, as discussed above.

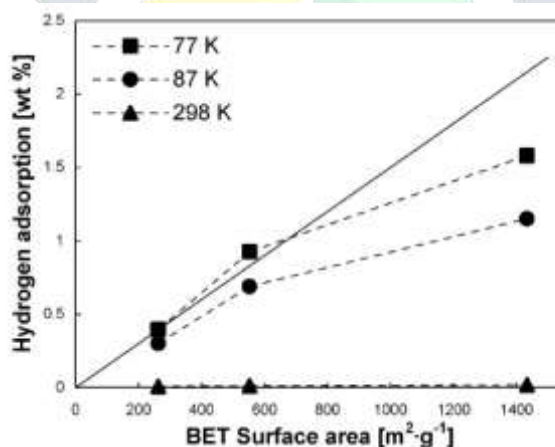


Figure 2.6 Comparison between the BET surface area and the hydrogen adsorption at 77, 87, and 298 K and nearly atmospheric pressure for the raw (262 m<sup>2</sup> g<sup>-1</sup>), air-treated (552 m<sup>2</sup> g<sup>-1</sup>), and KOH treated (1433 m<sup>2</sup> g<sup>-1</sup>) samples [2]

[The solid line represents an empirical relation obtained from electrochemical adsorption of hydrogen on many carbon samples.]

The KOH-treated sample has less high energy sites than the other two samples. KOH-treated sample has the highest surface area (S BET) (1433 m<sup>2</sup> g<sup>-1</sup>) and adsorbs 1.58 wt. % H<sub>2</sub> at 77K and 760 Torr. This is much more than the amount adsorbed by the raw sample at the same conditions.

**Engineering studies related to fixed bed adsorber and its application for fission gas adsorption at cryogenics temperature** [3] by Puwar Dhairyapalsinh, Prabhat Kumar, V.A.Subramani, B.Muralidharan and Bharti V.Dave, Indian Journal of cryogenics Vol 35A,2010

A comprehensive approach to deal with adsorption is described here. Both fundamental scientific as well as applied engineering approaches are needed for ensuring high performing fixed bed adsorber design. Mechanism of adsorption along with faster and more accurate design and simulation of adsorption processes is nowadays possible so it can be exploited for effective

utilization. With use of adsorption, many separations can be done which are impossible or impractical with other conventional methods such as distillation or absorption.

**Breakthrough studies of activated carbon and oxyisieve for helium purification at 77K** [4] by Nisith K. Das, Pradeep Kumar, Amitavasur, Rakesh K. Bhandari Indian Journal of cryogenics Vol. 35. No.1-4,2010.

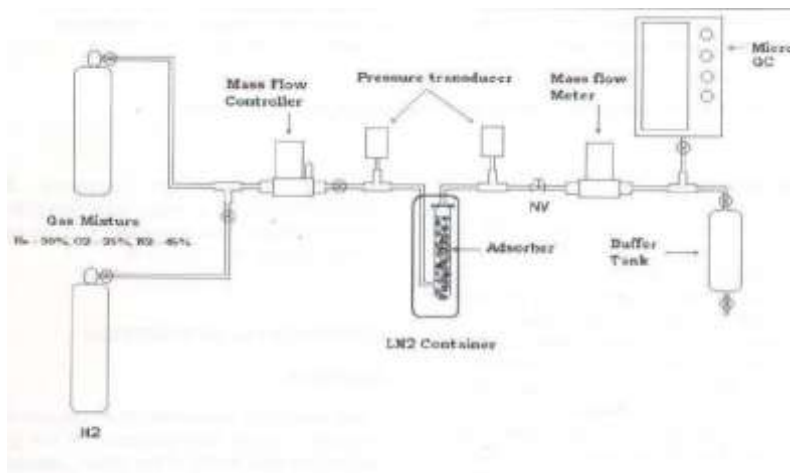


Figure 2.7 - Experimental Setup [4]

