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

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Abstract

The performance of 5A zeolite and a carbon sieve produced from coal for the separation of O_2 and N_2 from air has been studied. In static adsorption at 25°C, the zeolite took up more N_2 than O_2 . Conversely, for short adsorption times, the carbon sieve took up more O_2 than N_2 . This behavior was reflected when air was passed through adsorbent beds. For the zeolite, enriched O_2 was recovered in the outlet; for carbon, enriched N_2 was recovered. Possibilities for improving the performance of the carbon sieve are discussed.

INTRODUCTION

The possibility of concentrating O_2 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_2 than for either O_2 or Ar. Since then, many natural and synthetic zeolites have been found to preferentially adsorb N_2 over O_2 (2-5). Stronger adsorption of N_2 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),

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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 mor-denites (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 O₂ and N₂ into the cavities. The surface area of this zeolite was 480 m²/g, as calculated by the Dubinin-Polanyi equation (14) from CO₂ adsorption data at 25°C.

The carbon sieve selected for this study was prepared by heating a high volatile C bituminous coal in a N₂ atmosphere at a heating rate of 5°C/min to 800°C. The sample was held at 800°C for 2 hr in N₂ before cooling in N₂ 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 CO₂ adsorption at 25°C, of 714 m²/g. By contrast, the surface area calculated from N₂ adsorption data taken at 77°K, using the BET equation, was < 1 m²/g. Prior to adsorption of CO₂ or N₂, the carbon sample was outgassed at a vacuum of 10⁻⁶ Torr at 300°C overnight. A time of 30 min was allowed for each adsorption point. As described previously (10), large differences in CO₂ and N₂ 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 CO₂ (25°C) and N₂ (77°K) surface areas in turn do not make good sieves for the separation of N₂ and O₂.

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 (17) 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

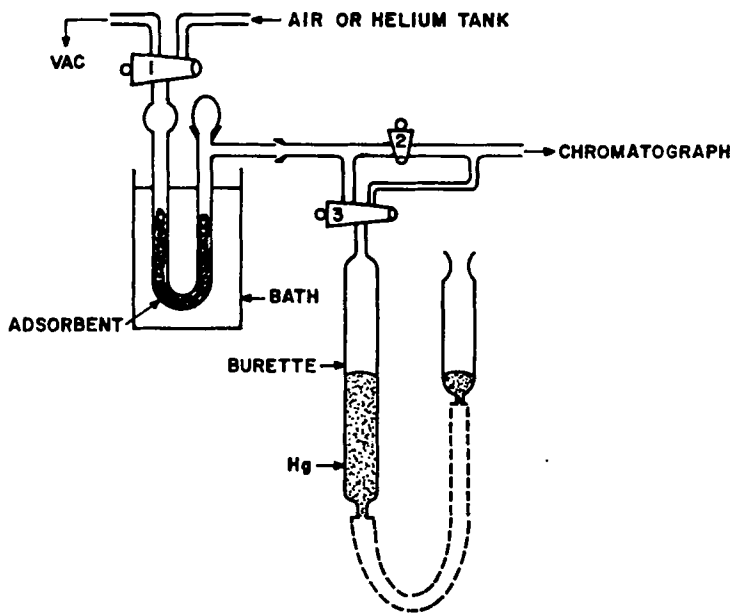


FIG. 1. Apparatus for measuring separation of O_2 and N_2 upon passage of air through a packed bed of adsorbent.

