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S. P. Nandi<sup>ab</sup>, P. L. Walker Jr.<sup>a</sup>

<sup>a</sup> Department of Material Sciences, Pennsylvania State University, University Park, Pennsylvania <sup>b</sup> Argonne National Laboratories, Argonne, Illinois

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## Separation of Oxygen and Nitrogen Using 5A Zeolite and Carbon Molecular Sieves

S. P. NANDI\* and P. L. WALKER, JR.

DEPARTMENT OF MATERIAL SCIENCES  
PENNSYLVANIA STATE UNIVERSITY  
UNIVERSITY PARK, PENNSYLVANIA 16802

### Abstract

The performance of 5A zeolite and a carbon sieve produced from coal for the separation of O<sub>2</sub> and N<sub>2</sub> from air has been studied. In static adsorption at 25°C, the zeolite took up more N<sub>2</sub> than O<sub>2</sub>. Conversely, for short adsorption times, the carbon sieve took up more O<sub>2</sub> than N<sub>2</sub>. This behavior was reflected when air was passed through adsorbent beds. For the zeolite, enriched O<sub>2</sub> was recovered in the outlet; for carbon, enriched N<sub>2</sub> was recovered. Possibilities for improving the performance of the carbon sieve are discussed.

### INTRODUCTION

The possibility of concentrating O<sub>2</sub> from air by selective adsorption at or near room temperature was shown to be possible by Barrer some years ago (1). He showed that chabazite, a natural zeolite, has a higher capacity for N<sub>2</sub> than for either O<sub>2</sub> or Ar. Since then, many natural and synthetic zeolites have been found to preferentially adsorb N<sub>2</sub> over O<sub>2</sub> (2-5). Stronger adsorption of N<sub>2</sub> has been attributed to its having a permanent quadrupole moment which interacts with cations in the zeolite structure (6).

A number of patents, commencing with the Skarstrom patent (7),

\*Present address: Argonne National Laboratories, Argonne, Illinois.

describe engineering processes for the separation of  $O_2$  from air using zeolites. Such separation processes now appear economically attractive, compared to cryogenic separation, for use in small- or medium-sized  $O_2$  plants, that is, up to about 15 tons/day. Zeolites used commercially include synthetic calcium Type 5A, calcium Type 10X, and various types of mordenites (8).

With the advent of carbon molecular sieves, there has been interest in the possibility of their use in concentrating  $O_2$  from air (9). Unlike the zeolites, carbon sieves are not highly crystalline but are composed of very small crystallites in which the carbon atoms are trigonally bonded (10). The crystallites, in turn, are cross-linked to yield a disordered cavity-aperture structure. The apertures, produced by the more or less close approach of basal planes from adjacent crystallites, are slit-shaped (11). The size of the slits can be altered, depending upon the organic precursor which is used to produce the carbon and heat treatment temperature, among other variables.

In comparison to zeolites, there is a negligible difference in the attraction of  $N_2$  and  $O_2$  to a carbon surface (12). Therefore, if separation is to be achieved using microporous carbons, it will be on the basis of molecular sieving with  $O_2$  (kinetic diameter, 3.43 Å) diffusing into the carbon more rapidly than  $N_2$  (kinetic diameter, 3.68 Å). In this laboratory we have recently produced a large number of carbon molecular sieves from thermosetting polymers, coconut shells, and coals, and examined the static and dynamic adsorption of  $O_2$  and  $N_2$  on many of the samples (13). In this paper the behavior of one of the better samples produced from coal is compared with commercial 5A zeolite. It is to be emphasized that great latitude exists in the preparation of carbon sieves and that the sample considered in this paper is not necessarily the best which can be made for  $O_2$  separation from air. Rather, comparison of the zeolite and carbon sieve is meant to emphasize their differing behaviors, which may suggest applications for carbon sieves to the reader.

