

1

O

f

1

Conf-931018--68

LA-UR- 93-3655

*Title:* CRYOGENIC ADSORPTION OF LOW-CONCENTRATION HYDROGEN ON CHARCOAL, 5A MOLECULAR SIEVE, SODALITE, ZSM-5 AND WESSALITH DAY

*Author(s):* R. Scott Willms  
Tritium Science and Technology Group  
Materials Science and Technology Division

*Submitted to:* IEEE/NPSS 15th Symposium on Fusion Engineering  
October 11 thru 15, 1993, Hyannis, Massachusetts

**MASTER**

**Los Alamos**  
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

REPRODUCTION OF THIS DOCUMENT IS UNLIMITED

Form No. 836 R5  
ST 2629 10/91

# Cryogenic Adsorption of Low-Concentration Hydrogen on Charcoal, 5A Molecular Sieve, UOP S-115, ZSM-5 and Wessalith DAY

R. Scott Willms  
Los Alamos National Laboratory  
Los Alamos NM 87545

## ABSTRACT

The separation of low-concentration hydrogen isotopes from helium is a processing step that is required for ceramic lithium breeding blanket processing. Cryogenic adsorption is one method of effecting this separation. In this study five adsorbents were considered for this purpose: charcoal, 5A molecular sieve, UOP S-115, ZSM-5 and Wessalith DAY. The first two adsorbents exhibit good equilibrium loadings and are shown to be quite effective at adsorbing low-concentration hydrogen isotopes. The latter three adsorbents display considerably lower equilibrium loadings. This study concludes that by using either charcoal or 5A molecular sieve, cryogenic adsorption would be an effective means of separating hydrogen isotopes from helium.

## INTRODUCTION

One of the tritium breeding blankets that has been considered for fusion machines is comprised of lithium ceramic. To remove tritium from such a blanket, a stream of helium containing 0.1-1%  $H_2$  is swept over the ceramic. The  $H_2$  exchanges with tritium in the ceramic, thus moving the tritium into the helium sweep gas. Once outside the blanket the tritium must be separated from the helium carrier. One method considered for this purpose is cryogenic adsorption which would collect all of the hydrogen isotopes and leave helium in the gas phase. The helium is available for recycle back to the breeding blanket. When saturated with hydrogen isotopes, the cryogenic adsorbent is regenerated, sending the liberated hydrogen isotopes to the fuel processing system and ultimately to reuse in the fusion machine.

To demonstrate the separation of low-concentration hydrogen isotopes from helium, five adsorbents were considered: coconut charcoal, Linde 5A molecular sieve, UOP S-115, ZSM-5 and Wessalith DAY. All of these materials are commercially available. Charcoal and molecular sieve have been used extensively in tritium processing for applications such as cryosorption vacuum pumps, for separation of impurities (water, methane, nitrogen, etc.) from hydrogen isotopes, and for collection of water in tritium effluent cleanup systems. Because of extensive tritium processing experience with these two materials, they were obvious choices for inclusion in this study.

UOP S-115, ZSM-5 and Wessalith DAY are molecular sieves (aluminosilicates), but differ from 5A molecular sieve in that they have had all or most of the Al eliminated from the

molecular sieve. This gives them the unique property of being hydrophobic rather than hydrophilic as is typical of most molecular sieves. This property is attractive because it would minimize or eliminate a small, semipermanent tritium inventory on the adsorbent in the water form which is expected for 5A molecular sieve.

A test stand for measuring the adsorption characteristics of these materials was constructed. Streams of various concentrations of  $H_2$  in He were passed through the liquid nitrogen-cooled adsorbent. Breakthrough curves were observed using gas chromatography. From these data adsorption isotherms were determined.

## EXPERIMENTAL DESCRIPTION

### A. Apparatus

The experimental setup used for this study is shown in figure 1. Automatic flow controllers were used to mix hydrogen and helium in the desired ratios and flowrates. This mixture was sent to an adsorber which was immersed in a liquid nitrogen bath. The adsorber exit pressure was measured and controlled by a back pressure regulator valve which exhausted to atmosphere. Part of the exhaust was sent to an MTI gas chromatograph for analysis of the hydrogen concentration.