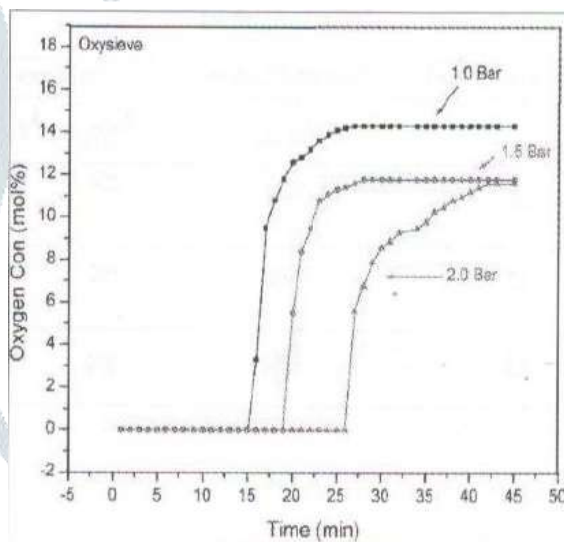


Figure 2.8 - The Breakthrough curves for oxygen [4]

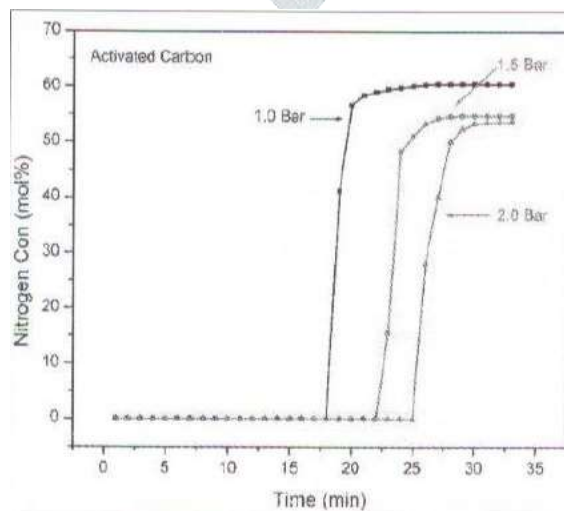


Figure 2.9 - Breakthrough curves for nitrogen, activated carbon as adsorbent [4]

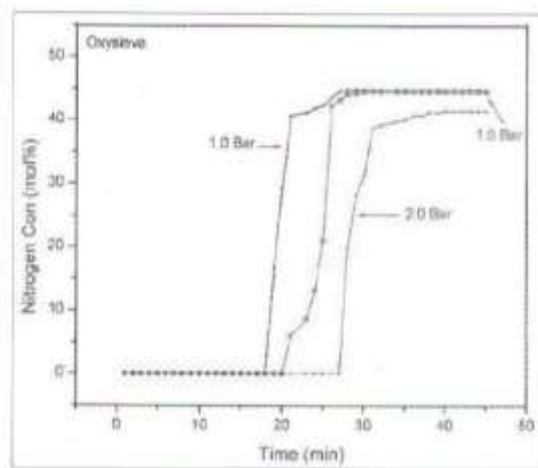


Figure 2.10 - Breakthrough curves for nitrogen, oxysieve as adsorbent [4]

The Breakthrough curves for oxygen are presented in fig 2.7, for oxysieve as adsorbent. Breakthrough curves for nitrogen are presented in figure 2.8 and figure 2.9, where activated carbon and oxysieve were used as adsorbent respectively. Fig 2.7 reveals that breakthrough curve for O<sub>2</sub> was obtained after a time lapse of 15 minutes at adsorption pressure of 1.0 bar with oxysieve as adsorbent. Furthermore, breakthrough for N<sub>2</sub> was appeared after a time interval of 18 minutes as shown in figure 2.9. All these imply that N<sub>2</sub> and O<sub>2</sub> at an appropriate adsorption step out of an oxysieve adsorption column. However, figure 2.8 reveals that breakthrough curve for N<sub>2</sub> was obtained after a time interval of 18 minutes at adsorption pressure of 1.0 bar with activated carbon as adsorbent. Therefore, high concentration of helium can be derived by cryoadsorption ahead of the breakthrough times for N<sub>2</sub> and O<sub>2</sub>.