## EXPERIMENTAL

### Adsorbents

Calcium Type 5A zeolite 9–12 mesh beads, supplied by Matheson Coleman and Bell, were used. Detailed, quantitative x-ray diffraction studies have been made to completely delineate the structure of the Type A

zeolite (8). In the 5A material, the 11.4 Å diameter cavities have two apertures per cavity which are unobstructed by exchangeable cations. Consequently, the eight oxygens forming the aperture present a free diameter of 4.2 Å, which allows rapid diffusion of O<sub>2</sub> and N<sub>2</sub> into the cavities. The surface area of this zeolite was 480 m<sup>2</sup>/g, as calculated by the Dubinin-Polanyi equation (14) from CO<sub>2</sub> adsorption data at 25°C.

The carbon sieve selected for this study was prepared by heating a high volatile C bituminous coal in a N<sub>2</sub> atmosphere at a heating rate of 5°C/min to 800°C. The sample was held at 800°C for 2 hr in N<sub>2</sub> before cooling in N<sub>2</sub> to room temperature. Heat treatment releases volatile matter from the coal (about 38 wt-% for this coal) and results in some crystallite growth. Heat treatment temperature (HTT) is a most important parameter, determining the effective aperture size in the carbon sieve. With increasing HTT the effective aperture size is first increased as volatiles are removed and is then decreased upon heating to higher temperatures as cross-links are increasingly broken and adjacent crystallites come more closely together.

The -150 mesh fraction of this char was taken for this study.\* It had a surface area, as calculated from CO<sub>2</sub> adsorption at 25°C, of 714 m<sup>2</sup>/g. By contrast, the surface area calculated from N<sub>2</sub> adsorption data taken at 77°K, using the BET equation, was < 1 m<sup>2</sup>/g. Prior to adsorption of CO<sub>2</sub> or N<sub>2</sub>, the carbon sample was outgassed at a vacuum of 10<sup>-6</sup> Torr at 300°C overnight. A time of 30 min was allowed for each adsorption point. As described previously (10), large differences in CO<sub>2</sub> and N<sub>2</sub> surface areas are characteristic of microporous carbons where the approach of basal planes of adjacent crystallites, forming the apertures, is between 4.8 and 5.3 Å. Carbons which do not exhibit large differences in CO<sub>2</sub> (25°C) and N<sub>2</sub> (77°K) surface areas in turn do not make good sieves for the separation of N<sub>2</sub> and O<sub>2</sub>.

### Static Adsorption of Nitrogen and Oxygen

A standard volumetric adsorption apparatus was used. All samples were initially degassed at 300°C. Isotherms were determined at 25°C, allowing 5 min for each adsorption point. Both gases could be removed completely from both samples, following an adsorption run, by outgassing for 30 min at 25°C.

\*As has been shown previously, a small particle size of carbon can be bonded together with an organic binder such as coal tar pitch (15) or furfuryl alcohol (11) to produce pellets or beads if this is desired. This step was not taken in this study.

### Dynamic Adsorption Studies

For measuring selective adsorption of  $N_2$  or  $O_2$  from air, the following experimental arrangement was used. The principal features of the apparatus are shown in Fig. 1. About 18 g of zeolite or 15 g of carbon were held in the U-tube. The sample was initially degassed at 300°C under high vacuum for 8 hr and then the U-tube was held at 25°C. Helium was introduced into the system to bring the tube to atmospheric pressure. Air was then passed at 10 to 30 cc (STP)/min by opening stopcock 1. Stopcock 3, connecting the calibrated buret, was kept closed. The effluent gases coming through stopcock 2 passed through the sampling valve of a chromatograph. Analysis of the gases could be performed at 1 to 5 min intervals. When the effluent gas analysis approached the analysis of air, flow was stopped by closing stopcocks 1 and 2. The gas remaining in the system was then collected in the calibrated buret by opening stopcock 3. The buret with the mercury reservoir could be operated like a piston pump. Gas was collected for a number of strokes until less than 2 cc of gas were

