Studies of Adsorption Characteristics of Activated Carbons in between 4.5 to 10 K for Cryopump Applications

V. Krishnamoorthy, Satya Swarup Udgata, Vijai Shankar Tripathi, Ranjana Gangradey, Srinivasan Kasthurirengan and Upendra Behera

1 I-Design Engineering Solutions Ltd., Ubale Nagar, Wagholi, Pune 412207, India
2 HEG R&D Centre, Mandideep, Raisen Dt. 462 046, India.
3 Cryopump Group, Institute of Plasma Research, Gandhinagar, Gujarat 382428, India
4 Centre for Cryogenic Technology, IISc, Bangalore 560012, India.

E-mail: svkrishnamurthi@gmail.com

Abstract. Cryosorption pump is the only solution to pump helium, hydrogen and its isotopes in fusion devices. To design such pumps, knowledge of adsorption characteristics of activated carbons in the temperature range from 4.5 to 77 K is needed, but is very scarce in the open literature. Hence an experimental setup is designed and developed to measure adsorption characteristics of activated carbons down to 4.5 K. For this purpose, a commercial micropore analyzer operating down to 77K is coupled to a two-stage GM cryocooler, to enable cooling the sample temperature down to 4.5 K. A heat switch is mounted in between the second stage cold head and the sample chamber helps to vary the sample temperature from 4.5 K to 77K without affecting the performance of the cryocooler. The details of the experimental setup is presented elsewhere. We present here the experimental results of adsorption of different types of activated carbons in the temperature range 4.5K to 10 K using Helium gas as adsorbate. These results are evaluated in terms of surface area, pore sizes and their distributions. Also the effect of epoxy based adhesive used in bonding the activated carbons to the panels is evaluated. These results will be useful towards the selection of the right activated carbons for the development of cryosorption pumps.

1. Introduction

The pumping of helium, hydrogen and its isotopes from fusion exhaust is possible only by the use of Cryosorption pumps, since they offer high pumping speeds and are capable of operating in the tokomak environment of radiation and high magnetic field. Normally, the cryo-condensation pumps operating at 4.2K, helps to condense all the gases except helium and hydrogen. To condense these gases, the porous sorbent is coated on the cryopanels. Among the various sorbent materials used for such applications, activated carbon provides the higher pumping speed and enables pumping of hydrogen and its isotopes in the presence of helium [1]. Also, activated carbon used requires moderate regeneration temperature (400K). Activated carbon adsorbent is suitable for use when handling large volume flow rates and to pump impure gases encountered in industrial processes particularly for fusion applications [3]. To have the sorbent adhered to the cryosurface, it needs to be bonded to the surface with an adhesive. Thus the fabrication of the cryosorption panel involves the selection of the right sorbent (with the proper isotherms and pore sizes) and the adhesive (high thermal conductivity and stability).
To have high pumping speeds for cryosorption pumps for helium, the knowledge of the adsorption characteristics of the activated carbons (mounted on the panel by special epoxy resins) is necessary. The sticking coefficient for helium for such cryopanels is also reduced because some of the pores of such activated carbons are also blocked by adhesive. So there is a need of choosing the best activated carbons with high sticking coefficient for helium. However, such data is not available in open literature in the temperature range below 77K [1]. Hence there is a need to characterize and analyze the adsorption characteristics of various activated carbons especially in the temperature range from 4.5 K to 10 K using a specially built experimental setup.

2. Experimental setup
There are no commercial instruments available to measure the characteristics of porous materials in the above temperature range. Hence the above experimental setup has been setup with the commercially available micropore analyzer suitable for use up to 77K along with the two stage GM Cryocooler and this is shown in Figure 1.

Fig. 1. Experimental setup to measure adsorption characteristic at 4.2K

A commercial micropore analyzer (Autosorb IQ) is procured from Quantachrome Instruments Inc, USA. This instrument is suitable for measurement of the adsorption characteristics of porous materials at 77 K using liquid nitrogen. This instrument has provision to degas the sample in which sample under study is heated and pumped out. After degassing, the sample under study is moved analyzer port, wherein the measurements are performed. The sample is maintained at 77 K with the help of a liquid nitrogen bath. The warm and cold zone volumes are measured automatically and used in the measurements.