**Low Temperature Adsorption Versus Pore Size in Activated Carbons** [5] by D. Martins, I. Catarino, D. Lopes, I. Esteves, J.P. Mota, G. Bonafait, “Low Temperature Adsorption Versus Pore Size in Activated Carbons”, Cryocoolers 16, 2011.

To select an appropriate adsorbent for nitrogen among activated carbons experimental analysis was done by D. Martins, I. Catarino, D. Lopes, I. Esteves, J.P. Mota, G. Bonffait to obtain the adsorption isotherms, data for heat of adsorption at 77K.

Three samples of charcoals were studied; their description is shown in Table 2.2: sample A is a machinable monolith while samples B and C are granules and pellets, respectively. Characterization analysis of the apparent surface area was performed using the Brunauer - Emmett-Teller (BET) equation and nitrogen isothermal data at 77 K obtained using a commercial Coulter Omnisorb 610R instrumentation.

Table 2.2 - Description of the three-charcoal studied [5]

Sample A	monolith, compacted carbon fibers based
Sample B	granular carbon, coconut shell based
Sample C	extruded pellets (2 mm), coal based

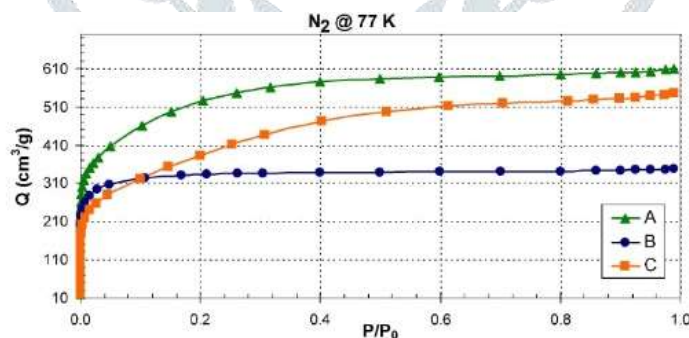


Figure.2.11 - Nitrogen isotherms at 77K [5]

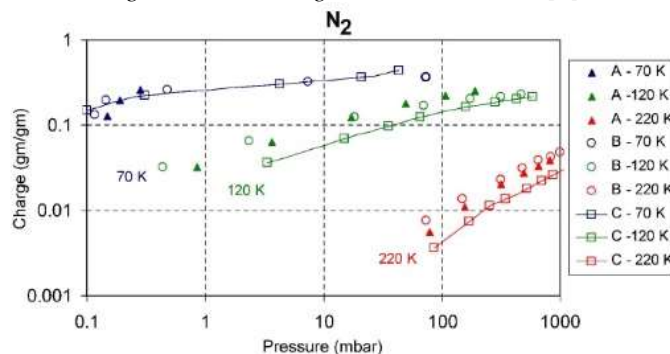


Figure 2.12 - Three selected adsorption isotherms for the gas nitrogen on the three charcoal samples [5]

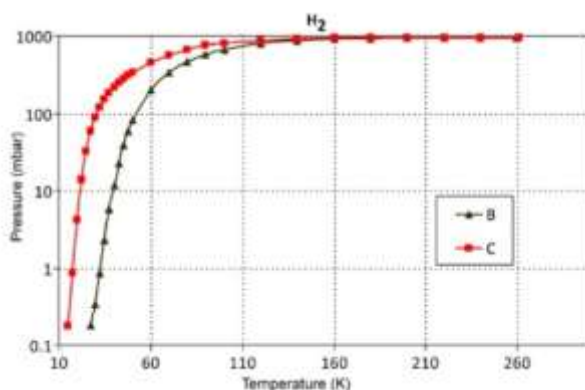


Figure 2.13 - “Sorption effect” (pressure versus temperature) for two charcoals under the same amount of hydrogen, same charcoal volume. [5]