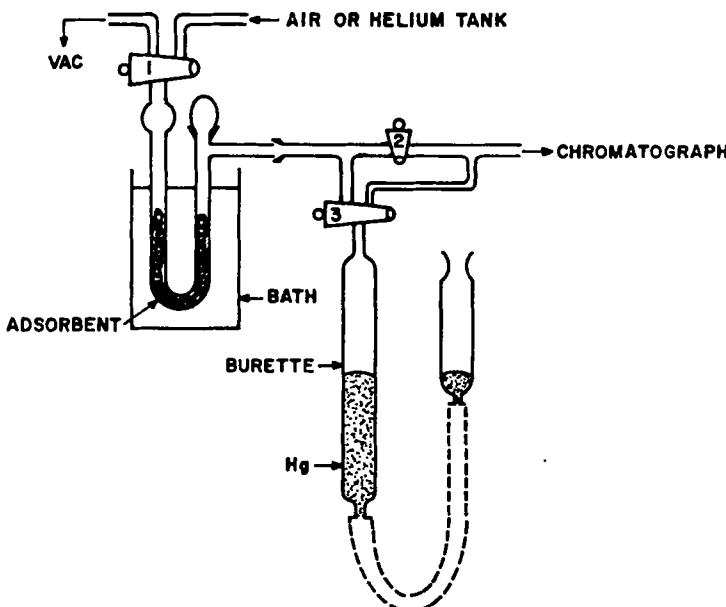


FIG. 1. Apparatus for measuring separation of  $O_2$  and  $N_2$  upon passage of air through a packed bed of adsorbent.

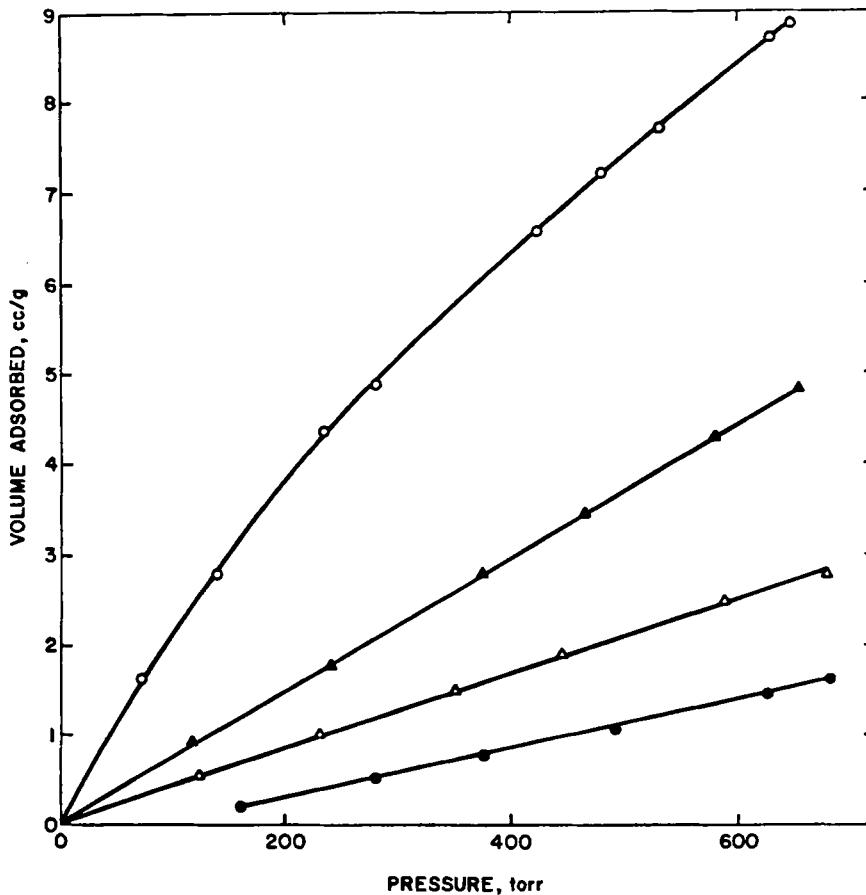


FIG. 2. Adsorption isotherms of N<sub>2</sub> (○) and O<sub>2</sub> (△) on 5A zeolite and carbon sieve at 25°C. Solid points are for carbon sieve.