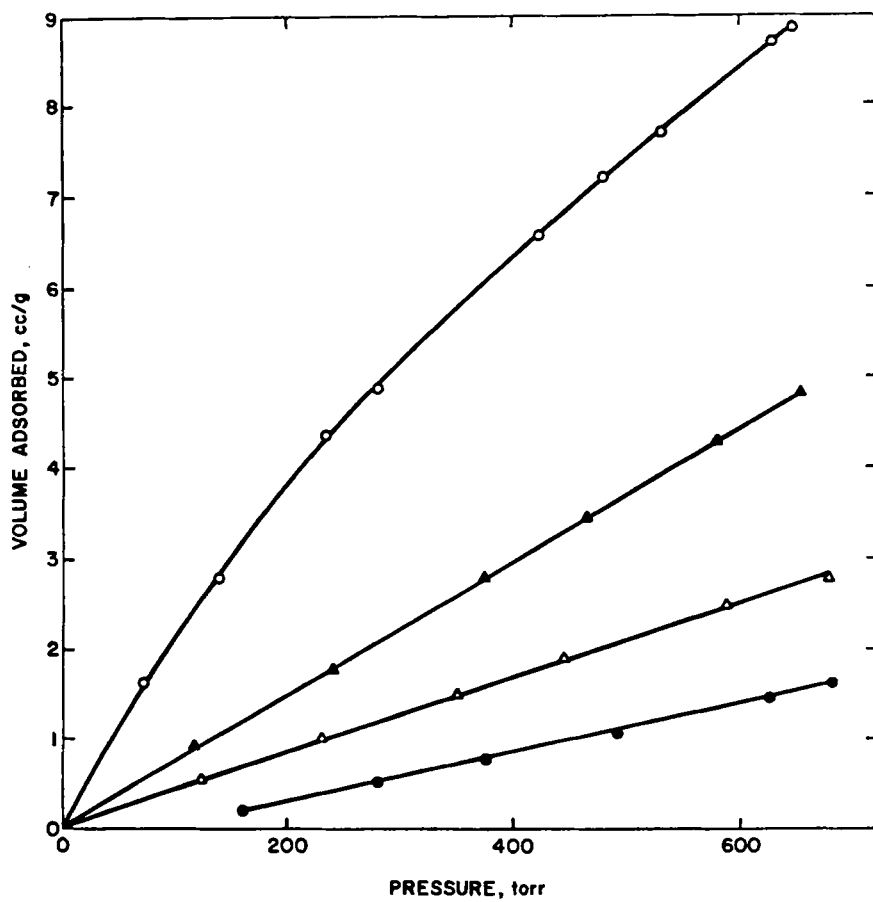


FIG. 2. Adsorption isotherms of N₂ (○) and O₂ (△) on 5A zeolite and carbon sieve at 25°C. Solid points are for carbon sieve.

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 $25^\circ C$ 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_∞ 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_∞ 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 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_2 . If the gas collected in the first cycle is not included, 6.3 cc/g of gas were collected, having an average N_2 concentration of 93.7 vol-%. In practice, in addition

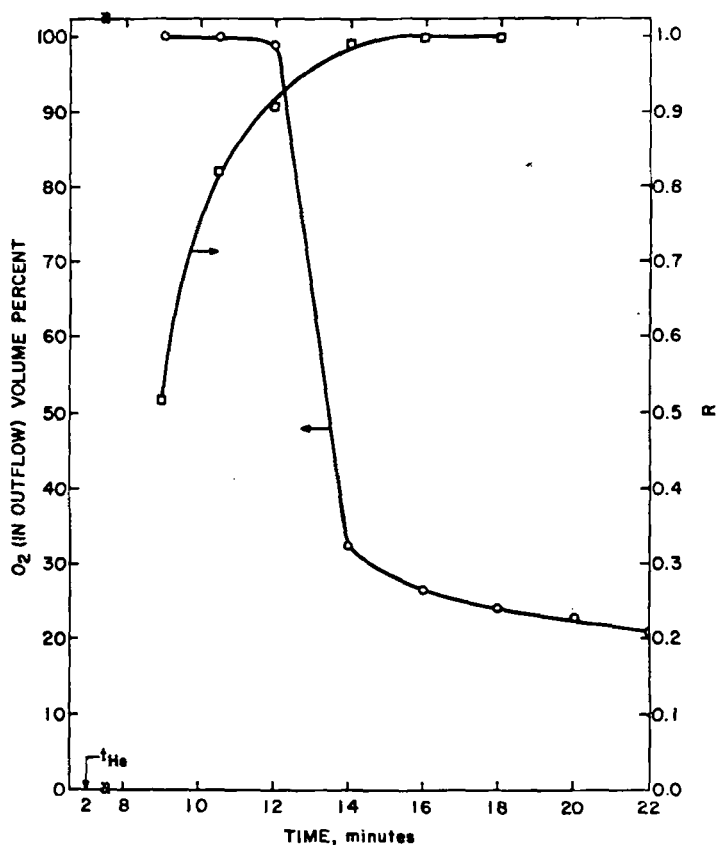


FIG. 3. Oxygen breakthrough curve for air entering bed of 5A zeolite at 25°C. Time to displace He from the system (t_{He}) was about 2 min.