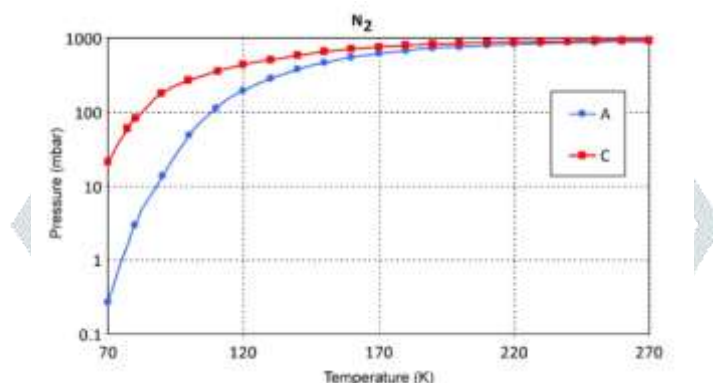


Figure 2.14 - “Sorption effect” (pressure versus temperature) for two charcoals under the same amount of nitrogen, same charcoal volume. [5]

**Development of a helium purification system using pressure swing adsorption by** <sup>[6]</sup> Nisith Kr. Das, Pradeep Kumar, C. Mallik and Rakesh K. Bhandari, CURRENT SCIENCE, VOL. 103, NO. 6, 25 SEPTEMBER 2012

A three-bed seven-step pressure swing adsorption (PSA) helium purification system has been developed exploiting PSA. It removes impurities like N<sub>2</sub> and O<sub>2</sub> from a ternary mixture leaving out high-purity helium from the gas mixture. In the present experimental setup, a feed gas stream containing helium (55.0 mol%), nitrogen (~35.0 mol%) and oxygen (~10.0 mol%) has been introduced into the system with predetermined pressure and flow rate. Lithium exchanged low silica X-zeolite (LiLSX) molecular sieve with an average pore diameter of 0.9–1.0 nm has been used as the adsorbing medium. Total cycle time of the PSA system was conveniently chosen to be 180 sec. The PSA system is operating successfully resulting in high-purity helium (>99.9%) with a yield of around 89%.

Table 2.3 - Characteristics of LiLSX molecular sieve [6]

Pilate diameter (mm)	1.8-2.0
Pore size (Å)	9
Particle density (g/cm <sup>3</sup> )	1.2
Pore volume (cm <sup>3</sup> /g)	0.39
Void volume (cm <sup>3</sup> )	0.62
Bed void fraction	0.40

This pilot-scale PSA system can produce high-purity helium (>99.9%) with a yield of over 89% with an adsorption pressure of 5 bar. The three-bed seven-step PSA helium purification system removes impurities such as N<sub>2</sub> and O<sub>2</sub> from a ternary mixture leaving behind high-purity helium. The merits of this technique over the existing ones can be summarized as an attaining helium purity of ~99.95 mol% using only LiLSX adsorbent which can take on two impurities, oxygen and nitrogen, leading to compactness and operational convenience of the system.

Table 2.4 - Operating parameters of the three-column PSA system [6]

Feed		Product	
Flow (slpm)	30	Flow (slpm)	~15.0
Pressure (bar)	5	Pressure (bar)	3.2
Temperature (°C)	30	Temperature	(°C) Ambient
Composition	mol%	Composition	mol%
He	~55	He	≥99.95
O <sub>2</sub>	~10	O <sub>2</sub> + N <sub>2</sub>	≤0.5
N <sub>2</sub>	~35		

**Cryogenic adsorber design in a helium refrigeration system** <sup>[7]</sup> by Zhongjun Hu, Ning Zhang, Zhengyu Li, and Q. Li  
Published by the American Institute of Physics, AIP Conference Proceedings 1434, 1737 (2012).