collected per stroke. The gas collected in the buret in the first step (stroke) consisted primarily of the gas remaining in the free space of the adsorption system. A time of 30 sec was allowed for each desorption step. Amounts of gas collected in each desorption step were measured and the gas analyzed.

## RESULTS AND DISCUSSION

### Adsorption Isotherms

Figure 2 presents data for  $N_2$  and  $O_2$  adsorption at 25°C on the 5A zeolite and the carbon sieve. All adsorption volume data in the paper are given at STP conditions. For the zeolite sample, equilibration was reached in the 10 min allowed for each adsorption point. Uptake of  $N_2$  exceeded that of  $O_2$ . Adsorption on the carbon sieve was slower than on the zeolite, and  $O_2$  uptake exceeded that of  $N_2$ . From plots of  $V_t/V_\infty$  vs  $\sqrt{t}$  for short adsorption times ( $t$ ) on the carbon sieve, the ratio of initial diffusion coefficients of  $O_2$  and  $N_2$  into the pore system was estimated at about 3.0. After 24 hr, adsorption of  $N_2$  was almost equal to that of  $O_2$ ; that is,  $V_\infty$  values were 2.18 and 2.39 cc/g, respectively. Thus, clearly, any significant separation which will be effected by the carbon sieve during short dynamic adsorption cycles depends upon differences in diffusion rates of  $O_2$  and  $N_2$  into the micropore system. In fact, as has been shown recently when sufficient time is allowed for adsorption equilibrium to be attained in some microporous carbons,  $N_2$  uptake can slightly exceed  $O_2$  uptake as a result of the greater interaction of the former molecule with two walls of a pore (12). That is,  $N_2$  is slightly larger than  $O_2$ .

### Dynamic Adsorption and Desorption

**Zeolite.** Figure 3 presents breakthrough curve results for air passing at 20 cc/min (space velocity of about  $1.3 \text{ min}^{-1}$ ) into the bed of 5A zeolite beads. Also shown is the ratio of outflow gas volume to inflow gas volume ( $R$ ) as a function of time of passage of air. From a time of 2 min (when helium is displaced from the apparatus) to about 12 min, essentially pure  $O_2$  was recovered in the outflow. This was equivalent to 2.4 cc/g of zeolite in the bed. Over the air flow rate range 15 to 30 cc/min, the amount of pure  $O_2$  recovered was independent of flow rate, indicating that gas transport to the surface of the zeolite particles was not the limiting step in adsorbent utilization (16).

There is frequently interest in recovering a gas stream high in  $N_2$  con-

centration upon regeneration of the zeolite. Figure 4 summarizes desorption results, following the adsorption run described in Fig. 3. Desorption was carried out at 25°C, as described in the experimental section. As expected, the gas derived from the first 30 sec cycle had a composition close to that of air. That is, it was primarily gas remaining in the free space of the apparatus following the adsorption run. The total volume of gas desorbed was 10.7 cc/g and had a concentration of 88.9 vol-% N<sub>2</sub>. If the gas collected in the first cycle is not included, 6.3 cc/g of gas were collected, having an average N<sub>2</sub> concentration of 93.7 vol-%. In practice, in addition