For measurements down to 4.5 K, the sample needs to be cooled to this temperature. This is done by using a Cryocooler (Model SRDK-415 from Janis Research Systems Inc. USA). This two stage GM Cryocooler provides a refrigeration power of ~ 1.5W at 4.2 K at its second stage and ~ 35W at 50 K in its first stage respectively. The sample under study is now mounted on the second stage cold head of the Cryocooler replacing the standard LN2 dewar. The thermal load of second stage to the second stage is minimized using the cooling power of the first stage as the thermal radiation shield.

Several layers of superinsulation are wrapped around first and second stage cold head to reduce radiation losses. Turbo molecular pumping system is used to evacuate the interspace of the vacuum jacket. Silicon diode sensors (DT670 and SI410, from M/s SI, USA) are used to monitor the temperatures of second stage cold head. The cold head temperature can also be increased above 4.2 K with the help of two cartridge heaters (each of 50 ohms). The sample temperature can be maintained at any specific temperature in the range from 4.5 K to 77 K using a temperature controller (Model 332 from M/s Lakeshore).

For 4.2 K measurements, the special sample chamber used is made of stainless steel mounted on the 2nd stage cold head of the Cryocooler and replaces the standard glass sample chamber used
normally for 77 K measurements. Also, for experiments at temperatures other than that of the cold head, the sample chamber needs to be raised in its temperature, without affecting the performance of the Cryocooler. For this purpose, a heat switch is interposed between the sample chamber and the cold head. The stainless steel sample chamber is of conflate type (5 cm diameter) sealed by copper gasket. A heat switch is mounted in between sample chamber and the cold head of the Cryocooler, which helps to carry out experiments at temperatures from 4.5 K to 100 K without affecting the performance of the Cryocooler.

This heat switch consists of two interpenetrating copper parts welded into a thin walled stainless steel cylinder such that they are separated by a narrow gap. Normally, the upper and lower copper blocks do not touch each other. Hence, when this gap is evacuated, the heat switch is open. The top part of the switch can be maintained at a temperature different from that of its bottom due to the poor heat transfer of the thin walled stainless steel cylinder connecting the upper and lower parts of the heat switch. However, when helium is filled in the gap, the heat switch is closed since the top part of the switch will be at the same temperature as that of its lower part i.e. that of the cold head.

Fig. 2. (a) Drawing of sample chamber mounting on the cold head. (b) Photograph of the sample mount on the cold heat exchanger of the GM cryocooler. 1. Sample chamber, 2. Radiation shield, 3. Heater, 4. Heat Switch, 5. Gas line for Heat Switch 6. Gas line for adsorption, 7. 2nd stage cold head.

The sample port has a volume of ~ 1 cm³ and is connected to the adsorption analyzer with the help of 0.125 in diameter stainless steel tube with appropriate end coupling. This smaller cross section pipe used to reduce void volume. Also similar pipe connections are used for gas entry into or evacuation of the heat switch. The sample needs to be degassed outside since the cold head of GM Cryocooler cannot be overheated. After GM Cryocooler reaches the set cold end temperature, the adsorption measurements are carried out by the analyzer by a dosing routine run by a predefined program.

3. Experimental Results
The adsorption characteristics of several types of activated carbons are studied using different adsorbates. The preliminary experiments were carried out with nitrogen gas as adsorbate at 77K and later these samples are evaluated at 4.2K-10K using helium gas as a adsorbate. In order to determine surface areas and the pore size distributions of the sample, the adsorption isotherms are needed.