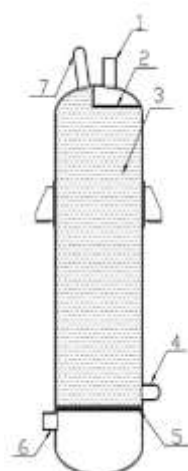


Figure 2.15 - Structure scheme of a cryogenic adsorber. (In fig 1 is the gas entrance, 6 is the gas exit, 3 is the adsorbent bed, 4 and 7 are filling holes, 2 and 5 are the filters.) [7]

The cryogenic adsorber is a necessary facility of helium purification in large scale cryogenic engineering. Active carbon is an effective adsorbent to adsorb some impurity components in helium. The dynamic adsorption capability determines the height of the adsorbent layer. When operating gas flow velocity increase, the gas stream breaks up into turbulence and the dust quantity of active carbon particles also increase. Therefore, the maximum permissible gas flow void tower velocity is limited under 0.25 m/s, which insures laminar gas flow. The diameter and adsorption layer height of the cryogenic adsorber are designed according to the gas flow velocity and the dynamic adsorption capability of the active carbon. A typical adsorber would bring about 0.5 kPa pressure drop due to the adsorbent resistance. To avoid the active carbon particles' dust flow out of the adsorber, deliberate structures of filters are set on both ends of the adsorption bed that consisted of several porous layers.

**Helium purification by Gas Adsorption method using coconut shell activated charcoal** <sup>[8]</sup> by Jitendra Bhushan, Akash Pandey, International Journal of Engineering Research & Technology, Vol. 3 Issue 11, November-2014. The gas is passed through oil and water separator vessel and three heat exchangers in series. The first heat exchanger acts as dryer and the second and third one condenses air and reduce the impurity in helium gas up to 0.84% only. Liquid air vessel then collects the condensed air, which is purged at regular interval. After that, a snow filter filters any ice coming with the impure stream. Now the impure helium gas, containing only 0.84% air impurity, enters the activated charcoal bed immersed in LN<sub>2</sub>. The adsorber bed reduces air impurity to less than 50 ppm and thus yields Grade 4.5 helium.

Table 2.5 - Specification of Helium Purifier [8]

Rate	21 Nm <sup>3</sup> /hr
Operating pressure and Temperature	120 bar (gauge) & 77K
Input gas purity	90% i.e. 10% air impurity
Output gas purity	99.995% (minimum) i.e. Grade 4.5 i.e. max. allowable impurity is 50 ppm
Run time for purification	6 (six) hours
Adsorbent	Coconut shell granular activated charcoal

Table 2.6 - Technical data of charcoal [8]

Characteristics	Property of Charcoal
Grade	AC 4/8
Particle type	Granular
Sieve size	-4 +8 BSS
BET Surface area, m <sup>2</sup> /gm, (min.)	1600
Moisture, percent by mass (min.)	4.5
Ash, percent by mass (max.)	4.0
Adsorption capacity in terms of Iodine number (min.), mg/gm	608

The results show that, in all the samples total impurity, consisting of moisture, nitrogen and oxygen is less than 5 vpm, which means purified helium is better than Grade 4.5 or 99.995% helium. So, Grade 4.5 helium has been obtained from 5% nitrogen impurity in input helium for 3 hours nonstop run.

**Design of Prototype Internal 20k Helium Gas Purification System for Helium Plant & Test Facility** <sup>[9]</sup> by Dhaval B. Prajapati, A.K.Sahu, J.M. Patel in International Journal of science technology and engineering, Volume 1 Issue 11, May 2015, ISSN 2349-784X.