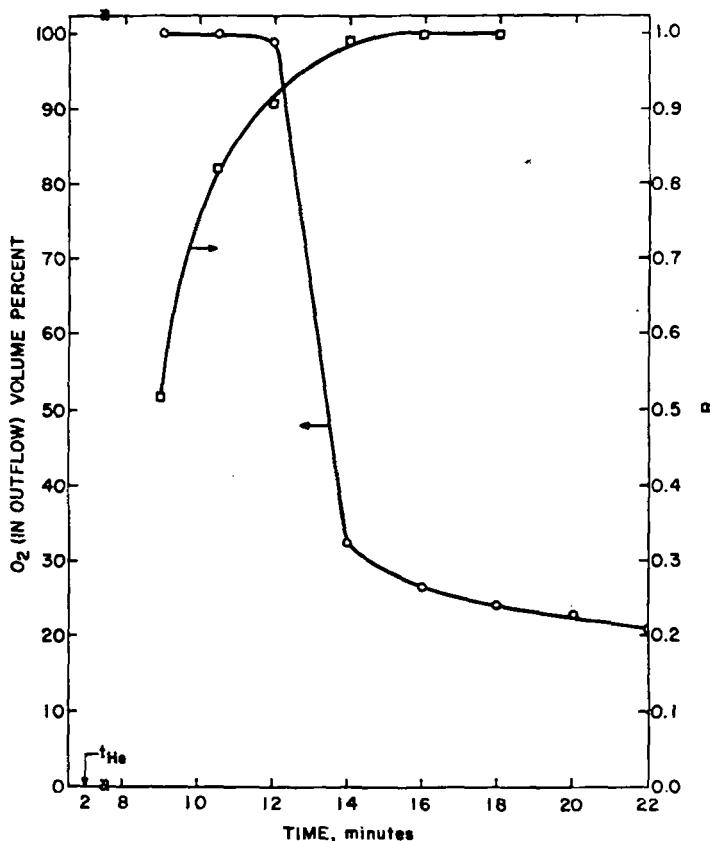


FIG. 3. Oxygen breakthrough curve for air entering bed of 5A zeolite at 25°C.  
Time to displace He from the system ( $t_{He}$ ) was about 2 min.

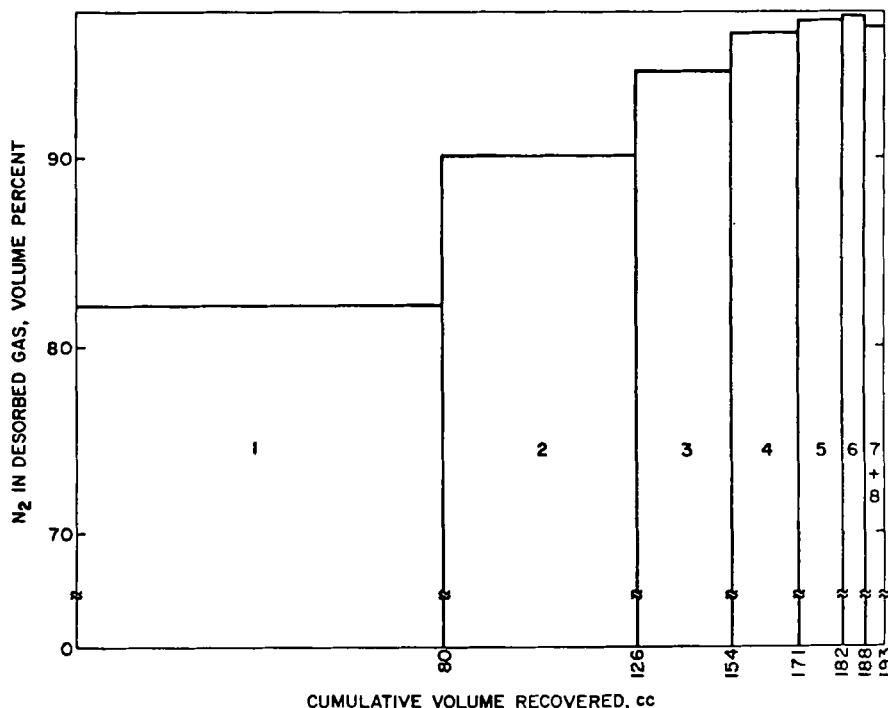


FIG. 4. Amount and composition of  $O_2$ - $N_2$  mixture recovered at  $25^\circ C$  upon cyclical removal of gas, following run shown in Fig. 3. Numbers in boxes identify cycle.

to using a "pressure swing" (7) to regenerate the zeolite bed, some elevation of bed temperature can also be used.