3.1 Experimental studies at 77K using nitrogen gas
The adsorption isotherms plot the specific volume adsorbed by the sample as a function of relative pressure (pressure/saturation vapor pressure) at a constant temperature. Figure 3(a) shows the adsorption isotherms for different activated carbon samples. Also included in the same figure is the adsorption isotherm for standard alumina sample (SARM-2005) for comparison, which has a surface
It is seen that activated carbon has higher volume of adsorption compared with the standard sample. Most of the carbon samples exhibit IUPAC classification type-I isotherms with an almost vertical rise at lower relative pressure range above 0.1, The alumina sample exhibit type-V isotherms, It almost rises to vertical at higher relative pressure range around 0.7

![Adsorption isotherms of Activated carbon for N2 gas at 77K](image)

Fig. 3. (a) Adsorption isotherms of Standard Alumina sample and the activated carbon samples for nitrogen gas adsorption at 77 K. (b) Adsorption isotherms of ACS-3 activated carbon samples with helium gas at 4.2 to 10K

### 3.2 Experimental studies at 4.5 to 10 K using helium gas

The experimental procedure of measurements at 4.5 K is different when compared to 77 K measurement. At 77K, the dead volume measurement is done using helium gas because adsorption of sample at 77K with helium is nearly zero. However, at 4.5 K, helium gas itself is chosen as the adsorbate. Hence, the blank (adsorption of the sample chamber without the sample) measurements at these temperatures are carried out separately. This data is used for the measurements with the sample mounted in the sample chamber. The typical adsorption isotherms of a typical activated carbon globule sample namely ACS 3 is shown in Figure 3(b). It is observed that the adsorbed volume gradually increases with lowering of temperature. The adsorption volumes are also higher at lower temperatures for helium as adsorbate.

Table 1 Total surface areas of the activated carbon samples by BET method at different temperatures.

| SAMPLES                                      | SURFACE AREA MEASUREMENT (m²/g) |
|----------------------------------------------|----------------------------------|
|                                              | 77K (Nitrogen as adsorbate)      | 4.2K (Helium as adsorbate) | 5K (Helium as adsorbate) | 8K (Helium as adsorbate) | 10K (Helium as adsorbate) |
| Blank                                        | 0.00                             | 0.12                       | 0.00                      | 0.00                      | 0.00                      |
| Carbon pellets                               | 1003.1                           | 1465.1                     | 1031.5                    | 894                       | 887.2                     |
| ACS-3                                        | 2038.2                           | 2700.3                     | 2639.45                   | 1963.4                    | 1736.8                    |
| ACFNW3                                       | 1773.2                           | 1951.01                    | 1924.1                    | 1589.3                    | 1335.2                    |
| Srilanka Charcoal Granules                   | 1364.5                           | 1801.2                     | 1797.6                    | 1188.5                    | 1069.2                    |
| ACF- FK3                                     | 2230                             | 2920.2                     | 2697.2                    | 2582.6                    | 2014.9                    |
| ACS3+SS plate+ adhesive                      | 1927                             | 2600.7                     | 2424.4                    | 1831.2                    | 1516.44                   |
| Charcoal granule Coarse                      | 1126.74                          | 1668.84                    | 1576.49                   | 1374.52                   | 1235.61                   |
4. Surface areas and pore size distributions

The adsorption surface areas of the samples can be determined by assuming that multilayer adsorption occurs over the sample surface starting from the initial monolayer. Thus, the standard BET technique is used in calculation of the surface areas of the activated carbons starting from the adsorption isotherms. The software provided along with the Autosorb IQ is used for the above calculations. The pore sizes are arrived at using the Density Functional Theory (DFT) method, using the experimentally measured isotherm data. The Autosorb IQ software enables the calculation of the pore size distributions.

Table 1 shows the surface areas of different activated carbon samples as determined by BET method with nitrogen as adsorbate at 77 K and helium as adsorbate in the temperature range from 4.5-10 K. We note that the surface areas are in general larger at lower temperature and the surface area with nitrogen at 77K nearly matches with that of helium in the temperature range between 5-8 K.

Pore size distribution is one of the important characteristic of a porous material. The volume adsorbed by the sample depends on the pore size and pore type. The overall pore sizes for the activated carbon is in the range from 10 to 50 Å. The pore sizes above 20 Å contribute less to the adsorption. Activated carbon samples ACS-3, ACF- NW3, ACF-FK2 have pore sizes below 20 Å and they are highly microporous [4]. On the other hand, SARM - Alumina sample has pore diameter of ~ 25 Å and it is mesoporous. Table 1 shows the average pore sizes measured for different activated carbon samples. To understand the influence of the pore size distribution on the adsorption, we chosen activated carbon globules ACS-3 for the analysis. Figure 4 shows the pore size distributions of activated carbon ACS3 at 77K and at 4.5 K.