The adsorbents were constructed of 1-welded 50 cc Whitey sample cylinders (SS-4CD-7 w-5). Outer cylinder dimensions are 13.45 cm long x 2.4 cm diameter. The wall thickness is 0.165 cm. The cylinder was filled with a measured amount of adsorbent and both ends were packed with stainless steel wool. 1/4" tubing was welded to both cylinder ends for connection to the test stand.

### B. Procedures

Before an experimental series, the bed was connected to the test stand and regenerated at 340 °C with a dry helium purge overnight. Between successive loadings (adsorber not disconnected from the test stand) the bed was regenerated at 200 °C for 30 minutes. If there was any chance that the adsorbent had had contact with air (and, thus, water) the more aggressive regeneration was repeated.

Table 1  
Summary of Adsorbents Tested

Adsorbent	Supplier	Type	Shape	Size	Amount Used (gm)
Charcoal (Coconut)	Calgon	PCB	Granules	Between 12 and 30 mesh	20.345
5A Molecular Sieve	Union Carbide (Linde)		Pellets	1/16"	41.436
S-115	UOP	S-115	Pellets	1/16"	36.859
ZSM-5	Mobil	MC-319	Pellets	1/16"	29.247
Wessalith DAY	Degussa	Z 1137	Pellets	2 mm	23.070

A run began by regenerating the adsorber and isolating it with its isolation valves. It was then immersed in liquid nitrogen. The target helium/H<sub>2</sub> flow for the run was started through the bypass valve and the back pressure regulator set. At "time zero" the flow was rerouted through the adsorber and the bypass valve was closed. Simultaneously, GC sampling was started. Samples were collected and analyzed every 72 seconds. This was continued until the hydrogen had completely broken through the adsorber (the exit concentration was equal to the inlet concentration).

For all experiments the total pressure was controlled at 790 torr (absolute).

Nominally runs for each adsorbent were carried out with 1000 sccm of He and various flowrates of H<sub>2</sub>. The H<sub>2</sub> flowrates were typically 1, 2.5, 5, 10, 25 and 50 sccm (see Table 2 for a listing of the actual conditions used for each adsorbent).

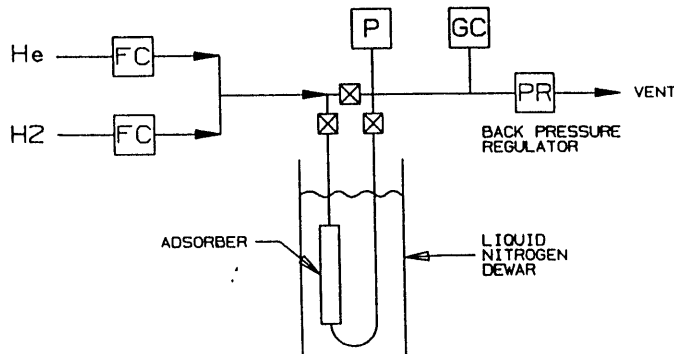


Figure 1 Schematic of Experimental Setup

### C. Adsorbents

The adsorbents used are summarized in Table 1. The charcoal used here is a Calgon type PCB granular activated carbon produced from coconut shells. Its specific surface area is about 1200 m<sup>2</sup>/gm [1].

Molecular sieves are aluminosilicates with included cations such as sodium, potassium and calcium. The cations are required to balance the electrical charge of the aluminum atoms. For 5A molecular sieve there is an equal amount of Al and Si, and

the major cation is Ca [3]. This makes for a highly polar, hydrophilic material. The 5A molecular sieve studied here was obtained from the Linde division of Union Carbide. The pellets are formed with a clay binder which constitutes 20% of the pellet. The specific surface area is reported by Danner [2] to be 572 m<sup>2</sup>/gm.

Molecular sieves have also been prepared with little or no Al resulting in a material which is non-polar and hydrophobic. One class of de-aluminated molecular sieves are essentially pure silica and have a unique structure often referred to as silicalite. They have been discussed by various authors [4-10]. The UOP S-115 and the ZSM-5 considered here are silicalites. The specific surface areas of these materials are approximately 400 m<sup>2</sup>/gm. The Si:Al ratio for S-115 is in the range of 140-200. It should be noted that both of the silicalites were prepared as pellets which means that they contain a binder. The ZSM-5 for instance contained considerable (35%) alumina as the binder.