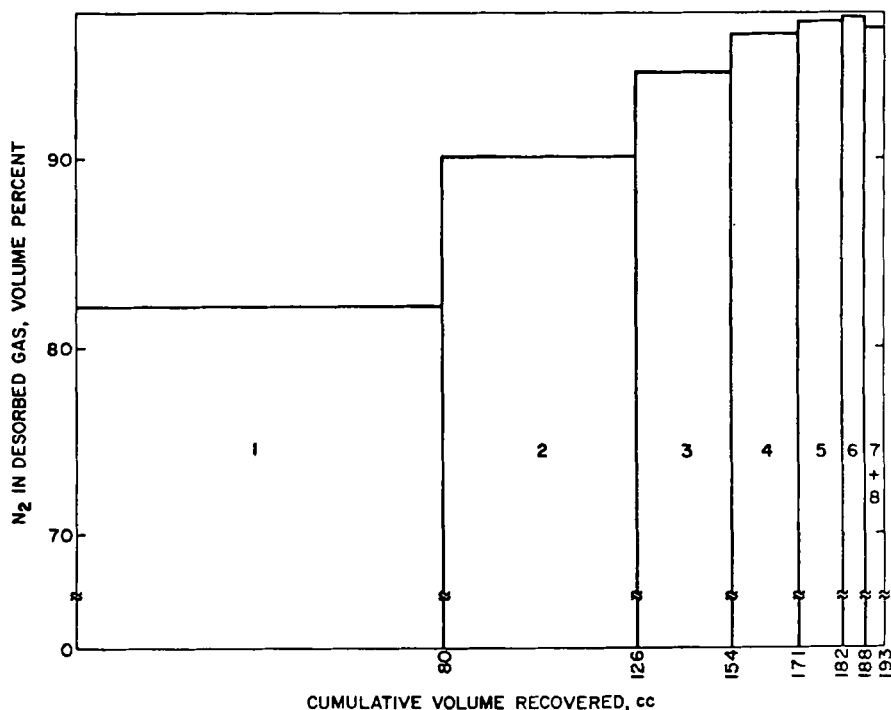


FIG. 4. Amount and composition of O_2 - N_2 mixture recovered at $25^\circ C$ upon cyclical removal of gas, following run shown in Fig. 3. Numbers in boxes identify cycle.

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 cc/min* (space velocity of about 0.7 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 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.