*Carbon Sieve.* Figure 5 presents breakthrough curve results for air passing at  $10 \text{ cc/min}^*$  (space velocity of about  $0.7 \text{ min}^{-1}$ ) into the bed of carbon sieve particles. In contrast to the zeolite bed, the first gas coming from the carbon bed was enriched in  $N_2$ . However, little pure  $N_2$  was produced prior to some  $O_2$  breakthrough. Because the breakthrough profile was not sharp, a significant amount of enriched  $N_2$  was produced; for example,  $3.2 \text{ cc/g}$  with a purity  $> 95\%$  was recovered.

Figure 6 presents desorption results on the carbon sieve. As expected,

\*As a result of the small size of carbon particles used ( $-150$  mesh), this volume flow rate was essentially the upper limit which could be used.

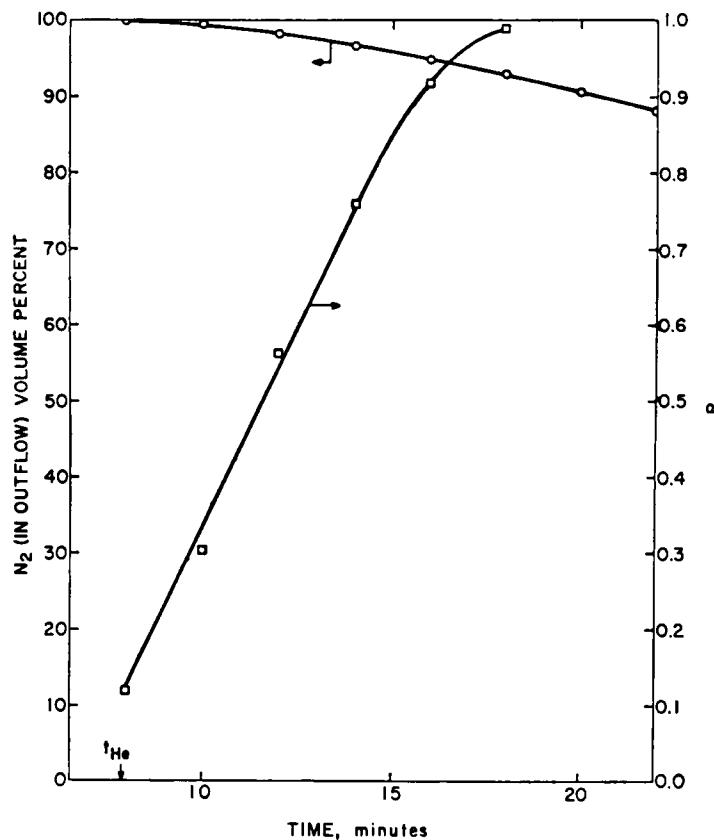


FIG. 5. Nitrogen breakthrough curve for air entering bed of carbon sieves at 25°C. Time to displace He from the system ( $t_{He}$ ) was about 4 min.