The Degussa Wessalith DAY is a de-aluminated Y structure molecular sieve. Its specific surface area is 800 m<sup>2</sup>/gm [11].

## RESULTS

### A. Breakthrough Curves

A typical breakthrough curve is shown in figure 2. This particular run was for charcoal and used 1000 sccm of He and 50 sccm of H<sub>2</sub> in the feed. For 32 minutes no hydrogen

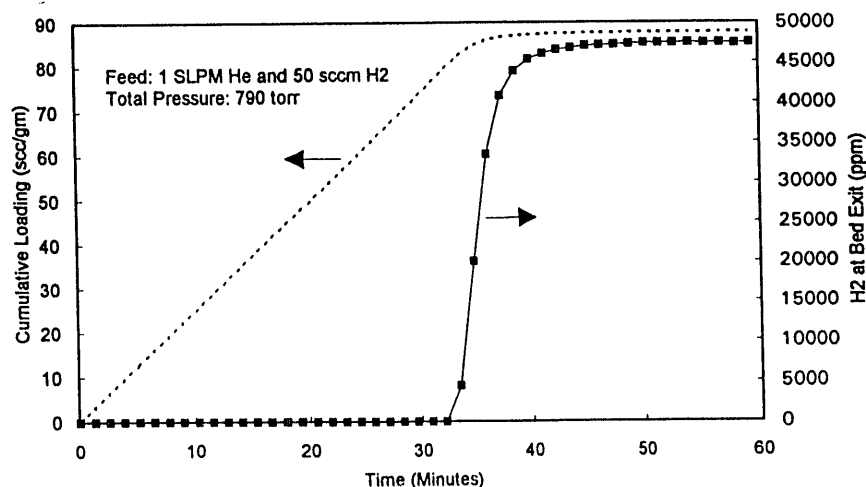


Figure 2 Typical Breakthrough Curve (Charcoal, 77 K)