![Pore size distribution of ACS-3 at 77K using nitrogen gas as adsorbate](image)

![Pore size distribution at 4.5 K](image)

(a) (b)

Fig. 4. (a) Pore size distribution of ACS-3 at 77K using nitrogen gas as adsorbate. (b) Pore size distribution of ACS-3 at 4.5 K

From the above figure it is seen that at 77K, the pore sizes have a distribution over the range from 10 Å to 35 Å. On the other hand, the 4.5K studies show that the major pore sizes are concentrated at about 15 Å. The pore size distributions at higher temperatures indicate a similar behaviour except that the peak around 15 Å gradually decreases with increasing temperatures.

5. Studies on Activated Carbon Coated on Adhesive Panel

To understand the actual performance of cryopanels, experiments have been conducted on small size cryopanels wherein the activated carbons are mounted using an epoxy based adhesive. ACS-3 charcoal globule is chosen because it offers higher volumes of adsorption compared to other samples. The base stainless steel cryopanel needs an adhesive coating onto which ACS-3 sample is adhered. It is observed that the epoxy based adhesive performs better than other types and hence this is chosen.

The adsorption characteristics of the cryopanels coated with activated carbon ACS-3 samples were studied as follows. Initially the plain ACS-3 samples were characterized. Next, a stainless steel sheet of size 20 mm x 10 mm x 1 mm is finely coated with adhesive on its surface and experimented for its adsorption characteristics. Subsequently, the same size stainless steel plate coated with the adhesive
and filled with activated carbon ACS-3 is studied for its adsorption characteristics. The performance characteristics of the various samples are shown in Table 2.

The results indicate that there is a reduction in the surface area of the ACS-3 coated onto the cryopanel and this value is ~ 10 % of that of the bare activated carbon ACS-3. This is easily understood since some of the pores are closed by the adhesive. Also, the average pore size of ACS-3 coated on the panel is found to be greater than that of the bare ACS-3. This is perhaps due to the interference of adhesives into the porous structure of the sample. Even though there is a decrease in the surface area and rearrangement of pore distribution, ACS-3 still exhibits micropore structure.

Table 2. Comparison of surface areas and average pore sizes of ACS-3 under different conditions.

| S.No | Sample under study                      | Surface area in 77K with N₂ (m²/g) | Average pore size in 77K with N₂ (Å) | Surface area in 4.5K with He(m²/g) | Average pore size in 4.5K with He (Å) |
|------|-----------------------------------------|------------------------------------|--------------------------------------|-----------------------------------|--------------------------------------|
| 1    | Activated carbon ACS-3                 | 2031.6                             | 7.60                                 | 2700.1                            | 6.21                                 |
| 2    | Stainless steel sheet                  | 0.00                               | 0.00                                 | 0.00                              | 0.00                                 |
| 3    | Stainless steel coated with Adhesive   | 0.00                               | 0.00                                 | 0.00                              | 0.00                                 |
| 4    | Stainless steel coated with Adhesive and ACS-3 | 1978.00 | 12.3                                  | 2600.7                            | 11.81                                |

6. Conclusion
An experimental setup has been designed and developed to measure adsorption characteristics of activated carbons down to 4.5 K. For this purpose, a commercial micropore analyzer operating down to 77K is coupled to a two-stage GM cryocooler, to enable cooling the sample temperature down to 4.5 K. A heat switch is mounted in between the second stage cold head and the sample chamber helps to vary the sample temperature from 4.5 K to 77K without affecting the performance of the cryocooler. The experimental results of adsorption of different types of activated carbons at 77K with nitrogen as adsorbate and in the temperature range 4.5K to 10 K with helium as adsorbate are presented. These results are evaluated in terms of surface area, pore sizes and their distributions. Also the performances of the small size cryopanels wherein the activated carbon ACS-3 is adhesively bonded is studied. It is observed that ACS-3 activated carbon is one of the best samples that can used for the development of cryopanels.

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