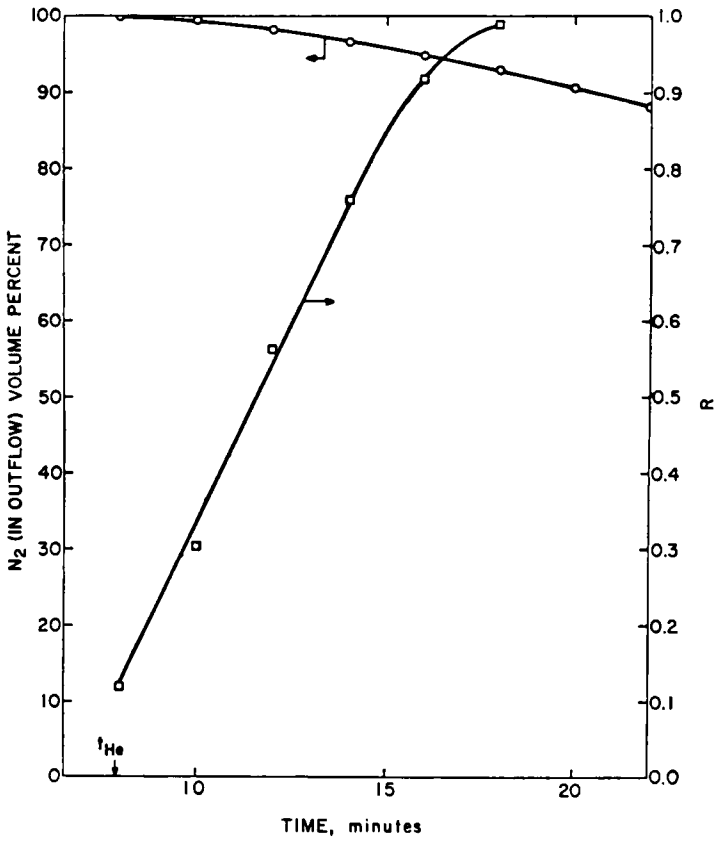


FIG. 5. Nitrogen breakthrough curve for air entering bed of carbon sieves at 25°C. Time to displace He from the system (t_{He}) was about 4 min.

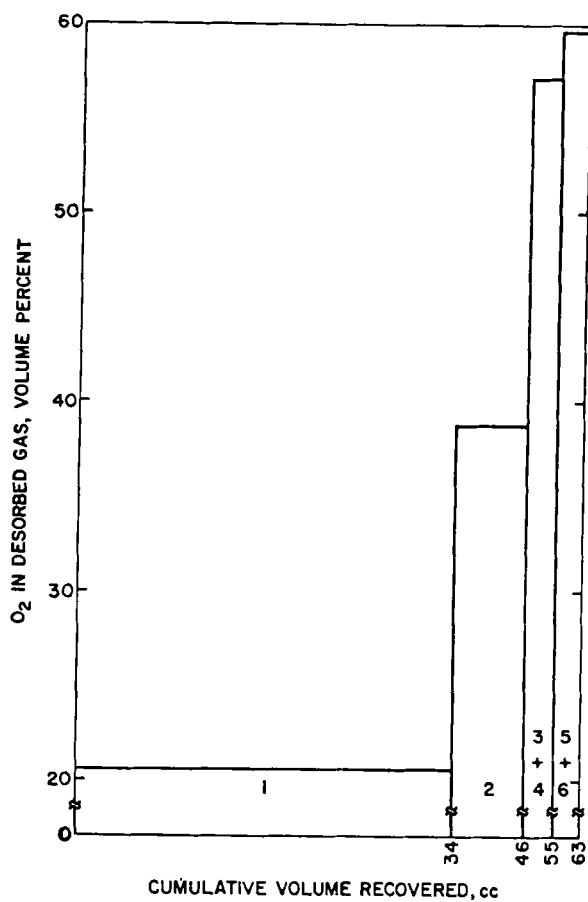


FIG. 6. Amount and composition of O_2 - N_2 mixture recovered at $25^\circ C$ upon cyclical removal of gas, following run shown in Fig. 5. Numbers in boxes identify cycle.

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% O₂-50% N₂.

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 O₂ and N₂ at room temperature for reasonably short times. Diffusion of O₂ and N₂ into the 5A zeolite is relatively rapid (10); differences in uptake are due to differences in heats of adsorption of O₂ and N₂. 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 O₂ and N₂.

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 O₂ or N₂); and, hence, if one is interested in separation of O₂ and N₂ 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 O₂ and N₂ using a carbon sieve, water uptake would be low.

Clearly, for the results presented in this paper the performance of the zeolite for O₂-N₂ 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 mμ. 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 O₂ to N₂ 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 O₂ and N₂ 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 \AA (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_2 to N_2 into the void system, one would also like to increase the magnitude of the O_2 diffusion rate. Thereby a greater utilization of the void system for O_2 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_2 parallels a decrease in the ratio of diffusion rates for O_2 and N_2 (13).

In any case, one suspects that a very reproducible organic precursor will have to be used to produce carbon sieves for O_2 - N_2 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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