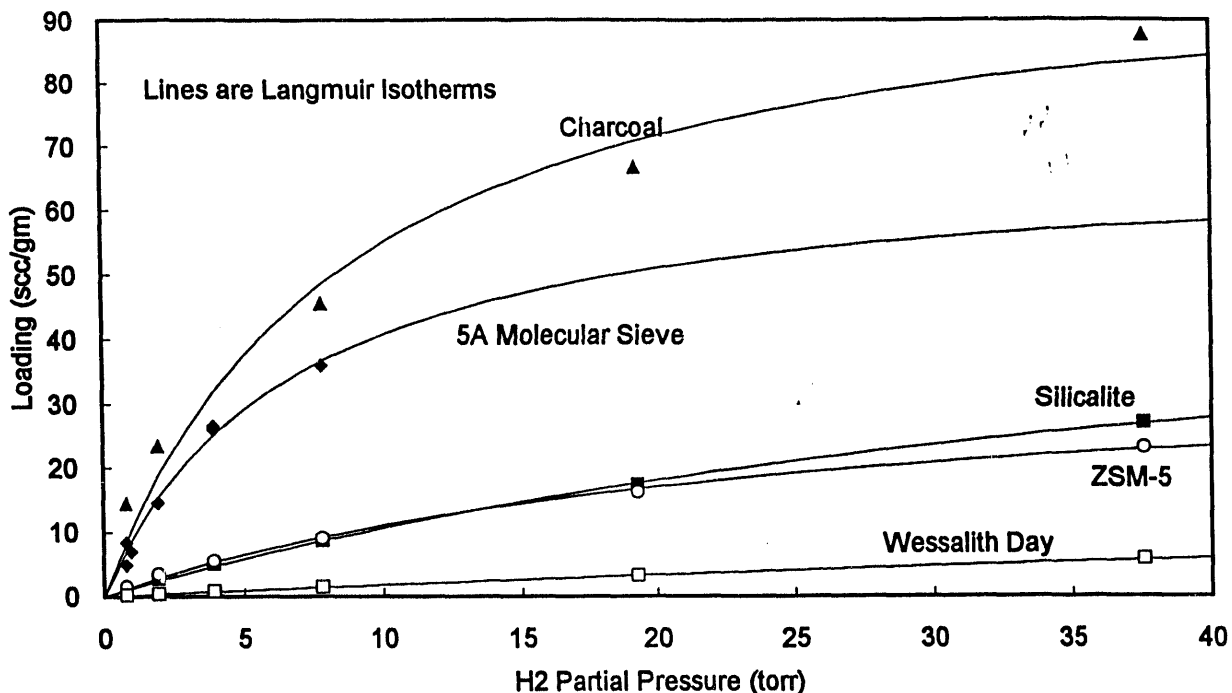


Figure 3 77 K Adsorption Isotherms for Five Adsorbents

was detected in the adsorber exhaust. The GC is able to detect hydrogen in concentrations greater than about 20 ppm. Thereafter, following a sigmoid curve, the hydrogen concentration increases over a period of about 10 minutes, ultimately matching the feed hydrogen concentration. This indicates that the bed has completely saturated.

The long period of no  $H_2$  in the exhaust followed by a relatively sharp breakthrough indicates that this material has a "favorable" adsorption isotherm (confirmed below). It also indicates that the "unused" portion of the bed is relatively small. See [3] for a discussion of this adsorption terminology.

Integration of the difference between the amount of hydrogen in the adsorber inlet and outlet can be used to determine the cumulative bed loading at any instant. The results of this calculation are shown on figure 2 (dashed line). The ultimate bed loading in this case was 87.7 scc  $H_2$ /gm adsorbent. Coupled with the 37.6 torr partial pressure of  $H_2$  over the bed, this run establishes one point on the charcoal isotherm.

#### B. Adsorption Isotherms

Table 2 summarizes all of the runs conducted. Besides listing the flowrates and partial pressures for each experiment, the results of the cumulative loading calculations are included.

The information in Table 2 was used to prepare figure 3 which shows on one adsorption isotherm plot, all of the runs carried out. Each data set was fit with a Langmuir equation which is:

$$\frac{v}{v_m} = \frac{Bp}{1+Bp} \quad (1)$$

where  $v$  is the amount adsorbed in STP volume/gm of adsorbent,  $v_m$  is the monolayer amount adsorbed,  $B$  is the Langmuir constant and  $p$  is the adsorbate partial pressure. It is apparent from figure 3 that this adequately models the data.

As expected from the sharp breakthrough curves, all of the isotherms are "favorable" (second derivative  $< 0$ ). A summary of the Langmuir parameters for each adsorbent are given in Table 3.

In the Langmuir model of adsorption the value of  $v_m$  represents the ultimate bed loading assuming that the surface of the adsorbent is saturated by a monolayer of adsorbate. This is the asymptotic value to which  $v$  will increase. In Table 3, the fact that  $v_m$  varies from 103 to 24.2 scc/gm for the five adsorbents, may at least in part be attributed to variations in specific surface area and adsorption site density. Indeed, except for Wessalith DAY, the values of  $v_m$  are roughly proportional to the material's specific surface area. The very low loading values for Wessalith DAY are surprising considering its large surface area.

Table 2  
Summary of Experiments Conducted

Adsorbent	He Flowrate (sccm)	H <sub>2</sub> Flowrate (sccm)	P <sub>H2</sub> (torr)	v (scc/gm)
Charcoal	1000	1	.789	14.5
	1000	2.5	1.97	23.4
	1000	10	7.82	45.6
	1000	25	19.3	66.7
	1000	50	37.6	87.7
5A Sieve	1000	10	7.82	36.0
	2000	10	3.93	26.0
	2000	10	3.93	26.0
	4000	10	1.97	14.5
	8000	10	0.99	7.0
	1000	10	7.82	36.0
	1000	5	3.93	26.5
	4000	4	0.789	8.4
	8000	8	0.789	5.0
UOP S-115	1000	2.5	1.97	2.7
	1000	5	3.93	5.1
	1000	10	7.82	8.7
	1000	25	19.3	17.4
	1000	50	37.6	27.0
ZSM-5	1000	1	.789	1.6
	1000	2.5	1.97	3.5
	1000	5	3.93	5.6
	1000	10	7.82	9.1
	1000	25	19.3	16.2
	1000	50	37.6	23.1
Wessalith	1000	1	.789	0.26
	1000	2.5	1.97	0.44
	1000	5	3.93	0.83
	1000	10	7.82	1.5
	1000	25	19.3	3.3
	1000	50	37.6	5.8

Of this group, charcoal is clearly the best adsorbent for separating H<sub>2</sub> from helium, though 5A molecular sieve also exhibits good performance. The three de-aluminated sieves show substantially poorer performance, with UOP S-115 and ZSM-5 showing comparable loadings and Wessalith DAY giving the worst loading figures.