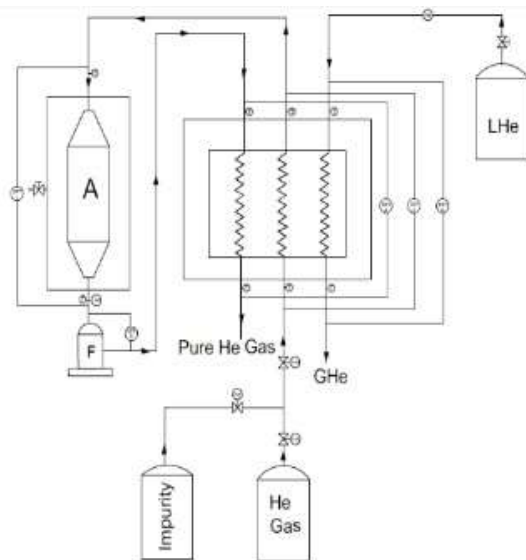


Fig 2.16 - Adsorber Bed Test Facility Simple PID [9]

The current work deals with the design and optimization of adsorption-based helium purification system at 20K and its test facility. In context to the design requirements it can be concluded that activated carbon especially coconut shell based seems to be more effective as compared to the different adsorbents discussed. In addition to this, calculation gives us for 1 m bed length and 0.0278m bed diameter, mass of adsorbent required is approximately 0.350 Kg of coconut shell-based charcoal. So, total minimum size of charcoal adsorber bed required is 1 m and, in this case, it is selected 1.5 m which is in safe zone and mass of adsorbent required for that 0.5 Kg.

For the Filter Element, 550 mesh size required to prevent to enter the charcoal particles into pure helium gas of greater than 20micron size. Optimized height and width of the mesh is 0.04m and 0.085m respectively.

For tube-in-tube three stream heat exchanger, the optimized length is 3m with 1 g/s mass flow rate of 300K hot helium stream & 2 g/s mass flow rate of 4.2K liquid helium stream which gives pressure drop within limit.

### 3. References

- [1] "Nitrogen Adsorption Isotherms for Zeolite and Activated Carbon" L.C. Yang, T.D. Vo, and H.H. Burris, cryogenics, 1982.
- [2] "Porosity, Surface Area, Surface Energy, and Hydrogen Adsorption in Nanostructured Carbons" by Alejandro Anson, Jacek Jagiello, JoseB. Parra, M. Luisa Sanjuan, Ana M. Benito, Wolfgang K. Maser, and M. Teresa Martinez, *J. Phys. Chem. B* 2004, 108, 15820-15826.
- [3] "Engineering studies related to fixed bed adsorber and its application for fission gas adsorption at cryogenics temperature" by Puwar Dhairyapalsinh, Prabhat Kumar, V.A.Subramani, B.Muralidharan and Bharti V.Dave, *Indian Journal of cryogenics* Vol 35A,2010
- [4] "Breakthrough studies of activated carbon and oxysieve for helium purification at 77K" by Nisith K.Das, Pradeep Kumar, Amitavasur, Rakesh K. Bhandari *Indian Journal of cryogenics* Vol. 35. No.1-4,2010.
- [5] "Low Temperature Adsorption Versus Pore Size In Activated Carbons", D. Martins, I. Catarino, D. Lopes, I. Esteves, J.P. Mota, G. Bonafait, *Cryocoolers* 16, 2011.
- [6] "Development of a helium purification system using pressure swing adsorption" by Nisith Kr. Das, Pradeep Kumar, C. Mallik and Rakesh K. Bhandari, *CURRENT SCIENCE*, VOL. 103, NO. 6, 25 SEPTEMBER 2012
- [7] "Cryogenic adsorber design in a helium refrigeration system" by Zhongjun Hu, Ning Zhang, Zhengyu Li, and Q. Li Published by the American Institute of Physics, *AIP Conference Proceedings* 1434, 1737 (2012).
- [8] "Helium purification by Gas Adsorption method using coconut shell activated charcoal" by Jitendra Bhushan, Akash Pandey, *International Journal of Engineering Research & Technology*, Vol. 3 Issue 11, November-2014.
- [9] "Design of Prototype Internal 20k Helium Gas Purification System for Helium Plant & Test Facility" by Dhaval B. Prajapati, A.K.Sahu, J.M. Patel in *International Journal of science technology and engineering*, Volume 1 Issue 11, May 2015, ISSN 2349-784X.