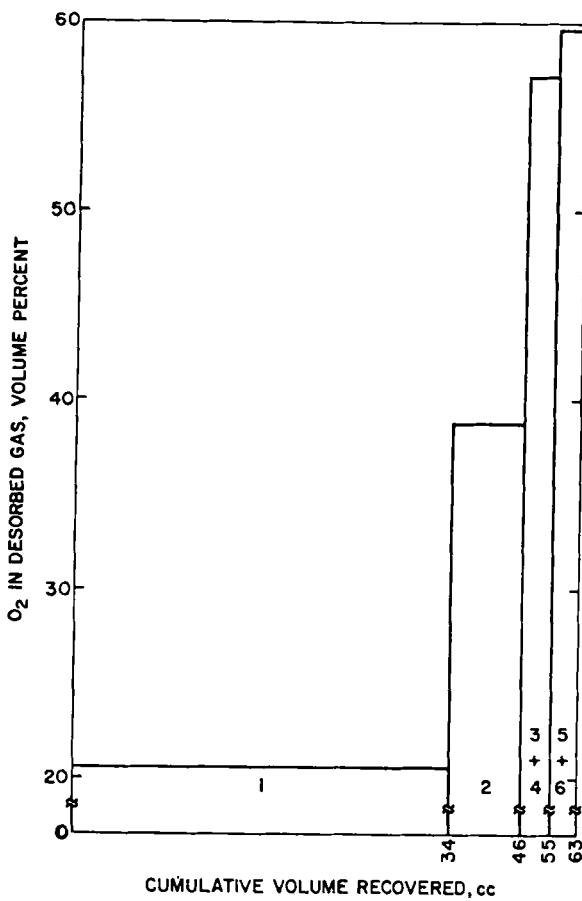


FIG. 6. Amount and composition of O<sub>2</sub>-N<sub>2</sub> mixture recovered at 25°C upon cyclical removal of gas, following run shown in Fig. 5. Numbers in boxes identify cycle.

the gas recovered in the first cycle had a composition close to that of air. Ultimately, 1.7 cc/g of additional gas was recovered in cycles 2 through 6: it had an average composition of 50% O<sub>2</sub>-50% N<sub>2</sub>.

### Zeolite vs Carbon Sieve

The main purpose of this paper has been to show the gross difference in behavior of zeolites and carbon sieves when they are in contact with O<sub>2</sub> and N<sub>2</sub> at room temperature for reasonably short times. Diffusion of O<sub>2</sub> and N<sub>2</sub> into the 5A zeolite is relatively rapid (10); differences in uptake are due to differences in heats of adsorption of O<sub>2</sub> and N<sub>2</sub>. Diffusion of the gases into the main void system of the carbon sieve, selected for this study, is much slower; it is activated (10). Differences in uptake for short times are due to differences in diffusion rates of O<sub>2</sub> and N<sub>2</sub>.

In addition to there being a difference as to which gas is taken up most readily by the zeolite and carbon sieve, there is at least one additional significant difference in behavior between these adsorbents. The zeolite adsorbs water strongly (preferentially to either O<sub>2</sub> or N<sub>2</sub>); and, hence, if one is interested in separation of O<sub>2</sub> and N<sub>2</sub> from a wet air stream, significant zeolite capacity is lost because of water uptake. Regeneration of the zeolite to remove the water requires heating to temperatures of about 300°C. Carbon surfaces are hydrophobic (17), and active sites can be kept hydrophobic in the presence of oxygen by prior dissociative chemisorption of hydrogen on these sites (18). Thus, during separation of O<sub>2</sub> and N<sub>2</sub> using a carbon sieve, water uptake would be low.

Clearly, for the results presented in this paper the performance of the zeolite for O<sub>2</sub>-N<sub>2</sub> separation was superior to that of the carbon sieve. It raises the question as to whether it will be possible to prepare carbon sieves which are competitive with zeolites for this application. Steps which need be taken to obtain improvement are obvious. First, the particle size of the carbon needs to be reduced to a value more comparable to that of the zeolite, that is <10 m $\mu$ . Enhancement in utilization of the particle for adsorption prior to breakthrough in the bed is particularly marked upon particle size reduction when the rate of diffusion within the particle is small. The small particles can then be bound together to produce pellets or beads, as is done for the production of zeolites.