Table 3  
Summary of Langmuir Parameters for Each Adsorbent

Adsorbent	v <sub>m</sub> (scc/gm)	B (torr <sup>-1</sup> )
Charcoal (Coconut)	103	0.114
5A Molecular Sieve	68.1	0.149
UOP S-115	59.3	0.0220
65% ZSM-5/35% Al <sub>2</sub> O <sub>3</sub>	37.1	0.0426
Wessalith DAY	24.2	0.00808

Five adsorbents have been tested for suitability at separating low concentration H<sub>2</sub> from He. From equilibrium loading considerations the adsorbents can be ranked from best to worst as: charcoal, 5A molecular sieve, UOP S-115  $\approx$  ZSM-5, and Wessalith DAY. Either of the first two materials would provide good performance for the subject application. Though charcoal provides the best loading performance, there may be other considerations which would also influence the choice of adsorbents such as stability, carbon content and hydrophobic/hydrophilic nature. This study indicates that cryogenic adsorption is a good means for separating low-concentration hydrogen isotopes from He. The isotherms presented here would be useful for the design of a practical adsorber.

## ACKNOWLEDGMENTS

The author would like to gratefully acknowledge the work of Richard Barton (Teacher Research Associates Program) and Jeff Urioste (Graduate Research Assistant Program) who collected the experimental data. Mobil Research and Development Corporation donated the ZSM-5, Degussa Corporation donated the Wessalith DAY and UOP donated the S-115. Gratitude is expressed to these three corporations.

## REFERENCES

- [1] Calgon Technical Bulletin
- [2] R.P. Danner, *The Adsorption of Binary Gas Mixtures on Molecular Sieves*, Ph.D. Dissertation, Lehigh University, 1966, p. 27.
- [3] R.T. Yang, *Gas Separation by Adsorption Processes*, Butterworths, 1987, pp 19-24.
- [4] E.M. Flanigen, R.W. Grose, "Crystalline Silica Adsorbent," US Patent 4,061,724, 1977.
- [5] E.M. Flanigen, J.M. Bennett, R.W. Grose, J.P. Cohen, R.L. Patton, R.M. Kirchner, J.V. Smith, "Silicalite, a New Hydrophobic Crystalline Silica Molecular Sieve," *Nature*, 271, 512 (1978).
- [6] G.T. Kokotailo, S.L. Lawton, D.H. Olson, W.M.J. Meier, "Structure of Synthetic Zeolite ZSM-5," *Nature*, 272, 437-438 (1978).
- [7] R.M. Dessau, "Selective sorption properties of zeolites," *Adsorption and Ion Exchange with Synthetic Zeolites—Principles and Practice*, W.H. Flank, Ed., ACS Symposium Series 135, Am. Chem. Soc., Washington, DC, 1980, pp 123-135.
- [8] K. Otto, C.N. Montreuil, O. Todor, R.W. McCabe, and H.S. Gandi, "Adsorption of Hydrocarbons and Other Exhaust Components on Silicalite," *AIChE J.*, 30, 2333-2340 (1991).
- [9] H. B. Abdul-Rehman, M. A. Hasanain, and K.F. Loughlin, "Quaternary, Ternary, Binary, and Pure Component Sorption on Zeolites. 1. Light Alkanes on Linde S-115 Silicalite at Moderate to High Pressures," *J&EC Res.*, 29, 1525-1535 (1990).
- [10] C-K. Lee and A.S.T. Chiang, "Lattice Model for the Adsorption of Benzene in Silicalite I," *AIChE J.*, 38(1), 128-135 (1992).
- [11] Degussa Technical Bulletin, Degussa AG, Frankfurt 11, June 1991.

**DATE**

**FILMED**

1 / 26 / 94

**END**