A second area of improvement for the carbon sieves is also critical. That is, the ratio of diffusion rates of O<sub>2</sub> to N<sub>2</sub> into the pore system must be increased beyond the value of 3.0 existing for the carbon used in this study. The problem is twofold. First, the sizes of O<sub>2</sub> and N<sub>2</sub> are very close.

Second, unlike the zeolite, there is a distribution in aperture sizes in the carbons leading into the cavities. To obtain improved carbon sieves, this distribution must be made narrower around an aperture size which should be about 5.1 Å (10). Fortunately, great flexibility exists in the preparation of carbon sieves of desired aperture size such as: choice of organic precursor, heat treatment temperature, slight oxidation to selectively gasify carbon atoms from the structure, and carbon deposition in the apertures by the cracking of a gaseous hydrocarbon.

In addition to increasing the ratio of rates of diffusion of O<sub>2</sub> to N<sub>2</sub> into the void system, one would also like to increase the magnitude of the O<sub>2</sub> diffusion rate. Thereby a greater utilization of the void system for O<sub>2</sub> uptake could be achieved before breakthrough occurs. Unfortunately, it has been generally found that an increase in the magnitude of the diffusion rates for O<sub>2</sub> parallels a decrease in the ratio of diffusion rates for O<sub>2</sub> and N<sub>2</sub> (13).

In any case, one suspects that a very reproducible organic precursor will have to be used to produce carbon sieves for O<sub>2</sub>-N<sub>2</sub> separation because of the close tolerances demanded. That is, the carbon sieve must be made reproducibly. This probably means the selection of thermosetting polymers as precursors and the elimination of candidates like coals and coconut hulls. This is unfortunate for it means that the price of the carbon sieves will be substantial.

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### REFERENCES

1. R. M. Barrer, *Proc. R. Soc. London, Ser. A*, **167**, 392 (1938).
2. R. M. Barrer, *Trans. Faraday Soc.*, **40**, 555 (1944).
3. R. M. Barrer and J. W. Sutherland, *Proc. Roy. Soc. London, Ser. A*, **237**, 439 (1956).
4. R. M. Barrer and W. I. Stuart, *Ibid.*, **249**, 464 (1959).
5. D. Domine and L. Hay, *Molecular Sieves*, Society of Chemical Industry, London, 1968, pp. 204-216.
6. R. M. Barrer, *J. Colloid Interface Sci.*, **21**, 415 (1966).
7. C. W. Skarstrom, U.S. Patent 2,944,627 (July 12, 1960).
8. D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974.
9. H. Juntgen, K. Knoblauch, H. Munzner, and W. Peters, *Chem.-Ing.-Tech.*, **45**, 533 (1973).

10. P. L. Walker, Jr., L. G. Austin, and S. P. Nandi, *Chemistry and Physics of Carbon*, Vol. 2 (P. L. Walker, Jr., ed.), Dekker, New York, 1966, pp. 257-371.
11. P. L. Walker, Jr., T. G. Lamond, and J. E. Metcalfe, III, *Second Conference on Industrial Carbon and Graphite*, Society of Chemical Industry, London, 1965, pp. 7-14.
12. P. Ehrburger, O. P. Mahajan, and P. L. Walker, Jr., "Adsorption of Oxygen and Nitrogen on Surface-Modified Carbons," *J. Colloid Interface Sci.*, In Press.
13. S. P. Nandi and P. L. Walker, Jr., *Fuel*, 54, 169 (1975).
14. M. M. Dubinin, *Chem. Phys. Carbon*, 2, 51-120 (1966).
15. J. E. Metcalfe, III, Ph.D. Thesis, The Pennsylvania State University, 1965.
16. L. A. Jonas and J. A. Rehrmann, *Carbon*, 12, 95 (1974).
17. P. L. Walker, Jr. and J. Janov, *J. Colloid Interface Sci.*, 28, 449 (1968).
18. R. C. Bansal, F. J. Vastola, and P. L. Walker, Jr., *Carbon*, 9, 185 (1971).

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